“Studies on Process Intensification of Treatment Techniques for Tannery Waste Effluent”

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by

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DECLARATION

I, **Shivendu,** declare that this thesis titled, **"STUDIES ON PROCESS INTENSIFICATION OF TREATMENT TECHNIQUES FOR TANNERY WASTE EFFLUENT"** and the work presented in it are my own. I confirm that:

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This is to certify that the thesis entitled **"STUDIES ON PROCESS INTENSIFICATION OF TREATMENT TECHNIQUES FOR TANNERY WASTE EFFLUENT"** being submitted by **Shivendu (2014RCH9057)** is a bonafide research work carried out under my supervision and guidance in fulfillment of the requirement for the award of the degree of **Doctor of Philosophy** in the **Department of Chemical Engineering**, Malaviya National Institute of Technology, Jaipur, India. The matter embodied in this thesis is original and has not been submitted to any other University or Institute for the award of any other degree.

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ABSTRACT

The treatment of recalcitrant bio-refractory pollutants especially common in wastewater emanating from the tannery industries is a major challenge to the industries due to the absence of an efficient treatment technology, high operational costs as well as in view of the stringent rules imposed by the various environmental and governmental regulatory bodies. Cavitation has emerged as an advanced oxidation technique for the treatment of bio-refractory pollutants in wastewater, either operated alone or in combination with other advanced oxidative reagents and/or processes. It provides an alternative approach to treat highly complex waste effluent with effective degradation of recalcitrant molecules and enhanced biodegradability index (BI) of pollutants. Combination of conventional pretreatment techniques such as coagulation with cavitation and treatment with various oxidation agents such as O_3, H_2O_2 and Fenton's reagent gives higher degradation efficiencies yielding intensified treatments. Hybrid oxidation processes provide better degradation efficiency when compared to individual process due to the enhanced generation of •OH radicals in the presence of process intensifying agents, reduction in process treatment time and enhanced contact/mass transfer thereby maximizing the extent of mineralization. The efficiency of these hybrid processes depends on the type of pollutant, formation of hydroxyl radicals and its effective interaction with pollutant molecules. This integrated approach is easy to be adopted into the conventional treatment processes through moderate modifications for installation into commercial practice, and therefore their process efficiencies was evaluated for maximum chemical oxygen demand (COD)/total organic carbon (TOC) reduction and increase in the BI (BOD:COD) of the waste effluent.

Alum coagulation followed by cavitation as a pretreatment tool for treatment of tannery waste effluent (TWE) was studied with the aim of reducing its COD, TOC, total suspended solids (TSS) etc. and enhancing its BI to make it suitable for anaerobic digestion (AD). The residual pH of alum treated TWE was around 4.5, where maximum COD and TSS reduction was achieved. The efficiency of pretreatment process was enhanced by subjecting coagulated tannery waste effluent (CTWE) to hydrodynamic cavitation (HC) and ultrasonication (US). In case of HC, process parameters such as inlet

pressure and dilution affected the treatment of CTWE and lower operating pressure (5 bar) was more favorable for the treatment of CTWE and enhanced the BI from 0.14 to 0.57 in 120 min. The CTWE samples when subjected to HC pretreatment with 50% dilution, the effect of HC pretreatment was that it caused a higher % reduction in COD and TOC as well as there was a significant reduction in the quantum of COD and TOC compared to non-diluted sample. On the other hand, pretreatment of TWE using coagulation followed by US demonstrated that BI of effluent was enhanced from 0.10 to 0.41 in 150 min. Energy efficiency evaluation for both processes at their optimized conditions based on the actual amount of COD reduced per unit energy delivered to the system, indicated that coagulation followed by HC for pretreatment of TWE was found to be six times more energy efficient as compared to coagulation followed by US.

Efficacy of US in combination with AOPs for the treatment of TWE enhances the degradation efficiency of organic pollutants. US treatment of TWE gave maximum 20.3% COD reduction at optimized amplitude of 40%. Combination of US with oxidizing agents such as hydrogen peroxide, Fenton reagent, ozone and hypochlorite was found to be not effective to treat raw TWE. Therefore coagulation was carried out prior to US to reduce the organic load from TWE samples using alum and aluminum chloride as coagulants. Alum had higher efficiency with reduction of 52.01% COD and 69.79% TSS at the optimized dosage of 1.5 g/100 mL as compared to aluminum chloride which had reduction of 46.3% COD and 55.7% TOC for the same dosage. Maximum 23.7% reduction in COD of CTWE was observed using US at 40% amplitude after 120 minutes. Combination of US with H_2O_2 was found effective in case of CTWE and 36.82% reduction in COD was obtained at optimized dosage of H_2O_2. The combination of US with sodium hypochlorite and ozone also improved the degradation efficiency and maximum 35.94% and 36.14% reduction in COD was observed respectively. However combination of US with Fenton’s reagent was the most effective hybrid process among all the hybrid processes to treat CTWE with maximum 66.96% reduction in COD. Therefore, these hybrid processes may be used as pretreatment tool for the treatment CTWE.

The degradation of organic pollutants in TWE using hybrid HC such as HC + ozone (O_3), HC + hydrogen peroxide (H_2O_2) and HC + Fenton's reagent was studied. HC treatment alone caused a reduction of 14.46% COD, 12.60% TOC, 10.01% total dissolved solids (TDS) and 34.82% TSS of the TWE samples at the optimum inlet pressure of 500 kPa within 120 min. It also caused an increase in BI value from 0.33 to 0.43 indicating increased biodegradability, whereas dilution of the TWE samples did not enhance the HC process efficiency. HC combined with O_3 was effective as COD and TOC reduction increased to 26.81% and 17.96% respectively at the optimum loading of 7 g/h of O_3. HC combined with H_2O_2 significantly enhanced the degradation efficiency to a maximum of 34.35% COD and 19.71% TOC reduction due to the enhanced generation of hydroxyl radicals. However, HC combined with Fenton's process was found to be the most efficient hybrid process for the treatment of TWE at a maximum reduction of 50.20% COD and 32.41% TOC respectively at $FeSO_4.7H_2O/H_2O_2$ ratio of 1:3 (w/w). The requirement of H_2O_2 per g of COD reduction for HC + Fenton reduced to 1.95 g/g compared to the requirement of 3.02 g/g for HC + H_2O_2 process. Moreover, HC + Fenton's treatment increased the BI value from 0.28 to 0.46, which is an increase by 64% compared to an increase by 30% using HC alone. Other enhanced benefits include higher rate of mineralization of organic matter with lower cost of treatment. Hybrid HC + Fenton was the most energy efficient approach than HC process with a 75% reduction in the energy requirement and 56% reduction in treatment cost per mg of COD reduction of TWE.

The efficacy of pretreated TWE for its application for enhanced production of biogas along with COD reduction by subjecting it to batch AD was investigated. HC was utilized for pretreatment of TWE using a slit venturi as the cavitating device operated at 5 bar pressure for 2 h. The HC treated TWE mixed with sewage seed (5 to 20% v/v) served as the substrate for AD which was carried out in small scale (200ml) and laboratory scale (2L) bioreactors. The biogas yield and percentage COD reduction was almost 2 times higher in HC treated TWE in comparison to raw TWE. Biogas yield of 68.57 mL/g volatile solids (VS) along with 43.17% COD reduction was obtained during AD of HC treated TWE in a 2 L bioreactor with 10% seed dosage. An ‘AD’ simulator was developed in MATLAB representing the AD digestion process and parameter optimization done by validations using experimental methane production data from the laboratory scale bioreactors. The ‘AD’ simulator effectively predicted for the long-term performance of the bioreactor for HC treated TWE in terms of concentration of organic polymers, organic monomers, volatile fatty acids (VFA) and concentrations of methane and carbon dioxide in the produced biogas for varying VS content of feed. The biogas production was enhanced by adding food waste to the feed samples for different loading time intervals (24 h/ 48 h) in two different reactors and yield of biogas studied for comparison of HC treated TWE to raw TWE samples. The biogas generation increased up to 7.8 and 11.8 folds for HC treated TWE samples with OLR of 24 h and 48 h respectively than for the raw TWE. The cost estimations proved that the cost of biogas produced by AD of the HC treated TWE mixed with food waste will recover the extra cost of HC pretreatment process when compared to AD of raw TWE alone, therefore establishing that HC as a pre-treatment tool has the potential for COD reduction of the recalcitrant TWE as well as for enhancing the biogas yield when it is subjected to AD. The hybrid techniques developed enhanced the BI of treated TWE and therefore may be used as a pre-treatment tool by integrating into existing biological treatment units in the conventional effluent treatment plants, in order to cause enhanced degradation of highly bio-recalcitrant organic pollutants.

LIST OF PUBLICATIONS

The following papers on the research work presented in this thesis have been published.

1. Shivendu Saxena, Virendra Kumar Saharan, Suja George, Enhanced synergistic degradation efficiency using hybrid hydrodynamic cavitation for treatment of tannery waste effluent, Journal of Cleaner Production, 198 (2018) 1406-1421.
2. Shivendu Saxena, Sunil Rajoriya, Virendra Kumar Saharan, Suja George, An advanced pretreatment strategy involving hydrodynamic and acoustic cavitation along with alum coagulation for the mineralization and biodegradability enhancement of tannery waste effluent, Ultrsonics Sonochemistry 44 (2018) 299-309.
3. Shivendu Saxena, Virendra Kumar Saharan, Suja George, Modeling & Simulation studies on Batch Anaerobic Digestion of hydrodynamically cavitated Tannery waste effluent for higher biogas yield, Ultrasonics-Sonochemistry 58 (2019)104692.

Dedicated

To

My Parents

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List of Abbreviations and Nomenclature

$\mathbf{X_n}$	Bacterial concentration (g/L) (n = 1 to 5)
$\boldsymbol{\mu_{mn}}$	Maximum specific growth rate (per h) for X_n (n = 1 to 5)
k	First order specific growth rate for the hydrolysis of organic polymers (per h)
$\mathbf{Y_n}$	Bacterial yield (g biomass/mM substrate) for X_n (n = 1 to 5)
$\mathbf{b_n}$	Bacterial decay rate constant (per h) for X_n (n = 1 to 5)
$\mathbf{K_{S,n}}$	Monad saturation constant (mM) (n = 1 to 6)
Ac	Acetate
Bu	Butyrate
Pr	Propionate
$\mathbf{f_n}$	Conversion factor for substrate (mM/g) (n = 1 to 5)
H	Henry's Law coefficient (atm/mol fraction)
I	Inhibitor
F	Function
$\mathbf{K_{I,n}}$	Inhibition constant (mM) (n =1 to 8)
$\mathbf{K_{La,n}}$	Mass transfer coefficient (per h) (n = 8,10,12)
$\mathbf{S_n}$	Substrate concentration (mM) (n = 1 to 13)
$\mathbf{S_n^e}$	Equilibrium substrate concentration (mM) (n = 5,6,7)
VS	Volatile solids (mg/L)
COD	Chemical oxygen demand (mg/L)
BOD	Biological oxygen demand (mg/L)
BI	Biodegradability index
TS	Total solids (mg/L)
TOC	Total organic carbon
TSS	Total suspended solids
TDS	Total dissolved solids
BI	Biodegradability index
FTIR	Fourier transform infrared spectroscopy
LCMS	Liquid chromatography – mass spectroscopy
TWE	Tannery waste effluent
AD	Anaerobic digestion
OLR	Organic loading rate (mL/h)
Rs	Rupees
Subscripts	
i	Substrate i
j	Bacteria j
g	Inhibition g

CHAPTER 1

Introduction and Literature Review

1.1 Introduction

Availability of clean drinking water from surface water resources, which is the prime factor that determines the well-being of our society, is under constant threat today due to the disposal of biological, municipal and industrial wastes/ wastewaters from the various industries/ manufacturing units. One of the easiest ways for the various contaminants present in wastewater to enter the aquatic system among the different routes is through direct dumping either from industries or from the effluent treatment plants. Leather industry considered as the prime economic driver for many developing countries (Lofrano et al., 2013), has led to an exponential growth in leather tanning/ processing sector. Leather tanning practices primarily comprises of following steps: (a) pre-treatment of raw animal skins/hides, (b) application of tanning agent on skin/hides, softening, curing, dyeing etc. and (c) drying and shining of the treated skins/hides to make leather suitable for product manufacturers. The processing of leather requires a wide variety of chemicals and large quantity of water in order to convert the raw hides / animal skins into the desired leather goods, thereby resulting in generation of large amount of wastewater with very high concentration of biological and chemical waste.

The tannery wastewaters are highly complex in nature with respect to both of its biological and chemical characteristics such as high alkalinity, high organic content, high phosphate and nitrate content, high pH, strong odor, dark color, heavy metals etc. They are mainly characterized in terms of their COD, BOD, TDS, TSS, chromium and phenolic content etc. The treatment of the tannery wastewater is highly essential before its disposal because of the presence of high organic and inorganic content in the form of phosphates and nitrates etc. which is one of the main cause of eutrophication in many water bodies, besides causing many health hazards (Marousek et al., 2017). Moreover, the dark color of the wastewater causes hindrance to sunlight pathway in the water body, because of which the plant photosynthesis happening inside the water is affected, which result in lowering the dissolved oxygen content in water hence adversely affects the aquatic life of the water body (Durai and Rajasimman, 2011; Saxena et al., 2016). The tannery wastewater which is collected and commonly treated at the common effluent treatment plants are not being fully treated, because of limitations such as low plant capacity, inefficiency to handle high intake load, treatment process limitations or inability to treat bio-refractory pollutants as well as process inefficiency due to the current practice of mixing different effluents generated from different locations. Regulatory bodies such as the Central Pollution Control Board in India, try to prevent the disposal of the wastewater into the environment by taking various regulatory measures i.e. imposing highly stringent laws such as closure of the industrial units or levying heavy fines as compensation for polluting the environment in case of their incompetency to meet the wastewater discharge standards. Even though several measures are being adopted to save the environment by the governmental and regulatory bodies these measures will not be fully successful without the technology development for efficient treatment of the recalcitrant pollutants present in tannery wastewater along with solving various technical hitches, high maintenance and operating costs etc. Therefore, treatment of TWE up to the quality levels prescribed by the various regulatory authorities is very essential in view of both biotic as well as abiotic wellbeing.

An extensive literature review was carried out to study the nature of tannery waste and wastewater characteristics and the various conventional and advanced treatment techniques applicable for wastewater treatment. Studies available on the advantage of using cavitation techniques such as HC and US over conventional pretreatment techniques for the treatment of tannery wastewater was reviewed in order to identify the research gaps and formulate the objectives of the proposed research work and are described in sections below.

1.2 Literature Review

Tanning is an art by means of which putrescible animal hides and skins are preserved from decay and converted into imputrescible substances known as “Leather”. The history of leather manufacturing is dated back to 12th century of BC. Leather industry, though economically viable is placed high on the list of major polluting industries and central pollution control board (CPCB) places tanneries under red ‘categories’. All the tanneries are obligated to comply with legal provisions under WATER (prevention and control of pollution) ACT, 1974 and environmental protection ACT 1986. They are fundamentally related to protect environmental resources including land, water and air from being polluted by the discharge of treated or untreated trade effluent (Gazette of India., 1988).

1.2.1 Tanning process

In any leather industry, leather production stages that generates TWE can be divided into four main categories i.e., a) pre-tanning (beam house operations), b) tanyard operations, c) post-tanning operations and d) finishing operations. Fig.1.1 presents the different stages of tannery operation, chemicals used in particular operation and the pollutants associated with each process.

1.2.1.1 Pre-tanning (Beamhouse operation):

Pre-tanning operations are primary operations that comprises of cleaning and conditioning steps in which raw material (skin/hide) is prepared for the tanning operation. These primary operation are categorized as follows

I. Soaking: eliminates the dirt, blood and preservatives from the stored skin and hide.
II. Fleshing and trimming: removes hair and extraneous matter from the skin and hides.
III. Deliming and bating: removes the hair residues such as roots, pigments and degrade the proteins in the dehaired, fleshed and alkaline hides.
IV. Pickling: reduces the pH of the hide (to around 3) to make it suitable for tanning.
V. Degreasing: removes the excessive amount of grease using organic solvents or surfactants, together with soaking, pickling or after tanning.

1.2.1.2 Tanning (Tanyard operation)

It is a process of stabilizing collagen fiber through a cross- linking action using natural or synthetic chemicals. Tanning agents can be classified in three main groups namely chrome tanning agent, vegetable tanning agents, and alternative tanning agents (e. g. Syntans, aldehydes, and oil tanning agents). Chrome tanning is being highly preferred in the industry in comparison to vegetable tanning.

1.2.1.3 Post-tanning (Wet finishing)

Post- tanning operations involve neutralization and bleaching, followed by retanning, dyeing, and fat liquoring. These processes are mostly undertaken in a single processing vessel. Specialized operations are also performed to add certain properties to the leather product (e. g. Water repellence or resistance, oleophobicity, gas permeability, flame retardancy, abrasion resistance, and anti- electrostatic properties).

1.2.1.4 Finishing

The crust that results after re-tanning and drying is subjected to a number of finishing operations. The purpose of these operations is to make the hide softer, to improve their resistance and to mask the unfinished surfaces by treating the hide with an organic solvent or water based dye and varnish.

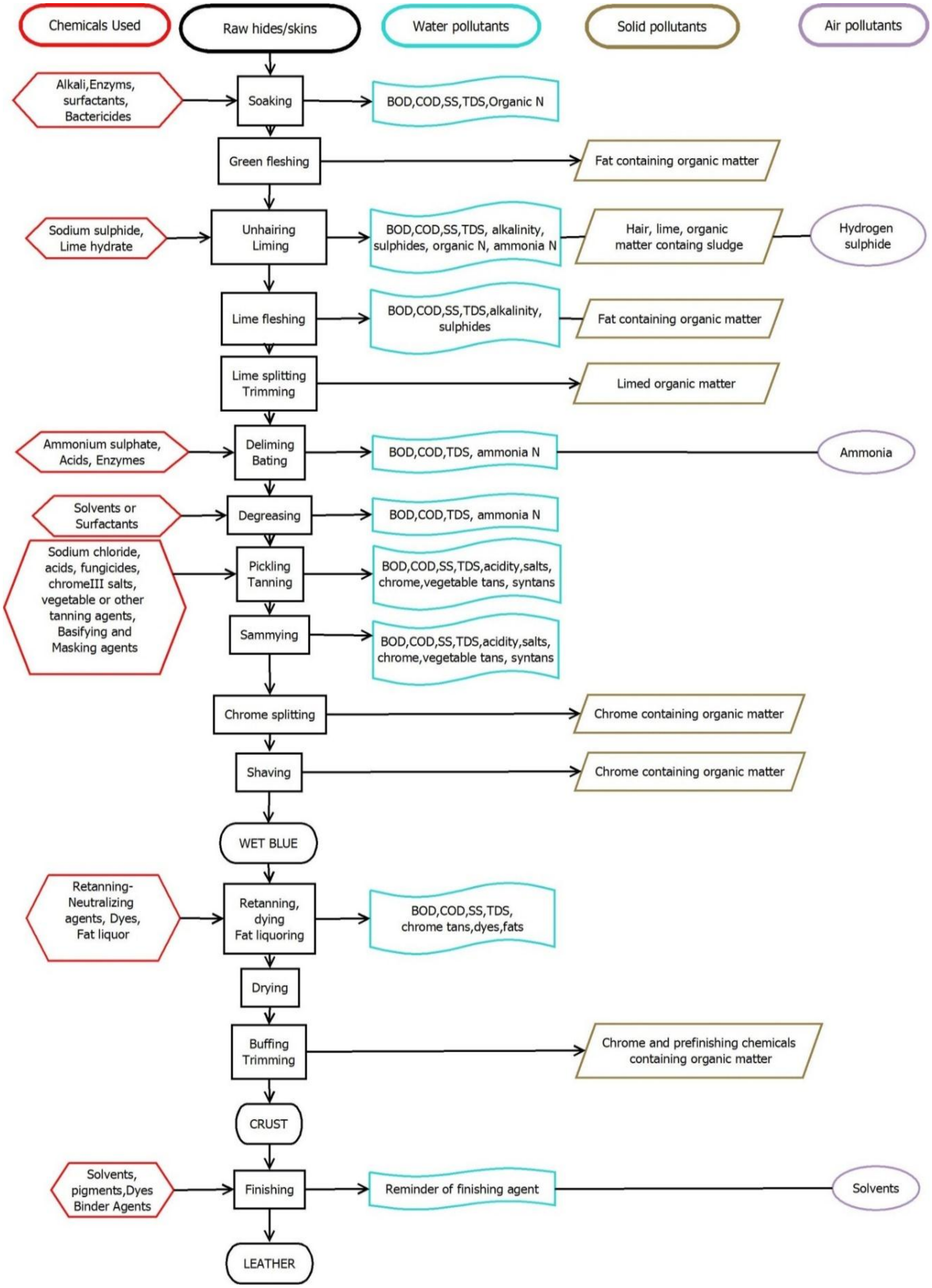


Fig. 1.1 Different stages of tannery operation, chemicals and the pollutants associated with these operations

1.2.2 Tannery wastewater characteristics

The tanneries are generally situated near the water bodies such as rivers, lakes, streams etc. as they need constant water supply. Most of the processes involved in leather production are wet-processes and the volume of wastewater produced by each of the major operation varies in a very wide range. The levels of the pollution in tannery wastewater vary depending upon the process adopted in leather making. More than 60 m^3 of water and 300 kg of chemicals are required for the processing of a ton of raw skin (Verheijen et al., 1996). Tannery wastewater is containing a complex mixture of organic and inorganic pollutants. Tannery wastewater is characterized by dark color, high BOD, high COD, high pH and high dissolved salts. Therefore disposal of these wastewaters into water bodies or onto land can cause irreversible damage to the environment in the vicinity. The composite wastewater from a tannery is highly colored and cause foul smell. It is also alkaline with a high amount of suspended and dissolved impurities. In spite of the highly acidic nature of the spent chrome tan liquor and spent liquor, the total mixed wastewater of a tannery in most cases is alkaline, which is due to lime present in spent lime liquor in excessively high amount. Generally BOD of the composite wastewater varies from 2000 to 3000 mg/l. Table 1.1 shows approximate quantities of waste water generated and pollution load in different steps conducted to leather processing (Dixit et al., 2015) and Table 1.2 presents the characteristics of composite tannery effluent as reported in literature.

Table 1.1 Quantity of waste water generated and pollution load in different steps conducted to leather processing (Dixit et al., 2015)

Pollution load	**Leather processing operations load kg/tonne hide**					
	Soaking	**Unhairing /liming**	**Deliming and bating**	**Chrome tanning**	**Post tanning**	**Finishing**
Waste water generated (m^3)	9-12	4-6	1.5-2	1-2	1-1.5	1-2
COD	22-33	79-122	13-20	7-11	24-40	0-5
BOD	7-11	28-45	5-9	2-4	8-15	0-2
Suspended solids	11-17	53-97	8-12	5-10	6-11	0-2
Total Kjeldhal Nitrogen	1-2	6-8	3-5	0.6-0.9	0.3-0.5	-
Sulphides	-	3.9-8.7	0.1-0.3	-	-	-
Chlorides	85-113	5-15	2-4	40-60	5-10	-
Sulphates	1-2	1-2	10-26	30-55	10-25	-
Chromium	-	-	-	2-5	1-2	-

Table 1.2 Characteristics of composite tannery wastewater

pH	**TDS (mg/L)**	**TS (mg/L)**	**SS (mg/L)**	**VSS (mg/L)**	**COD (mg/L)**	**BOD (mg/L)**	**Chromium (mg/L)**	**Sulphide (mg/L)**	**Reference**
7.4	….	….	2690	1260	3700	1470	….	440	Apaydin et al., (2009)
7.08 ±28	….	10265 ±1460	2820 ±140	1505 ±90	4800 ±350	….	95 ±55	….	Ganesh et al., (2006)
7.08-8.7	13300-19700	….	600-955	….	4100-6700	630-975	11.5-14.3	….	Kongjao and Damronglerd, (2008)
….	15152	…..	2004	1660	8000	930	11.2	228	Koteswari and Ramanibai, (2003)

7.70	36800	….	5300	1300	2200	….	….	….	Lefebvre et al., (2005)
10.872	6810	….	….	….	11153.65	2906	32.87	507.5	Leta et al., (2004)
7.79	….	….	915	578	2155	….	50.9	35.8	Orhon et al., (2000)
10.5	17737	18884	1147	….	3114	1126	83	55.00	Ram et al., (1999)
7.7	….	….	….	….	2426	….	29.3	286	Szpyrkowicz et al., (2005b)
7.9-9.2	21620				2533	977	258	860	Mandal et al., (2010)

1.2.3 Methodologies for tannery wastewater treatment

The tannery effluent is conventionally treated using various physical, chemical and biological methods. The physico-chemical treatment of organic effluent consists of adsorption, coagulation, precipitation, flocculation, sedimentation, filtration, ion exchange and chemical oxidation. The biochemical methods include biodegradation, bio-sorption etc. Biological methods such as aerobic and anaerobic treatment techniques are suitable for degrading the organic present in TWE. Many advanced treatment technologies are being used in recent years, such as membrane based processes, advanced oxidation technologies such as Fenton’s reagent, photo catalytic oxidation and hybrid methods comprising of different AOPs and sonication techniques such as US and HC, in order to bring the treated water quality to the required discharge standards. The review on the various treatment technologies adopted for treatment of tannery wastewater with their advantages and disadvantages are described in section below

.1.2.3.1 Coagulation/flocculation

Coagulation has been traditionally used in tannery industry to reduce COD and suspended solids. The physico-chemical treatment technique of chemical flocculation has been widely practiced, particularly for the industrial wastewater with high organic-inorganic load, and is an indispensable part of any wastewater treatment plant. Coagulation is a process in which an external chemical is added into the wastewater solution having charged suspended particles. These chemicals neutralize the charged particle due to which large flocs are generated which evidently settles down in the form of sludge. Most of the frequently used coagulants generally fall into two categories i.e. aluminum based coagulant and iron based coagulant. The effectiveness of these coagulants mainly depends on their capability to form multi-charged polynuclear complexes, and cause the destabilization and neutralization of colloidal matter present in TWE. Some advantages of coagulation when used in pretreatment include minimum sludge formation during secondary treatment due to the removal of suspended solids, simplicity, cost effectiveness, and good removal efficiencies on an industrial level. However, coagulation/flocculation is a highly pH dependent process and its effectiveness mainly rest on the TWE characteristics to be treated (Song et al., 2004) and is not very effective for most of the recalcitrant waste produced in tannery processing. There are several studies on coagulation/flocculation of TWE that has been reported by many researchers (Ates et al., 1997; Lofrano et al., 2006; Song et al., 2004) and the extent of removal attained are summarized in Table 1.3. In table 1.3 coagulants such as ferrous sulphate, ferric chloride and alum have been primarily used for the treatment of raw tannery waste water. From the table it was observed that COD reduction is varied in the range of 30 % to 80 %. This deviation in COD reduction can be attributed to the nature of TWE and the additives which are used along with the coagulant to enhance the COD reduction. In the study reported by Ates et al., (1997), Kabdasli et al., (1999) and Lofrano et al., (2006)coagulant such as Ferrous sulphate, ferric chloride , alum and polyelectrolyte were used to treat raw and sulphide oxidized wastewater and more than 70 % COD reduction was observed. In the study reported by Haydar and Aziz, (2009) in which alum in combination with anaionic and cataoinic polymer was used as a coagualant for the treatment of raw tannery wastewater, resulted in a maximum COD reduction of 36.2% for alum+ anionic polymer and 48.3 % for alum+ cationic polymer.

Table 1.3 Studies on treatment of Tannery wastewater using coagulation

Coagulant	Type of wastewater	Initial characteristics	Removal	References
$FeS0_4.7H_20$, alum, $FeCl_3$ and with polyelectrolyte	Raw wastewater & sulphide oxidize wastewater	COD = 4183-6144 Cr= 125- 198 TSS = 2070-2640	COD 70-80% SS >90% Cr >98%	Ates et al., (1997)
$FeCl_3.6H_20$, $FeS0_4.7H_20$ and alum with anionic polyelectrolyte	Raw wastewater & sulphide oxidize wastewater	COD = 4480-5235 TKN= 295-325 Cr= 60-65	COD = 80% TKN = 80% Cr = 100%.	Kabdasli et al., (1999)
Aluminium sulphate and ferric chloride	Raw tannery wastewater	SS= 260±45 Cr = 16.8±2.3 COD= 3300±150	SS=38-46% COD = 30-37% Cr= 74-99%	Song et al., (2004)
Ferric chloride, ferrous sulphate, aluminium sulphate and polyaluminium ferric chloride (PAFC).	Raw tannery wastewater	COD=12415-14820 TSS=9660-10660	COD >75% TSS>95%	Lofrano et al., (2006)
Alum with cationic and anionic polymers	Raw tannery wastewater	Alum + cationic polymer Turbidity = 1184, Cr = 56.9 COD = 2700, TSS = 1078 Alum + anionic polymer Turbidity = 1302, Cr = 70.3, COD = 2480, TSS = 1104	Alum + cationic polymer Turbidity = 97%,TSS = 93.5%, TCOD = 36.2%Cr = 98.4% Alum + anionic polymer Turbidity = 99.7%, TSS = 96.3%, TCOD = 48.3%, Cr = 99.7%	Haydar and Aziz, (2009)
Aluminium sulphate hexadecahydrate (alum)	Raw tannery wastewater	Cr = 350 COD = 1250 BOD = 550 TS = 115,000	COD= 65% TS = 17% BOD =68% Cr = 34%	Dasgupta et al., (2015)

1.2.3.2 Biological Treatment

The biological treatment processes such as aerobic and anaerobic processes involve micro-organisms generally bacteria, fungi and nematodes to decompose organic content in wastewater through normal biological process. Biological treatment of wastewater is preferred worldwide over physical or chemical treatment process, due to its better effectiveness and more economic nature in comparison to most physico-chemical treatment methods. Biological approaches are the eco-friendly methods and involve the stabilization of waste by decomposing them into harmless inorganic solids either by aerobic or anaerobic processes. Biological treatments of tannery wastewater use the activated sludge process (ASP) and up flow anaerobic sludge blanket (UASB) process. In countries with a hot climate, aerobic treatments are used and where a lot of land is available, facultative (preferably aerated/facultative) lagoons are also used. Anaerobic treatments are generally used for sludge digestion of tannery effluents.

1.2.3.2.1 Aerobic treatment

The aerobic biological treatment is the process of biological degrading of organic pollutant by microbial action in the presence of oxygen. Aerobic treatment involves using open lagoon, activated sludge treatment, trickling filters and oxidation ditches. Continuous oxygen supply is required for biological degradation of organic waste; therefore in most of the cases diffusion based aeration system is utilized to maximize the air supply for proper functioning of helpful microorganisms. The reaction product of aerobic treatment process is carbon dioxide and large quantity of biomass. The general application of aerobic treatment process is for wastewater having low to medium organic load (i.e. COD < 1000 ppm). Aerobic treatment process is generally used for the treatment of municipal sewage waste, wastewater effluent from pulp and paper related industries and food processing unit such as meat processing industries. One of the main drawbacks involved in aerobic treatment process is the high power consumption by large air diffusers for the continuous aeration of aerobic treatment chamber. Several studies have been reported on the aerobic treatment of TWE using ASP by many workers (Kim et al., 2014; Noorjahan, 2014; Ramteke et al., 2010; Sharma and Malaviya, 2013; Sivaprakasam et al., 2008) and the reduction in COD/BOD attained in their studies are summarized in Table 1.4. The different classes of microorganisms which have been used for the treatment of TWE in their studies are also presented in Table 1.4. Studies reported by Kim et al., (2014),Noorjahan, (2014), Ramteke et al., (2010) and Sivaprakasam et al., (2008); for the treatment of TWE have shown more than 80% COD reduction. However , in the study reported by Nanda et al., (2010) the bacterial species Nostoc sp. was used for the treatment of TWE which caused only 37.8% reduction in COD. Sharma and Malaviya, (2013), used fungal species Aspergillus niger SPFS2-g for the treatment of TWE and reported 81.58% reduction in COD. Elmagd and Mahmoud, (2014) conducted a study using mixed culture and achieved more than 98% reduction in COD of TWE.

Table 1.4 Studies on treatment of Tannery wastewater using aerobic treatment

Microorganisms	Initial COD/ BOD	% COD removal	% BOD removal	References
Brachymonas denitrificans	COD = 4500-7700 BOD = 1800-2400	98.3	-	Kim et al., (2014)
Aspergillus niger	COD = 2637 BOD = 900	88.73	96	Noorjahan, (2014)
Aspergillus flavus		95.4	96.33	
Mixed culture	COD = 3250 BOD = 1690	98.3	98.4	Elmagd and Mahmoud, (2014)
Aspergillus niger SPFS2-g	COD = 5776±30.1	81.58	-	Sharma and Malaviya, (2013)
E. coli	COD = 2016±2 BOD= 1520±10	98.46	90	Ramteke et al., (2010)
Vibrio sp.		87.5	-	
Pseudomonas sp.		96.15	-	
P. aeruginosa, B. flexus, E. homiense, S. aureus	COD = 2512 BOD = 1484	80	-	Sivaprakasam et al., (2008)
Nostoc sp.	COD = 892±44.5 BOD = 740.1±36.2	37.8	57.5	Nanda et al., (2010)

1.2.3.2.2 Anaerobic treatment

In contrast to aerobic treatment process, AD process is carried out in the absence of oxygen. Anaerobic treatment process requires a closed chamber as absence of oxygen is a prerequisite for the treatment process, therefore to make the system free off oxygen gaseous nitrogen is purged through the anaerobic chamber containing organic waste. AD treatment is generally implemented in the case of wastewater with concentrated waste (with medium to high organic content (COD more than1000 ppm) which are easily biodegradable). The end product of AD in the reactor is the biogas which consists of methane and carbon dioxide with minute fraction of hydrogen and hydrogen sulphide along with active biomass. The methane produced during the anaerobic treatment method is of economic importance which reduces the overall operational cost of the treatment. In terms of total sludge produced during anaerobic treatment, it is relatively very less in comparison to aerobic treatment process. However, unlike aerobic treatment the effluent from anaerobic chamber needs to be treated prior to discharge in open environment. The anaerobic treatment of TWE is mainly performed by using either the anaerobic filters (AF) composed of Upflow anaerobic filters (UAF) and down-flow anaerobic filters (DAF) or Upflow Anaerobic Sludge Blanket (UASB) reactors (Dixit et al., 2015; El-sheikh et al., 2011; Lefebvre et al., 2006). Several studies reported on the treatment of TWE based on anaerobic treatment, are summarized in Table 1.5 and it was observed that upflow anaerobic reactor was the most preferred choice for the treatment of tannery wastewater. In the study carried by Lefebvre et al., (2006) and Banu et al., (2007), UASB and hybrid UASBR were used for the treatment of tannery wastewater, and 70±10.2 % and 86-88% reduction in COD was reported respectively. The increase in the COD reduction in the latter case can be attributed to hybrid approach and type of wastewater. In the study reported by Genschow et al., (1996)and Daryapurkar et al., (2001) a total 65% and 98% reduction in COD was observed for use of two stage UAF for the treatment of tannery wastewater.

Table 1.5 Studies on treatment of Tannery wastewater using anaerobic treatment

Reactor	Type of Wastewater	Initial COD	% COD Removal	References
UASB	Tannery soak liquor	2270	78%	Lefebvre et al., (2006)
UAFBR	Tannery wastewater	2762±490	70±10.2%	Song et al., (2003)
Hybrid UASBR	Tannery wastewater	16500	86-88%	Banu et al., (2007)
Two stage UAF	Tannery wastewater	900	98%	Daryapurkar et al., (2001)

Two stage UAF	Tannery wastewater	5710	65%	Genschow et al., (1996)

Many pretreatment strategies are also being adopted in order to increase the AD rate or for enhancing the biodegradability of organic pollutants by enhancing the rate of limiting steps of the digestion process mainly hydrolysis and acidogenesis reactions, thereby increasing the biogas yield. Low temperature thermal treatment is one of the pretreatment strategies for treating mixed sludge and sewage sludge studied by Ferrer et al., (2009) and Liao et al., (2016) respectively, and reported to be economical in terms of less energy required and having a promising scale up potential, however the high exposure time for waste treatment, limits its applicability for sludge treatment. High temperature thermal pretreatment approach such as hydrothermal treatment and steam explosion has been used for waste effluent and sludge treatment. Kepp et al., (2000) reported steam explosion at 165-180°C and Zabranska et al., (2006) reported steam explosion at 140°C for the pretreatment of mixed sludge which resulted in increased biogas production. Although the high temperature thermal treatment is easily scalable and eliminates sanitation problems, the high energy demand as well as the risk of recalcitrant formation in the dewatered biomass during the thermal process, limits its usage as a pretreatment strategy. Studies also report on application of electrochemical treatment (Yu et al., 2014), potassium ferrate oxidation (Wu et al., 2015) and ozonation (Cesaro and Belgiorno, 2013) as other pretreatment techniques for solid waste and mixed sludge used to increase the biogas production. Xie et al., (2007), Hogan et al., (2004), and Neis et al., (2008) reported on the application of sonication for the treatment of mixed sludge which resulted in increase in biogas production by AD. The increase in biogas generation was comparatively higher using US technology in comparison to all above mentioned pretreatment approaches, however the high operational costs and the low processing volumes in an US reactor system limits its use for large scale treatment. Another cavitation technique such as the HC exhibits similar effects as ultrasound, but its energy consumption is lower in comparison to ultrasound disintegration (Saxena et al., 2018a) and may be considered as a better effective approach for mineralization of organic contents in wastewater.

From the literature survey carried out, it was observed that conventional wastewater treatment techniques such as the physical methods of coagulation, precipitation, chemical methods of flocculation, adsorption/ ion exchange as well as the biological methods of aerobic and AD process have not been able to completely degrade or satisfactorily treat the tannery wastewater because of its complex nature. These treatment techniques are generally operated in combination such as physico-chemical (coagulation flocculation), physico-biological (open air lagoons) or bio-chemical (coagulation followed by aerobic/anaerobic treatment) processes. The aerobic and anaerobic treatment of industrial waste effluent is a potential alternative in comparison to inorganic treatment processes. However, the cost of operation is a major concern for the operational success of biological treatment processes. Therefore, AD has been in focus in treatment processes in comparison to aerobic process because it reduces the sludge volume along with the production of useful gases, most notably methane. In spite of the economic advantage of anaerobic treatment process, its application is restricted in TWE treatment due to varying pH range and presence of large quantity of recalcitrant compounds, therefore pretreatment of waste effluent is a prerequisite. Due to the limitations of the above chemical and biological treatment processes, alternative and advanced treatment technologies are necessary to be developed for the pretreatment of tannery effluent.

1.2.3.3 Advanced treatment methods

The TWE even after subjected to conventional treatment process still contains many refractory and recalcitrant organic pollutants (ROPs) and therefore, require further treatment for environmental safety. In recent years there has been a shift in the treatment approach of industrial waste effluent using different techniques such as membrane technologies (MTs) (Dixit et al., 2015; Lofrano et al., 2013), membrane bioreactor (MBR) (Dixit et al., 2015; Giulio Munz et al., 2008; Suganthi et al., 2013), and advanced oxidation processes (AOPs) such as Fenton's reagent, ozonation, UV/H_20_2, photo catalytic oxidation and electrochemical oxidation (Dixit et al., 2015; Naumczyk and Rusiniak, 2005; Schrank et al., 2005; Srinivasan et al., 2012) reported by many researchers.

1.2.3.3.1 Membrane Technology

Membrane treatment process of industrial waste is the mechanical separation technique by passing through semipermeable membranes, however presence of high concentrations of organic matter causes fouling of the pores of the membranes which is a major concern (Srinivasan et al., 2012; Stoller et al., 2013). To separate the toxic waste from wastewater, membrane technologies (MTs) are used which allows the separation/purification by passing through permeable membranes. One of the major advantages of MTs over some of the other purification techniques such as distillation, sublimation or crystallization is that MTs work without heating therefore resulting in low energy consumption. Recent studies by Labanda et al., (2009); Ranganathan and Kabadgi, (2011) indicate application of MTs for leather industries especially in chromium removal from TWE. In the study reported by Gallego-Molina et al., (2013), MTs was used for purification/reuse of wastewater and chemicals of deliming/bating liquor and also for the removal of salts (Lofrano et al., 2013). Several membrane-based technologies such as cross flow microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and supported liquid membranes (SLMs) are being used for the removal of pollutants from TWE (Dixit et al., 2015; Lofrano et al., 2013). Though MTs are well suited for the treatment of industrial waste effluent but clogging of membrane and high process cost are some major drawbacks associated with membrane based treatment techniques.

1.2.3.3.2 Membrane bioreactor

A membrane bioreactor (MBR) is the combination of a membrane process like microfiltration or ultrafiltration with a suspended growth bioreactor, which is widely used for treating municipal and industrial wastewater. MBRs are much more efficient in comparison to Activated sludge process (ASPs) in terms of less or no sludge formation and also no effect of bulking which may affect process performance (Dixit et al., 2015; G Munz et al., 2008; Suganthi et al., 2013). The presence of tannins in TWE reduces the kinetics of nitrification without large differences between the biomass selected with either the conventional activated sludge treatment process (CASTP) or the MBR used (Munz et al., 2009).

In all these studies on the conventional methods of TWE treatment used such as coagulation, adsorption and membrane-based techniques resulted only in the concentration or accumulation of the toxic waste with no degradation. On the other hand the biological treatment method caused degradation of the organic waste, however most of the toxic elements present in tannery wastewater as well as intermediates formed during the biological degradation process hindered the biological treatment processes. Therefore, advanced oxidation methods are being studied for the treatment of recalcitrant compounds present in tannery wastewater which are not readily biodegradable in order to break the complex biomolecules into simpler forms.

1.2.3.3.3 Advanced oxidation processes

In advanced oxidation processes, strong oxidizing agents such as hydrogen peroxide, ozone, hypochlorite, and Fenton's reagent are used to generate hydroxyl radicals that cause the disintegration of complex and recalcitrant organic content. AOPs are more cost effective and environment friendly methods for the treatment of toxic waste materials. Treatment of waste is carried out through the hydroxyl radicals produced by oxidizing agent, which attacks the molecules of waste effluents and breaks it into simpler form. The hydroxyl radicals utilized in AOPs are produced by use of one of the following methods using Fenton's reagent, Ozonation, UV/H_20_2, photo catalytic oxidation, cavitation and electrochemical treatment. In recent year's various hybrid treatment approaches such as sonication in combination with different AOPs are also being studied for the treatment of complex industrial waste effluents (Bagal and Gogate, 2014; Rajoriya et al., 2018). As TWE comprising of many bio-refractory compounds which are recalcitrant in nature as well as with high concentration of harsh and toxic chemicals, advanced treatment techniques such as advanced oxidation using cavitation, sonolysis, Fenton's process, electrooxidation or photocatalytic methods etc., or in combination of above processes may be more effective in mineralization of the complex molecules. There are several studies reported on treatment of TWE based on advanced oxidation processes using Fenton's reagent, ozonation, UV/H_20_2, photo catalysts and electrochemical treatment which are presented in Table 1.6.

In Fenton based oxidation process, reaction between ferrous ion (Fe^{+2}) and H_2O_2 produces hydroxyl radicals and the ferric ion which further reacts with H_2O_2 to produce more highly reactive oxy-hydroxyl radicals and these hydroxyl radicals oxidize the organic pollutants present in waste effluent. Dantas et al., (2003) conducted a study in which Fenton reagent was used to treat the raw tannery wastewater of COD 1803 mg/L and achieved 70% COD removal within 20 min at pH 2.5. In the study reported by Lofrano et al., (2007), ~~synthetic~~ solution of synthetic tannins and oils was also treated with Fenton reagent and more than 80% COD reduction was attained in case of synthetic tannins and 95% reduction in COD was observed in case of oils. Though Fenton process was successfully applied at the laboratory or small scale, the high cost of chemical reagents used in this treatment technique limited its application on an industrial scale.

Ozone also has a potential to oxidize the organic as well inorganic pollutants present in waste effluent. The reactivity of ozone mostly depends on the nature of pollutants present in waste effluent (Pang et al., 2011) and it has higher capability to oxidize organic compounds such as unsaturated hydrocarbons, aromatic rings etc. as well as to oxidize inorganic compounds such as sulfides etc. In ozonation process, ozone either directly reacts with organic molecules or it gets dissociated into hydroxyl radicals which have higher oxidation potential than ozone. In studies reported by Houshyar et al., (2012), Di Iaconi et al., (2010), Preethi et al., (2009) and Dogruel et al., (2004), ozonation was used for the treatment of different types of TWE. Di Iaconi et al., (2010) and Dogruel et al., (2004) treated the biologically treated tannery wastewater using ozone as the oxidizing agent and achieved 30% reduction in COD. Houshyar et al., (2012) treated the pre-alkalized tannery wastewater using ozone and achieved maximum 70% reduction in COD over a time period of 120 minutes. Whereas Preethi et al., (2009) applied the ozonation process for diluted raw TWE of 2000 mg/L COD over a period of 120 minutes and reported the maximum of 70% COD removal at pH of 11 for an ozone flow rate of $6\times10^{-3}m^3min^{-1}$.

Photo catalytic oxidation process has gained a large interest in past few decades in the area of wastewater treatment due to its ability to mineralize the complex recalcitrant molecules at room temperature and pressure conditions. The major characteristics of photocatalytic reactions are production of free radicals which are produced by the interaction of photons with dissolved gases and water molecule present in the solution. One of the major advantage of photo-catalytic oxidation process is the possibility of using sunlight or near UV light for photochemical activity, which can make treatment process more cost effective (Han et al., 2012; Konstantinou and Albanis, 2004). Schrank et al., (2004) conducted the study for the treatment of coagulated TWE with inlet COD of 2365 mg/L using TiO_2 as a photo catalyst in presence of UV and observed 6% and 11% reduction in COD and TOC respectively at pH 3. In the same study it was reported that maximum 15% of BOD was removed at pH 7. Sauer et al., (2006) also conducted the study for the treatment of coagulated TWE using UV/H_2O_2 in which initial COD was varied in the range of 200-800 mg/L. They treated 2 L of coagulated TWE using 80W high pressure mercury vapor lamp and varying concentration of H_2O_2 and reported maximum 60% reduction in COD at 0.5 g/L H_2O_2 concentration in 4 h of treatment. In a study of combination of Fenton reagent and UV radiation used as a treatment technique for equalized TWE of 11,878 mg/L COD, it is reported that 90% removal in COD and 50% removal in TSS (Modenes et al., 2012) was obtained. The effective use of sunlight for UV irradiation could be a major advantage in this treatment technique due to which it reduces the operating cost of the plant and can be implemented on industrial scale. However, photo catalytic oxidation has a limited application for the treatment of TWE, such as lower efficiency in case of the slurry treatment as solid particle interferes the light and also use of UV irradiation makes the process highly energy intensive which results into the increased operational cost.

Use of electricity for the water treatment process has been traced back to 1889 in UK. However, its industrial application as electrochemical reactors for metal recovery from pollutant of metal plating industry was applied only in 1960s (Szpyrkowicz et al., 2001). Although in earlier times its application were limited due to high capital cost, but recent developments in this field have made the process more cost efficient in comparison to other technologies (Sundarapandiyan et al., 2010). Kurt et al., (2007) used the electrochemical oxidation process for treating the raw TWE using iron electrodes with 840 mg/L H_2O_2 dose and observed the 70% COD reduction at pH 3 within 10 minutes. Sengil et al., (2009) used the two different electrodes for the treatment of tannery liming wastewater and observed the mild iron electrode was more efficient as compared to aluminum electrodes. In case of mild iron electrodes maximum 82% COD was removed whereas in case of aluminium electrodes only 62% COD was removed at optimized conditions. The electrochemical oxidation process is highly dependent on the electrode used and treatment conditions (Costa et al., 2008). Due to high saline condition of tannery waste water, it is a perfect candidate for direct and indirect electro-oxidation process (Costa et al., 2008; Sundarapandiyan et al., 2010; Szpyrkowicz et al., 2001). It has been reported in literature that the kinetics of electrochemical process is 100 times faster than biological oxidation process (Lofrano et al., 2013).

Table 1.6 Studies on treatment of Tannery wastewater using AOPs

AOPs	Type of Wastewater	Initial COD/TOC	Reduction in pollutants	Conditions	References
Fenton reagent	Raw tannery wastewater	1803	COD = 70%	Time= 20 min pH=2.5 Volume = 500 mL Fe^{2+} =1.0 g/L H_2O_2= 15 g/L	Dantas et al. (2003)
Ozone	Biologically treated wastewater,	835	COD = 30%	Time = 50 min O_3 = 42.8 mg/min	Dogruel et al. (2004)
Photocatalysis (UV/TiO_2)	Coagulated/flocculated tannery wastewater	2365	COD = 6% , TOC = 11%,	Time = 2 h pH = 3 TiO_2 = 1 g/L 15 W mercury lamp	Schrank et al. (2004)
UV/H_2O_2	Coagulated tannery wastewater	200-800	COD = 60%	Time = 4 h H_2O_2 = 0.5 g/L pH = 2.5 80 W mercury lamp	Sauer et al. (2006)
Fenton	~~Synthetic~~ solution of synthetic tannins(ST) and oils	300	ST: COD = 80-90% Oils: COD = 95%	Time = 30 min ST: pH =3 H_2O_2 = 600 Fe^{2+} = 500 Oils: pH =3 H_2O_2 = 600 Fe^{2+} = 750	Lofrano et al. (2007)
Electrochemical treatment	Raw tannery wastewater	2810	COD = 70%	Electrodes = Iron Area = 45 cm^2 pH = 3 Time 10 min Electric power = 15 W H_2O_2 = 840 mg/L	Kurt et al. (2007)
Electrochemical	Equalized tannery	1005	TOC = 40.5%	Time = 5 h	Costa et al. (2008)

treatment	wastewater		Phenol = 83.9%	Current density = 100 mA/cm^2	
Electrochemical treatment	Tannery liming drum waste water	25300	COD = 62% (aluminium electrode) COD = 82% (MS electrode)	Time = 10 min Current density = 35 mA/cm^2 pH = 3	Sengil et al. (2009)
Ozone	Diluted raw tannery waste water	2000	COD = 70%	Time = 90 min pH = 11 $O_3 = 6\times10^{-3}$	Preethi et al. (2009)
Electrochemical treatment	Synthetic tannery waste water	10715	COD = 89%	Time = 120 min Salt (NaCl) = 30 g/L pH = 9 Current density = 12 mA/cm^2	Sundarapandiyan et al. (2010)
Ozone	Biologically treated tannery wastewater	2900	COD = 97% TSS = 96% TKN = 91%	Time = 60 min O_3= 150 g/m^3	Di Iaconi et al. (2010)
Photo-Fenton (UV/Fe^{2+}/H_2O_2)	Equalized tannery wastewater	11878	COD = 90% TSS = 50%	Irradiation time = 540 min Fe^{2+} = 0.4 g/L H_2O_2 = 15 g/L	Modenes et al. (2012)
Ozone	Pre-alkalized tannery wastewater	2177	COD = 70%	pH = 6 & 9 Time = 120 min O_3 = 8 g/h	Houshyar et al. (2012)

1.2.3.3.4 Cavitation

Cavitation is one of the emerging techniques for the treatment of bio-refractory pollutants present in wastewaters in the last few decades (Gogate and Pandit, 2004a). Cavitation is the process of formation of bubbles/cavities in the liquid medium and their subsequent growth and collapse occurring within a very short span of time with high energy release which results in the creation of localized 'hot spots' in the aqueous medium. These act as centers for the formation of $^{\bullet}OH$, $^{\bullet}H$, $HO^{\bullet}_2$ radicals and H_2O_2 which cause the degradation of the pollutant molecules (Rajoriya et al., 2016). Fig. 1.2 presents the general phenomenon of cavity formation, growth and subsequent collapse of bubble in a liquid medium. Cavitation may occur through the formation of bubbles or cavities in the liquid or it can be a result of the enlargement of cavities that are already present in the bulk liquid. These bubbles are suspended in liquid or may be trapped in tiny cracks in the liquid-solid interface for a miniscule time period before they collapse in the liquid medium.

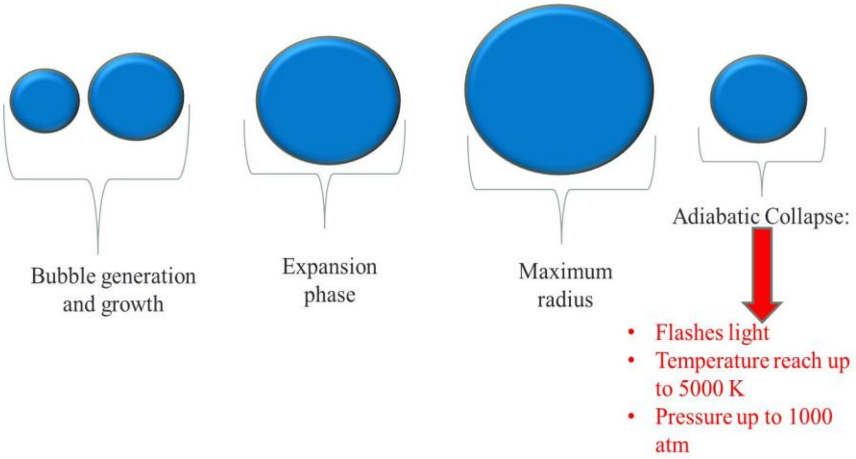


Fig. 1.2 Cavity formations, growth and subsequent collapse of bubble in a liquid medium

Different types of cavitation are classified on the basis of the method of cavity production. The four different type of cavitation are described as follows (Gogate and Pandit, 2001):

- HC which takes place due to the pressure fluctuations in the fluid flowing through mechanical constrictions such as venturi and orifice.

- Acoustic cavitation also known as US occurs due to the pressure variation when sound waves pass through the liquid medium.
- Optic cavitation occurs due to the rapture of liquid when high intensity light passes through a liquid medium.
- Particle cavitation is produced by any type of elementary particle such as a proton, neutron, etc. rupturing a liquid, as in a bubble chamber.

Out of these four types of cavitation, only hydrodynamic and acoustic cavitation generates the desired conditions which are required to degrade organic molecules present in liquid medium. The basic degradation mechanism of organic pollutants for both the processes (HC and US) is based on the production of free radicals. The organic pollutants present in wastewater can be oxidized by reactive species ($^{\bullet}OH$, $^{\bullet}H$, $HO_2^{\bullet}$, and also H_2O_2) generated during the cavitation process. The reactions involved during oxidation of organic molecules during cavitation are as follows: (Rajoriya et al., 2016),

$$H_2O \xrightarrow{\text{Cavitation}} H^{\bullet} + HO^{\bullet}$$

$$^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2$$

$$^{\bullet}OH + \text{organic molecules} \rightarrow CO_2 + H_2O + \text{some intermediates}$$

Hydrodynamic cavitation (HC):

HC occurs in a flowing liquid by pressure gradients caused by the geometrical variations as well as due to velocity fluctuations in the fluid system. It is generated when the liquid passes through a mechanical constriction such as venturi, orifice, or valve etc. As the liquid passes through a constriction, the pressure head gets converted into kinetic head under the effect of reduced area and as a result the kinetic energy of the liquid increases. Under sufficient throttling, the local pressure at the vena contracta falls below the threshold pressure i.e. vapour pressure of the liquid at the operating temperature and liquid gets vaporized which result in formation of number of cavities (Rajoriya et al., 2016). These generated cavities are further collapsed when pressure of the downstream section of cavitating device recovers. The pressure variation in flowing liquid due to change in flow area of the cavitating device is shown in Fig 1.3. The cavity collapse occurring within a very short period of time with high energy release results in the creation of localized ‘hot spots’ in the aqueous medium where temperature and pressure can rises up to 5000 K and 1000 atm respectively. These hot spot act as centers for the formation of $^{\bullet}OH$, $^{\bullet}H$, $HO^{\bullet}_2$ radicals and H_2O_2 that cause the degradation of the pollutant molecules.

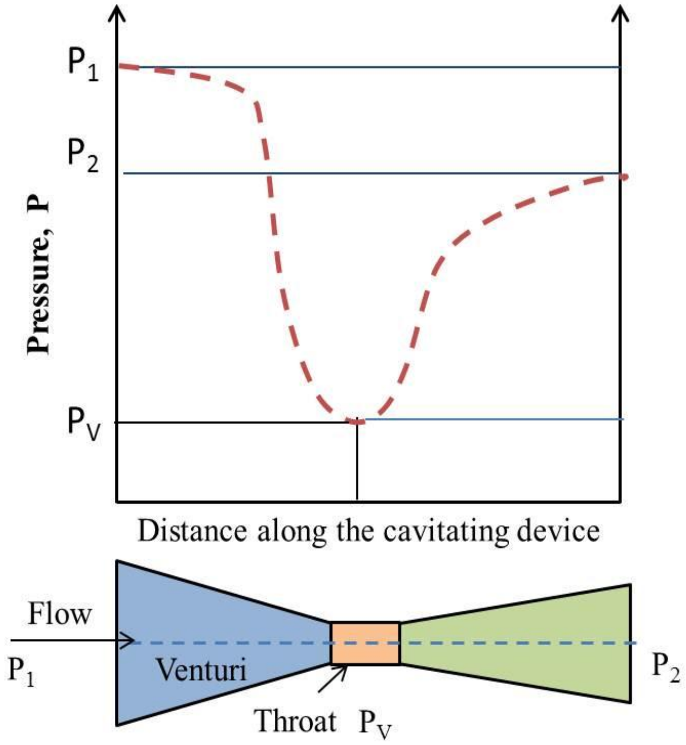


Fig. 1.3 Mechanism of HC

Various studies based on HC treatment of waste effluents containing different organic pollutants are summarized in Table 1.7.Joshi and Gogate, (2012), Patil et al., (2014), Bagal and Gogate, (2013), and Gogate and Patil, (2015) conducted the different studies for the degradation of different pesticides such as Dichlorvos, Imidacloprid, 2,4-dinitrophenol and Triazophos respectively using HC as the treatment technique. They observed that HC had the potential to degrade these bio-refractory pollutants and achieved 16%, 23.85%, 12.4% and 50% reduction in Dichlorvos, Imidacloprid, 2,4-dinitrophenol and Triazophos respectively. HC was also used for the degradation of Rhodamine B in which 59.3% reduction was observed for an initial concentration of 10 ppm at 4.8 atm HC operating pressure and pH of 2.5 over a process period of 2 h (Mishra and Gogate, 2010). Another study reported by Barik and Gogate, (2016), where reduction of 4-chloro 2-aminophenol using HC was investigated and observed that concentration of 4-chloro 2-aminophenol reduced by 24.6 % at 4 bar operating inlet pressure and pH of 6 in a 120 minutes. HC has not been used for treating TWE; however studies, reported in the literature indicate that HC has potential to degrade the organic molecule.

Table 1.7 Studies based on % reduction in organic pollutant concentration using HC treatment

Pollutant	Initial concentration	% Reduction	Operating conditions	Reference
2,4-dinitrophenol	20 ppm	12.4	Pressure = 4 bar Time = 120 min pH = 4 Device = orifice plate	Bagal and Gogate, (2013)
4-chloro 2-aminophenol	20 ppm	24.6	Pressure = 4 bar Time = 120 min Device = orifice plate pH = 6	Barik and Gogate, (2016)
potassium ferrocyanide (K4Fe(CN)6)	20 ppm	44.02	Pressure = 6 bar Time = 120 min Device = venturi pH= 2	Jawale et al., (2014)
Triazophos	20 ppm	50	Pressure = 5 bar Time = 120 min Device = orifice plate pH = 3	Gogate and Patil, (2015)
Imidacloprid	20 ppm	23.85	Pressure = 4 bar Time = 120 min Device = venturi pH = 3	Patil et al., (2014)
Dichlorvos	20 ppm	16	Pressure = 5 bar Time = 60 min pH = 3 Device = orifice plate	Joshi and Gogate, (2012)
Rhodamine B	10 ppm	59.3	Pressure = 4.8 bar Time = 120 min Device = venturi pH = 2.5	Mishra and Gogate, (2010)
Imidacloprid	25 ppm	26.5	Pressure = 15 bar	Raut-jadhav et al.,

			Time = 120 min pH = 2.7 Device = venturi	(2013)
P-nitrophenol	5 g/L	53.4	Pressure = 2.93 bar Time = 90 min Device = venturi	Pradhan and Gogate, (2010a)
Methyl parathion	20 ppm	44	Pressure = 4 bar Time = 120 min Device = orifice plate	Patil and Gogate, (2012)
Chlorpyrifos	0.11 ppm	72.7	Pressure = 5 bar Time = 60 min Device = orifice plate pH = 3	Randhavane and Khambete, (2017)

Acoustic cavitation (Ultrasonication (US)):

In US, cavitation occurs due to the high-frequency sound waves i.e. ultrasound spectra ranging from 16 kHz to 100 MHz passing through the liquid medium. The general mechanism of the US is defined by two terms known as compression and rarefaction as shown in Fig. 1.4. The sequential effect of rarefaction and compression cycle results in the formation of bubbles i.e., known as cavities, their growth and finally their collapse (Rajoriya et al., 2016). Rarefaction is a phenomenon during which the negative acoustic pressure becomes so high that it can separate liquid molecules. During this phenomenon as the distance between two adjacent molecules exceed from the critical molecular distance, cavities are formed by utilizing the void area between the separated molecules. When the negative acoustic pressure becomes positive, compression of the liquid molecules takes place and at this moment cavities are forced to constrict. The collapse phase of cavitation is adiabatic in nature and at the time of collapse the local temperature and pressure rises up to 5000 K and 1000 atm respectively which provides energy spots on a time scale for the various chemical and physical transformations. Under the effect of these energy spots the promptness of the processes could be increased, the yield of the process can be enhanced, reaction mechanism can be altered and cause positive feasibility of the process: even in the mild conditions.

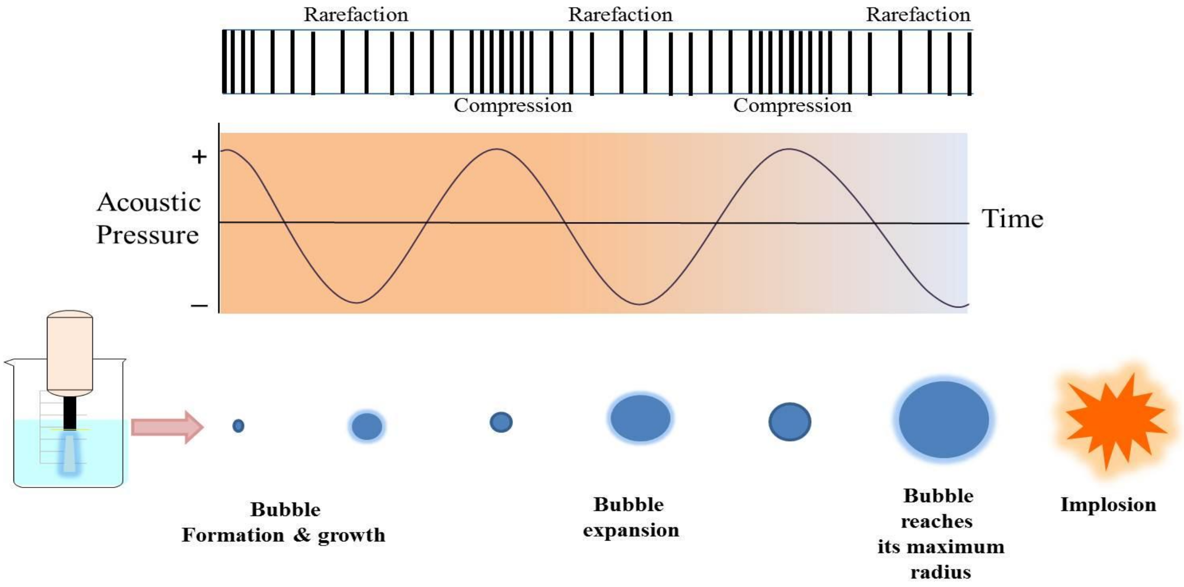


Fig. 1.4 Mechanism of acoustic cavitation

Many studies reported on the use of US process for the destruction of complex organic molecules present in wastewater, which is highly desirable due to its capacity of producing high intensity ultrasonic waves (Pang et al., 2011). Recent literature report indicated that US is capable of degrading recalcitrant matter such as organic dyes (Priya and Madras, 2006; Wang et al., 2011; Zhang et al., 2007), phenolic compounds (Liu et al., 2009), pesticides (Wang et al., 2007, 2006), aqueous carbon tetrachloride (Francony and Pctrier, 1996), benzene compounds (Nanzai et al., 2009), herbicides (Bahena et al., 2008), polycyclic aromatic hydrocarbons (David, 2009) and chloro-aromatic compounds etc. (Ku et al., 2005; Lim et al., 2008). Table 1.8 present the various studies in which different organic pollutants have been removed using US techniques. Bagal and Gogate, (2012) conducted the study for the degradation of Alachlor which is used as herbicides using US and reported that at pH of 3, 86.4% alachlor concentration was reduced using US. Degradation of different pesticides such as Carbofuran, methyl parathion and 2,4-dinitrophenol was studied using US in different studies conducted by Ying Shih et al., (2010), Shriwas and Gogate, (2011) and Guo et al., (2005) respectively and have reported 22%, 10.2% and 23.5% reduction in their pollutant concentrations respectively. In a study conducted by Neppolian et al., (2002) for the degradation of methyl tert-butyl ether (MTBE) which is widely used as a gasoline additive, almost 84% reduction was achieved from an initial MTBE concentration of 2.84×10^{-2} mM/150mL over a period of 5 h using US as the degradation technique. Use of US for degradation of tannery waste has not been reported so far.

Table 1.8 Studies based on % reduction in organic pollutant concentration using US

Pollutant	**Initial concentration**	**% Reduction/ Removal**	**Operating conditions**	**Reference**
Alachlor	20 ppm	86.4	Time = 120 min pH = 3 frequency = 20 kHz power = 100 W	Bagal and Gogate, (2012)
Methyl parathion	20 ppm	10.2	Time = 60 min pH = 2.5 frequency = 20 kHz power = 270 W	Shriwas and Gogate, (2011)
Methyl tert-butyl ether	2.84×10^{-2} mM/150 mL	84	Time = 5 h pH = 5.8 frequency = 20 kHz	Neppolian et al., (2002)
p-nitrophenol	0.5% (w/V)	48.3	Time = 90 min pH = 3.7 frequency = 20 kHz power = 1 kW	Pradhan and Gogate, (2010b)
Carbofuran	20 mg/L	22	Time = 120 min pH = 3 frequency = 20 kHz power = 300 W	Ying Shih et al., (2010)
2,4-dinitrophenol	20 mg/L	23.5	Time = 4 h Frequency = 20 kHz Power = 800 W	Guo et al., (2005)

1.2.3.4 Hybrid treatment methodologies

In the previous section, various treatment approaches applied for TWE and various kind of organic matter have been discussed. However, these treatment approaches have some serious limitations that still need to be addressed. From the treatment techniques, it’s evident that no individual system is simple and efficient enough for complete treatment of the tannery waste. In case of aerobic treatment, the high concentration of poorly biodegradable compounds such as tannins and toxic metals inhibit the biological treatment processes (Schrank et al., 2004). Application of anaerobic treatment process on a full scale approach had a number of shortcomings such as i) Regular synthesis of sulfide due to reduction of sulfate, acted as electron acceptors in the absence of oxygen and nitrates; ii) presence of large concentration of protein in waste hindered biomass processing in anaerobic reactor, hindered reaction kinetics, and hence inhibited sludge formation, and iii) further treatment of anaerobically treated waste was required in order to achieve permissible COD limit (Mannucci et al., 2010). Some of the major drawbacks of membrane based processes are the significant fouling due to clogging, adsorption and formation of cake layer by pollutants like residual organics, dyes, and other impurities onto the membrane (Srinivasan et al., 2012; Stoller et al., 2013). Some of the above processes may not be economically feasible because of high costs that are required and the lack of expertise required to implement and sustain such processes. If the treatment process is too long, it becomes non-feasible for treating huge amount of waste generated. In large scale treatment process high chemical cost of Fenton reagent is one of the major concern and drawback of this process. In case of photo catalytic oxidation process, particle hindrance and high energy demand limits its application for the treatment of waste effluent. The electrochemical process require both electricity as well as chemical reagents which results in high operational cost. It has been mentioned in literature that when HC or US alone have been applied for the treatment of waste effluent, both have a low efficiency for the treatment of organic pollutant. Therefore, to overcome these drawbacks combination of different treatment techniques is preferred to treat TWE effectively. Several studies have been reported where hybrid treatment approaches are used for the treatment of TWE. A study reported by Suganthi et al., (2013) where hybrid membrane bioreactor was used in combination with electrocoagulation and activated sludge process was used for the removal of COD and color present in TWE. In two different studies, activated carbon adsorption used in combination with coagulation and MBR for the treatment of tannery wastewater by Ayoub et al., (2011) and Munz et al., (2007). Furthermore studies conducted by Mandal et al., (2010), Srinivasan et al., (2012) and Szpyrkowicz et al., (2005a) where biological treatment was used with different oxidation processes such as Fenton oxidation, ozonation and electrochemical treatment respectively. These different studies reported for the treatment of tannery wastewater observed that combination of different treatment approaches enhanced the degradation of organic pollutants present in TWE and resulted in effective and significant treatment techniques. Therefore, it is evident that hybrid combinations of various advanced processes such as cavitation with coagulation or with different AOPs as well as AD may be used for the effective treatment of TWE.

1.2.3.5 Cavitation based hybrid oxidation methods:

Application of cavitation (HC & US) and cavitation based hybrid oxidation techniques have been reported to increase the biodegradability index and reduce toxicity of pollutant present in wastewater and could be applied as a pretreatment tool (Padoley et al., 2012; Rajoriya et al., 2018).

1.2.3.5.1 Cavitation coupled with hydrogen peroxide (H_2O_2):

Several studies report that addition of hydrogen peroxide (H_2O_2) during the cavitation process enhanced the degradation efficiency of cavitation to degrade organic molecules. Under the hot spot conditions during cavitation, H_2O_2 dissociates into hydroxyl radicals ($^{\bullet}OH$) and increases the quantum of $^{\bullet}OH$ radicals which significantly enhance the degradation process. It was also observed that when H_2O_2 was present in excessive amounts, it could also act as a scavenger for the $^{\bullet}OH$. Then reactions involved during the process of cavitation coupled with H_2O_2 are as follows: (Rajoriya et al., 2016):

$$H_2O_2 \xrightarrow{\text{Cavitation}} 2\,^{\bullet}OH$$

$$H_2O \xrightarrow{\text{Cavitation}} {}^{\bullet}H + {}^{\bullet}OH$$

$$^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2$$

$$^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O$$

$$^{\bullet}OH + HO_2^{\bullet} \rightarrow H_2O + O_2$$

$$HO_2^{\bullet} + H_2O_2 \rightarrow {}^{\bullet}OH + H_2O + O_2$$

$$^{\bullet}OH + \text{organic molecules} \rightarrow CO_2 + H_2O + \text{some intermediates}$$

Numerous studies as presented in Table 1.9 show the combined effect of HC + H_2O_2/ US + H_2O_2 on the degradation of various organic pollutants (Bagal and Gogate, 2013, 2012; Patil et al., 2014; Raut-Jadhav et al., 2013; Ying Shih et al., 2010). Bagal and Gogate, (2013) studied the combined effect of HC with H_2O_2 for the degradation of 2, 4-dinitrophenol (DNP). The degradation of DNP increased with increase in H_2O_2 concentration till an optimum ratio of 1:5 for DNP: H_2O_2 at constant inlet pressure of 4 bar in 120 minutes. Further increase in molar ratio of DNP: H_2O_2 did not enhance the degradation rate due to scavenging effect of H_2O_2 and maximum 21.3% degradation of DNP was observed. Whereas in case of HC alone only 12.4% degradation in DNP concentration was attained. Patil et al., (2014) observed almost complete degradation of Imidacloprid using combination of HC with 80 mg/L dose of H_2O_2 at pH 3 in 120 minutes of treatment. Mishra and Gogate, (2010) examined the combined effect of HC + H_2O_2 on the degradation of Rhodamine B and observed almost complete degradation of Rhodamine B occurred using HC at 4.84 atm inlet pressure and 200 mg/L dose of H_2O_2 at pH 2.5.

US also showed significant synergistic effect on the degradation of organic pollutant as presented by HC. In a study conducted by Ying Shih et al., (2010), using the combination of US with H_2O_2 for the degradation of Carbofuran, it was observed that reduction in Carbofuran increased with increase in concentration of H_2O_2. Maximum 44% reduction in Carbofuran with 20% reduction in TOC was attained within 120 minutes at optimum dose 200 mg/L of H_2O_2. Further increase in H_2O_2 dose decreased the degradation of Carbofuran due to the H_2O_2 at higher concentrations beyond the optimum dose, acting as a scavenger. Bagal and Gogate, (2012) observed almost complete degradation of Alachlor using US + H_2O_2 as the combined treatment approach. Since this treatment approach significantly enhanced the degradation rate of organic pollutants and increased the efficiency of treatment process, hence it could be better solution for the treatment of more complex waste effluents like TWE.

Table 1.9 Studies based on % reduction in organic pollutant concentration using HC/US + H_2O_2

Treatment method	**Pollutant**	**Initial concentration**	**% Reduction**	**Operating conditions**	**Reference**
HC + H_2O_2	2,4-dinitrophenol	20 ppm	21.3	Pressure = 4 bar, Time = 120 min pH = 4, Device = orifice plate H_2O_2 = 100 mg/L	Bagal and Gogate, (2013)
HC + H_2O_2	Potassium ferrocyanide ($K_4Fe(CN)_6$)	20 ppm	51.29	Pressure = 6 bar, Time = 120 min Device = venturi, pH= 2 $K_4Fe(CN)_6$:H_2O_2 (mol:mol) = 1:5	Jawale et al., (2014)
HC + H_2O_2	Imidacloprid	20 ppm	99.14	Pressure = 4 bar, Time = 120 min Device = venturi, pH = 3 H_2O_2 = 80 mg/L	Patil et al., (2014)
HC + H_2O_2	Dichlorvos	20 ppm	17	Pressure = 5 bar, Time = 60 min pH = 3, Device = orifice plate H_2O_2 = 16 ppm	Joshi and Gogate, (2012)
HC + H_2O_2	Rhodamine B	10 ppm	99.3	Pressure = 4.8 bar, Time = 120 min pH = 2.5, Device = venturi H_2O_2 = 200 mg/L	Mishra and Gogate, (2010)
HC + H_2O_2	Imidacloprid	25 ppm	100	Pressure = 15 bar, Time = 45 min Device = venturi, H_2O_2 = 3.91 mmol/L	Raut-jadhav et al., (2013)
US + H_2O_2	Alachlor	20 ppm	98.6	Time = 120 min, pH = 3 frequency = 20 kHz, power = 100 W H_2O_2 = 0.2 g/L	Bagal and Gogate, (2012)
US + H_2O_2	Methyl parathion	20 ppm	15	Time = 60 min, pH = 2.5 frequency = 20 kHz, power = 270 W H_2O_2 = 200 ppm	Shriwas and Gogate, (2011)
US + H_2O_2	Carbofuran	20 mg/L	44	Time = 120 min, pH = 3, frequency = 20 kHz, power = 300 W H_2O_2 = 200 mg/L	Ying Shih et al., (2010)

1.2.4.5.2 Cavitation coupled with ozone (O_3):

Ozone being a strong oxidising agent has a higher oxidation potential than H_2O_2 and Fenton reagent, and therefore it can be easily coupled with cavitation for enhanced degradation of organic pollutants. Under the mechanical effect of cavitation, ozone gets easily dispersed into the bulk of the liquid solution which result in an increase in the mass transfer rate of ozone from gas phase to bulk solution and also generates extreme conditions of hot spots as it easily dissociates into $^{\bullet}OH$ radicals. During the cavitation, ozone disintegrated into molecular oxygen and atomic oxygen ($O(^3P)$) which further reacts with water molecules and produces $^{\bullet}OH$. Reactions involved during the process of cavitation coupled with ozone are as follows (Rajoriya et al., 2016):

$$O_3 \xrightarrow{\text{Cavitation}} O_2 + O(^3P)$$

$$H_2O \xrightarrow{\text{Cavitation}} {}^{\bullet}H + {}^{\bullet}OH$$

$$O(^3P) + H_2O \rightarrow 2\,{}^{\bullet}OH$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2$$

$${}^{\bullet}OH + \text{organic molecules} \rightarrow CO_2 + H_2O + \text{some intermediates}$$

The hybrid treatment approach combining HC/US with ozone had been used by many researchers for the degradation of organic pollutants (Barik and Gogate, 2016; Gogate and Patil, 2015; Guo and Feng, 2009; Randhavane and Khambete, 2017; Song et al., 2007) and are as presented in Table 1.10. Barik and Gogate, (2016) investigated the synergistic effect of combined HC + ozone treatment technology for the degradation of 4-chloro 2-aminophenol. It was observed in the study that hybrid treatment methodology enhanced the degradation rate of 4-chloro 2-aminophenol and in combined treatment of 4-chloro 2-aminophenol 73.38% degradation was obtained whereas in case of HC alone, maximum 24.6% reduction was observed. Gogate and Patil, (2015) and Randhavane and Khambete, (2017) had also used the hybrid methodology combining HC + Ozone for the degradation of Triazophos and Chlorpyrifos respectively in their individual study. Both had observed the complete degradation of their respective pollutant using combined treatment whereas only 50% and 72.7% degradation of Triazophos and Chlorpyrifos respectively using HC alone. As combination of HC + Ozone, combination of US + Ozone also showed the same synergistic effect. Song et al., (2007) conducted the study for the degradation of p-nitrotoluene using combination of US + ozone and 85% reduction in TOC was observed using hybrid methodology whereas only 8% reduction in TOC was observed using US alone. In a different study Bisphenol A completely degraded by using US + Ozone whereas in the same study only 34.6% degradation was observed using US alone (Guo and Feng, 2009).

Table 1.10 Studies based on % degradation of organic pollutant using HC/US + Ozone

Treatment method	**Pollutant**	**Initial concentration**	**% Reduction**	**Operating conditions**	**Reference**
HC + Ozone	4-chloro 2-aminophenol	20 ppm	73.38	Pressure = 4 bar Time = 120 min Device = orifice plate pH = 6 O_3 = 400 mg/h	Barik and Gogate, (2016)
HC + Ozone	Triazophos	20 ppm	100	Pressure = 5 bar Time = 90 min Device = orifice plate pH = 3 O_3 = 1.95 g/h	Gogate and Patil, (2015)
HC + Ozone	Chlorpyrifos	0.11	100	Pressure = 5 bar Time = 45 min Device = orifice plate pH = 3 O_3 = 100 mg/h	Randhavane and Khambete, (2017)
US + Ozone	Bisphenol A	0.10 mg/L	100	Time = 60 min pH = 6.5 frequency = 20 kHz O_3 = 10 mL/min	Guo and Feng, (2009)
US + Ozone	P-nitrotoluene	100 mg/L	85 (TOC)	Time = 90 min pH = 10 frequency = 20 kHz power = 400 W O_3 = 3.8 g/h	Song et al., (2007)

1.2.3.5.3 Cavitation coupled with Fenton reagent:

The hybrid treatment methodology combining cavitation with Fenton's reagent increases the generation of $^{\bullet}OH$ radicals and enhances degradation rate of organic molecules present in sample solution. The advantage of combining HC with Fenton's reagent is that it produces hydroxyl radicals by the dissociation of H_2O_2 under the cavitational effects, and by the reaction between ferrous/ferric ions and H_2O_2 that occurs simultaneously generating highly reactive hydroxyl and oxy-hydroxyl radicals useful for the degradation of organic molecules. In Fenton process, ferrous ion (Fe^{2+}) reacts with H_2O_2 and produces the ferric ion and $^{\bullet}OH$ simultaneously. Later Fe^{3+} reacts with H_2O_2 and form the intermediate complex which further converted into Fe^{2+} and oxy- hydroxyl radicals ($^{\bullet}OOH$). It should be noted that when Fe^{2+} is present in excessive amounts self-quenching of $^{\bullet}OH$ starts and generates the Fe^{3+} ions. The reactions involved during the combined treatment process of cavitation with Fenton reagent are as follows (Rajoriya et al., 2016):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^-$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe\text{-}OOH^{2+} + H^+$$

$$Fe\text{-}OOH^{2+} \rightarrow Fe^{2+} + HOO^{\bullet}$$

$$H_2O_2 \xrightarrow{\text{Cavitation}} {}^{\bullet}OH + {}^{\bullet}OH$$

$${}^{\bullet}OH + \text{organic molecules} \rightarrow CO_2 + H_2O + \text{some intermediates}$$

Being a potential oxidizing agent Fenton has been widely used by many researchers in combination with HC/US for the degradation of organic pollutants (Bagal and Gogate, 2013, 2012; Cai et al., 2016; Gogate and Patil, 2015). Table 1.11 presents the numerous studies based on % degradation of organic pollutants using hybrid methodology combining HC/US + Fenton reagent. In most of the cases more than 90% degradation of respective organic pollutants was observed using combination of these two techniques. Pollutants like 2, 4-dinitrophenol, and Imidacloprid were completely degraded using HC + Fenton whereas only 12.4% and 23.85% degradation was observed using HC alone as the treatment approach (Bagal and Gogate, 2013; Patil et al., 2014). Combination of HC

+ Fenton like above mentioned hybrid treatment approaches showed the synergistic effect and same was observed in study conducted by Mishra and Gogate, (2010) for the degradation of Rhodamine B(Mishra and Gogate, 2010). It was observed that Rhodamine B was completely degraded using HC with Fenton reagent whereas approximately 25% reduction was observed at optimum condition in case of HC alone. US + Fenton also showed similar synergistic effect in all studies as presented in Table 1.11. The 2, 4-dinitrophenol was also degraded in the study as reported by Guo et al., (2005) using US + Fenton and it was observed that 98% degradation was attained whereas maximum 23.5 % degradation was observed at optimized conditions when US was used as the treatment technique. As observed that HC/US + Fenton have a great potential to degrade complex organic compounds therefore it indicates that it could be a better treatment methodology for the degradation of recalcitrant organic pollutants present in TWE.

Table 1.11 Studies based on % degradation of organic pollutants using HC/US + Fenton

Treatment method	Pollutant	Initial concentration	% Reduction	Operating conditions	Reference
HC + Fenton	2,4-dinitrophenol	20 ppm	100	Pressure = 4 bar, Time = 60 min pH = 4, Device = orifice plate H_2O_2 = 0.3 g/L, $FeSO_4$ = 0.6 g/L	Bagal and Gogate, (2013)
HC + Fenton	Azo dyes Orange G	20 mg/L	99.8	Pressure = 0.55 L/s, Time = 60 min pH = 3, Device = orifice plate H_2O_2 = 0.5 g/L, Fe^0 = 0.5 g/L	Cai et al., (2016)
HC + Fenton	Triazophos	20 ppm	83.12	Pressure = 5 bar, Time = 120 min Device = orifice plate, pH = 3 H_2O_2 = 80 ppm, $FeSO_4$ = 80 ppm	Gogate and Patil, (2015)
HC + Fenton	Imidacloprid	20 ppm	100	Pressure = 4 bar, Time = 60 min Device = venturi, pH = 3 H_2O_2 = 80 mg/L, $FeSO_4$ = 20 mg/L	Patil et al., (2014)
HC + Fenton	Dichlorvos	20 ppm	91.5	Pressure = 5 bar, Time = 60 min, pH = 3, Device = orifice plate, H_2O_2 = 16 ppm, $FeSO_4$ = 48 ppm	Joshi and Gogate, (2012)
HC + Fenton	Rhodamine B	10 ppm	100	Pressure = 4.8 bar, Time = 30 min Device = venturi, pH = 2.5, H_2O_2 = 200 mg/L, $FeSO_4$ = 40mg/L	Mishra and Gogate, (2010)
HC + Fenton	P-nitrophenol	5 g/L	63.2	Pressure = 2.93 bar, Time = 90 min, Device = venturi, H_2O_2 = 5 g/L $FeSO_4$ = 1 g/L	Pradhan and Gogate, (2010a)
HC + Fenton	Methyl parathion	20 ppm	93.8	Pressure = 4 bar, Time = 120 min Device = orifice plate, H_2O_2 = 100 mg/L $FeSO_4$ = 400 mg/L	Patil and Gogate, (2012)
US + Fenton	Alachlor	20 ppm	100	Time = 60 min, pH = 3 frequency = 20 kHz, power = 100 W	Bagal and Gogate, (2012)

				H_2O_2 = 0.07 g/L, $FeSO_4$ = 0.07 mg/L	
US + Fenton	Methyl parathion	20 ppm	98.5	Time = 60 min, pH = 2.5 frequency = 20 kHz, power = 270 W H_2O_2 = 200 ppm $FeSO_4$ = 600 ppm	Shriwas and Gogate, (2011)
US + Fenton	P-nitrophenol	0.5% (w/V)	66.4	Time = 90 min, pH = 3.7 frequency = 20 kHz power = 1 kW, H_2O_2 = 5 g/L $FeSO_4$ = 1 g/L	Pradhan and Gogate, (2010b)
US + Fenton	Azo dye Acid black 1 (AB1)	0.081 mM	98.83	Time = 30 min, pH = 3 frequency = 40 kHz H_2O_2 = 8 mM $FeSO_4$ = 0.25 mM	Sun et al., (2007)
US + Fenton	Carbofuran	20 mg/L	100	Time = 30 min, pH = 3 frequency = 20 kHz power = 300 W H_2O_2 = 200 mg/L $FeSO_4$ = 5 mg/L	Ying Shih et al., (2010)
US + Fenton	2,4-dinitrophenol	20 mg/L	98	Time = 60 min, pH = 4.1 Frequency = 20 kHz Power = 400 W H_2O_2 = 300 mg/L $FeSO_4$ = 60 mg/L	Guo et al., (2005)

1.3 Research gaps:

One of the major challenges with the operation of tannery industry is the large quantity of water required for proper functioning as well as the large quantity effluent discharge from the industry. The effluent from tannery is rich in organic content such as dyes, protein, lipids and surfactant along the high concentration of salts and ions like chromium in its various oxidation states. The type of waste in terms of organic and inorganic contaminant within the effluent depends on the process involving in leather production. The literature survey indicates that various treatment processes have been examined for treating the TWE, ranging from the conventional physico-chemical treatment methods to the advanced and hybrid treatment methodologies. However, most of these treatment approaches have various serious limitations that still need to be addressed. It is evident that no individual system is simple and efficient enough for the complete treatment of TWE and each system have its own limitations or drawbacks. The research gaps which are observed during the literature survey are summarized as follows:

1. Conventional physico-chemical treatment processes such as adsorption, coagulation/flocculation and membrane separation have such limitations, that the organic load was only precipitated out of the waste effluent but not degraded. The aforementioned approaches have their own drawbacks such as; coagulation produces a large volume of sludge, adsorption result in selective concentration of toxic material and creates a problem for storage and disposal. Moreover, another major drawback associated with coagulation is that due to addition of coagulants during the treatment process, it increases the total dissolved solids content of the treated effluent as well as alters the pH of the medium which further needs to be treated. Coagulation/flocculation is effective only at a particular pH and efficiency of this treatment approach highly depends on raw wastewater characteristics.
2. In case of membrane technology, the major drawbacks which are associated with membrane applications are the significant fouling due to clogging, adsorption and formation of cake layer by pollutants like residual organics, dyes, and other impurities onto the membrane. The membrane based processes may not be

economically feasible because of its high costs and expertise required to implement and sustain the operation of such processes.

3. The cost of operation is a major concern for the operational success of biological treatment processes and aerobic treatment is cost intensive process over the AD. In case of TWE, high salt content was used during the preservation of skins, the high concentration of salt in waste effluent hinders the efficiency of biological treatment. The high concentration of poorly biodegradable compounds such as tannins and toxic metals also restrict the digestion processes. If the process is too long, it becomes infeasible for treating huge amount of waste generated. Although AD has economic advantage over aerobic digestion, however its application is restricted in TWE treatment due to varying pH range and presence of large quantity of recalcitrant compounds, therefore pretreatment of waste effluent is a prerequisite, to increase the BI and degradation of the recalcitrant molecule present in TWE.
4. Advanced oxidizing agents such as Fenton, ozone and H_2O_2 utilize expensive chemicals and are generally required to be performed under the guidance of experts. Most of the advanced treatment methods are highly selective in nature in terms of waste treatment. Dosage requirement are high for reduction of COD to permissible limits for industrial effluents.
5. In the last decade, cavitation has emerged as an advanced oxidation technique for the treatment of bio-refractory pollutants and various hybrid treatment approaches using cavitation in combination with different oxidizing agents have been applied for the treatment of complex industrial waste effluents. As it has been found that cavitation processes enhance the biodegradability index and reduces the toxicity of pollutants and therefore it can be used as a pretreatment tool for the treatment of TWE, which has not been studied.
6. Though, many studies have been reported on the treatment of tannery effluents using various techniques including coagulation, aerobic, anaerobic, advanced oxidation techniques etc., whereas the use of cavitational reactors for the pretreatment of tannery effluent has not yet been reported in literature to the best

of our knowledge for the mineralization of TWE and for biodegradability index enhancement.

7. Cavitation is responsible for disintegration of complex/bio-refractory molecules and enhancement of BI, therefore HC, being an economic and energy efficient treatment technique, can also be used as a pretreatment strategy to increase the AD rate of TWE by enhancing the rate of limiting steps of the digestion process mainly hydrolysis and acidogenesis reactions and for increasing the biogas yield.
8. A hybrid treatment strategy may be adopted by combining the cavitation processes with treatment techniques such as coagulation, AOPs and biological treatment for the treatment of TWE.

1.4 Objectives of research

Cavitation is being applied for the pre-treatment of various kind of organic matter and is highly effective in terms of degradation of complex biomolecules with the help of hydroxyl radical produced in the process of cavitation. In the present study hybrid approaches have been applied for the treatment of TWE using coagulation, cavitation and anaerobic degradation. Based on the observed research gaps, the applicability of cavitation as a pretreatment technique for the degradation of complex organic components in TWE was extensively studied with the following specific objectives:

1. Pretreatment of TWE using alum coagulation followed by cavitation using HC & US techniques.
2. Advanced hybrid treatment of TWE using a hybrid technique of US in combination with advanced oxidizing reagents using hydrogen peroxide/Fenton’s reagent / sodium hypochlorite/ ozone.
3. Advanced hybrid treatment of TWE using HC coupled with various oxidizing agents such as hydrogen peroxide, Fenton’s, and ozone.
4. Modeling and simulation studies for the batch AD of hydrodynamically cavitated TWE mixed with food waste for enhanced biogas generation.

1.5 Organization of the thesis

The doctoral thesis has been divided into six chapters. The highlights of each chapter are presented as follows:

Chapter 1 provides an introduction of the problem statement, an extensive literature review on the work done in the area of treatment of tannery wastewater including conventional and advanced hybrid processes, research gaps, and objectives and the organization of the thesis.

Chapter 2 presents the study on an advanced pretreatment strategy, which has been adopted by combining the conventional pretreatment i.e. coagulation with cavitation a recent advanced oxidation technique for pretreatment which will help in breaking the larger recalcitrant organic molecules thereby enhancing the BI value prior to the secondary biological treatment process. The effect of different treatment process parameters such as coagulant dosage, residual pH, operating inlet pressure during cavitation, and dilution on the treatment of TWE was studied. The main aim was to evaluate the applicability of coagulation followed by HC or US for the pretreatment of TWE with an objective of biodegradability enhancement increasing its BI value with simultaneous reduction in its COD and TOC and the energy efficiency of the processes was studied.

Chapter 3 presents the study on the effectiveness of the hybrid treatment method of US in combination with various advanced oxidizing reagents as a combined treatment for the degradation of organic pollutants in TWE. In this hybrid method of US, various oxidation agents such as hydrogen peroxide, Fenton reagent, sodium hypochlorite and ozone were studied for the treatment of TWE and also in combination with conventional precipitation technique i.e. coagulation which has not been reported earlier. The process efficiency of this integrated approach was evaluated in terms of maximum COD reduction of TWE studying the effect of various process parameters such as coagulant dosages, US amplitude, concentration of oxidizing agents etc. on COD reduction of TWE and the energy requirements.

Chapter 4 presents the study on the hybrid treatment technique of combining HC with various oxidation agents such as O_3, H_2O_2 and Fenton's reagent which may give higher degradation efficiencies and therefore yielding intensified treatment. The use of hybrid HC coupled with oxidative agents, has been reported for treatment of various dyes mostly on laboratory scale, however no study has yet been reported for treatment of TWE. In this study, advanced treatment for reduction of COD and TOC along with increase in BI of the tannery effluent taken from an effluent treatment plant was the main focus of the study so as to evaluate the efficiency of treatment process. The effects of various process parameters such as the fluid flow inlet pressure to the cavitational device, sample dilution ratio, concentration of various oxidative agents etc. on the BI, degradation efficiency as well as the rate kinetics were studied. The various organic components present in the raw and treated samples were also analyzed using FTIR and LCMS. The most effective hybrid technique was identified on the basis of COD and TOC reduction of TWE and supported with energy and cost effectiveness.

Chapter 5 evaluates the performance of AD using HC treated TWE as the substrate for higher biogas yield in comparison to raw TWE. Performance of anaerobic digesters of both small and larger volume was experimentally studied using raw as well as HC treated TWE and biogas generation along with COD reduction in substrate was analyzed. Effect of seed concentration and organic loading on biogas generation was studied. Mathematical models were used to develop a simulator to represent the AD process as well as differentiating the AD performance with respect to two different feeds i.e. raw and HC treated TWE and the effect of model parameters were validated in the propagation of the various degradation reactions as well as for the prediction of long term performance of the digester for varying feeds.

Chapter 6 presents the major conclusions drawn from the present study and the recommendations for future work.

CHAPTER 2

Pretreatment of Tannery Waste effluent (TWE) Using Alum Coagulation Followed by Cavitation (Hydrodynamic cavitation (HC) & Ultrasonication (US))

2.1 Introduction:

The treatment of tannery effluent due to the higher concentration of organic load with low biodegradability is a serious environmental challenge today. In the last decade, studies of coagulation in combination with nano-filtration as well as adsorption techniques using activated carbon and cationic/anionic polymers showed higher removal efficiencies in terms of COD and TSS for the pretreatment of tannery effluents (Ayoub et al., 2011; Haydar and Aziz, 2009b; Reiera-Torres et al., 2010). However, these methods are incapable to break the larger complex molecules into smaller molecules which can be further treated with subsequent biological treatment processes. In order to enhance the BI, coagulation followed by cavitation either using HC or US can be applied for the pretreatment of tannery effluents. Coagulation as a physicochemical process used for the removal and settlement of particulate and colloidal particles present in industrial wastewater (Al-amoudi and Lovitt, 2007; Leonard et al., 1995; Yoon and Luttrell, 1992). Various chemicals such as aluminum sulfate (alum), ferric chloride, and ferrous sulfate etc. have been used as coagulants in previous studies (Kabdasli et al., 1999; Lofrano et al., 2006; Song et al., 2004). Some advantages of coagulation when used in pretreatment include minimum sludge formation during secondary treatment due to the removal of suspended solids, simplicity, cost effectiveness, and good removal efficiencies on an industrial level. In last decade, cavitation has also emerged as an advanced oxidation technique for the treatment of bio-refractory pollutants (Gogate and Pandit, 2004b) . It was reported that cavitation processes enhance the biodegradability index and reduces the toxicity of pollutants and therefore can be used as a pretreatment tool for the treatment of real industrial effluents (Padoley et al., 2012; Raut-Jadhav et al., 2013).

Though, many studies have been reported on the treatment of tannery effluents using various techniques including coagulation (Deghles and Kurt, 2016, 2015; Schrank et al., 2005; Sher et al., 2013; Song et al., 2004) whereas, the use of cavitational reactors for the pretreatment of tannery effluent has not yet been reported in literature to the best of our knowledge. An advanced pretreatment strategy has been adopted in this study by combining the conventional pretreatment i.e. coagulation with cavitation which is a recent advanced oxidation technique in the TWE pretreatment stage itself for breaking the larger recalcitrant organic molecules and in order to enhance the BI value prior to the secondary biological treatment process. The presence of suspended particle may hinder or reduce the efficiency of cavitation process; therefore coagulation process could be applied prior to cavitation in order to reduce the particle concentration by precipitating suspended organic matter present in TWE. Moreover, the effect of different process parameters such as coagulant dosage, residual pH, operating inlet pressure during cavitation, and dilution on the treatment of TWE was studied. The main aim was to evaluate the applicability of coagulation followed by HC and US for the pretreatment of TWE with an objective of biodegradability enhancement increasing its BI value by simultaneous reduction in its COD and TOC.

2.2 Experimental details

2.2.1 Chemicals

All the chemicals used in this study were purchased from Lobachemie, India and were of analytical grade (AR). Aluminum sulfate was used as the coagulant. Chemicals such as ferrous ammonium sulfate, concentrated sulfuric acid, silver sulfate, mercuric sulfate, potassium dichromate and ferroin indicator were used for COD analysis. BOD analysis were carried out using sodium thiosulfate, alkali iodide azide, manganous sulfate, starch, potassium dihydrogen phosphate, dipotassium hydrogen orthophosphate, disodium hydrogen phosphate, ammonium chloride, calcium chloride, magnesium sulfate and ferric chloride. Orthophosphoric acid and sodium peroxidisulfate were used for TOC analysis. Distilled water was used for the dilution study. All the chemicals were used as received from suppliers without any further purification.

2.2.2 Tannery waste effluent (TWE)

TWE samples were taken from a common effluent treatment plant (CETP) (sources are not given due to the confidentiality issues) located at the industrial area of Jaipur, India and the sample collection was carried out at the main inlet point to the CETP before the equalization tank. The study was conducted using two different types of tannery effluent samples. The characteristics of both samples are given in Table 2.1, and the variation in the sample characteristics was due to sample collection on different days. Sample 1 which was collected initially was used for pretreatment studies using coagulation followed by HC and sample 2 was used for pretreatment studies with coagulation followed by US. TWE was stored in a deep freezer and allowed to achieve room temperature before conducting experiments.

Table 2.1 Characteristics of TWE

Parameters	Sample 1	Sample 2
COD (mg/L)	18800-23000	11000-12800
TOC (mg/L)	3512-3868	2050-2300
BOD (mg/L)	2540-2960	1040-1100
Biodegradability index (BI)	0.12-0.14	0.9-0.10
pH	11.98-12.54	12.2-12.5
TDS (mg/L)	28430-32300	22350-24870
TSS (mg/L)	25000-35200	10860-11630
Conductivity (mS/cm)	66.2-69.7	44.6-46.0
Turbidity (NTU)	3592-3785	3260-3441

2.2.3 Experimental setup

2.2.3.1 Hydrodynamic cavitation reactor

Schematic representation of HC reactor set-up used in the present study is shown in Fig. 2.1. HC reactor set-up comprises of a closed loop circuit with a storage tank (20 L), manual valves, pressure gauges, a flow meter, and a high-pressure piston pump (power rating 2.2 kW). Pipes used in the HC reactor have an internal diameter of 19 mm. The bottom of the storage tank was connected to the suction side of the pump. The discharge from the pump was distributed into two lines: main line and bypass line. The main line consists of a cavitating device (slit venturi) and the flow rate in the main line was maintained by regulating the speed of the motor through variable frequency drive (VFD). The dimensions of the slit venturi used in this study are given in Table 2.2. Studies already reported by (Rajoriya et al., 2017a) on the same HC reactor and slit venturi have identified the optimized cavitation conditions such as inlet pressure and cavitation number for obtaining the highest cavitational intensity, which was used as basis for performing the cavitation phenomena in our experimental studies.

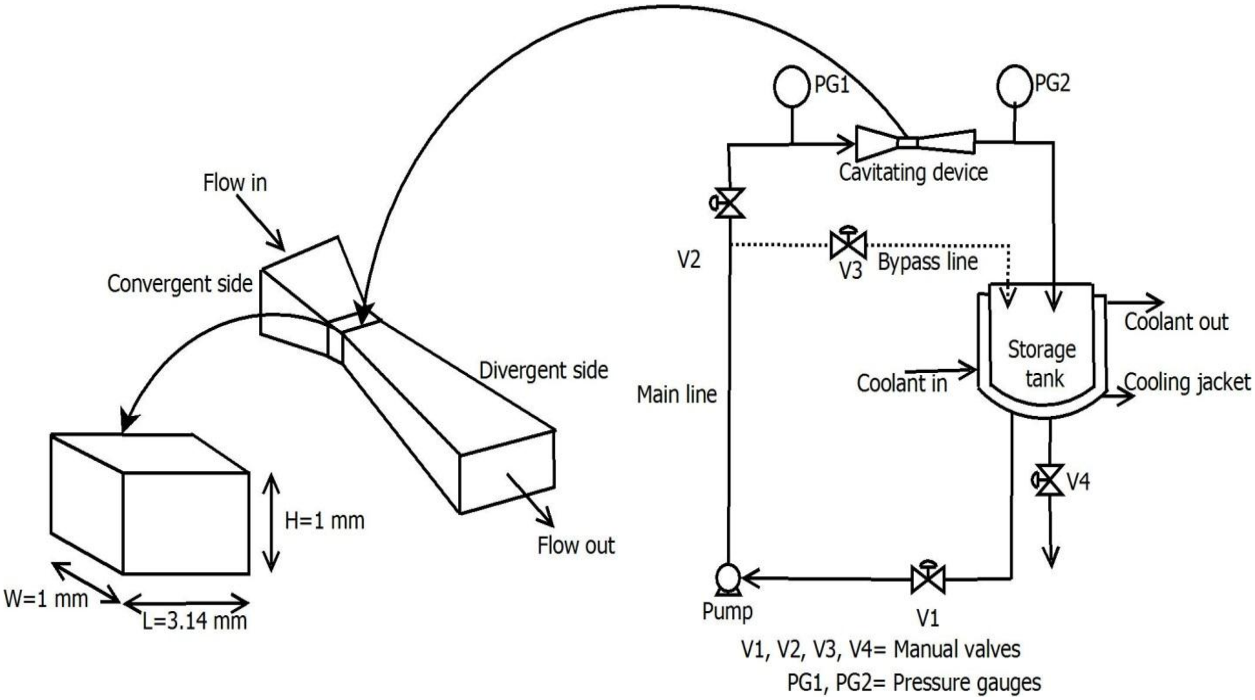


Fig. 2.1 Schematic representation of slit venturi based HC reactor setup

Table 2.2 Dimensions of slit venturi

Cavitating device	Dimension of throat	Venturi length	Length of convergent section	Length of divergent section	Half angle of convergent section	Half angle of divergent section
Slit venturi	Length(L) =3.14 mm Width(W) =1 mm Height(H) =1 mm	100.6 mm	20.6 mm	79 mm	23.5°	6.5°

2.2.3.2 Ultrasonication set-up

A schematic diagram of the US reactor set-up is shown in Fig. 2.2. All the experiments related to US were conducted using ultrasonic horn (VCX 750, Sonics, USA). Ultrasonic horn with 13 mm diameter was operated at 20 kHz with a maximum power output of 750 W. The ultrasonic horn was kept in a sound abatement wooden compartment to reduce the noise produced during sonication process. Adjustable jack was used in order to maintain the height of sample inside compartment so that horn tip could be properly immersed in sample. The temperature of the TWE sample was maintained by cooling water circulation through the jacket surrounding the batch reactor.

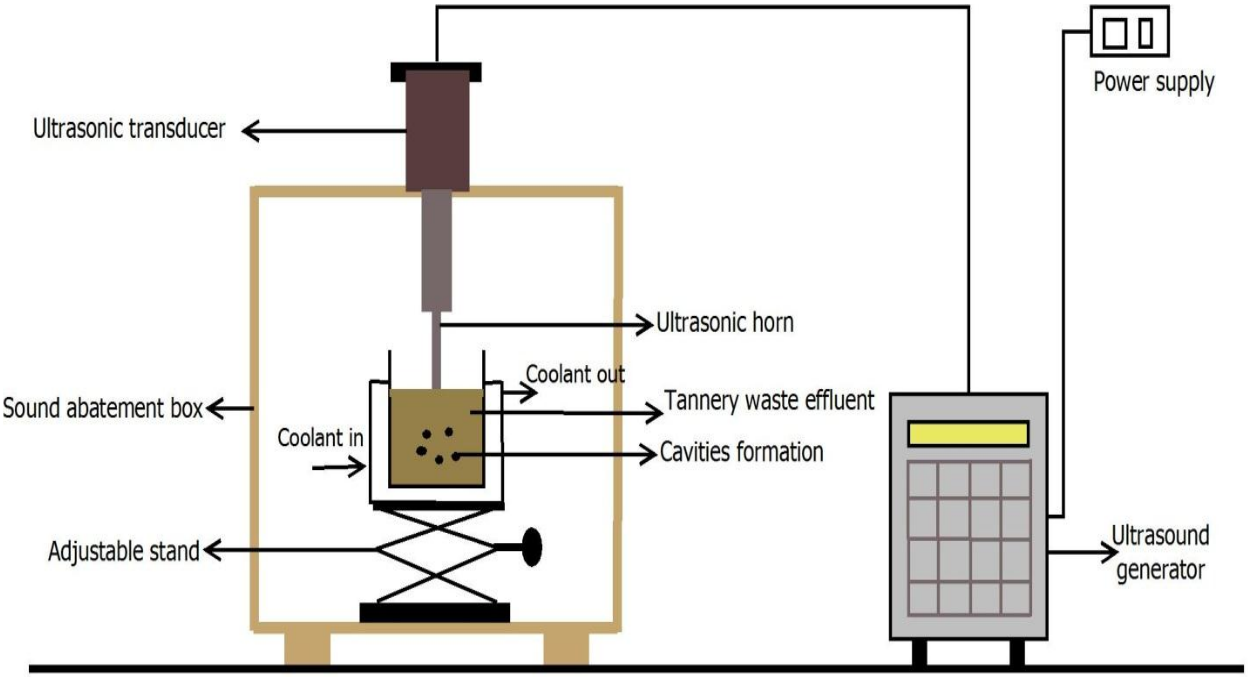


Fig. 2.2 Schematic diagram of US reactor set-up

2.2.4 Experimental procedure

The TWE samples were first treated using coagulation and thereafter supernatant obtained was further subjected to HC and US. In the coagulation process two different methodologies were adopted for the treatment of TWE based on the initial pH of the effluent waste. A block diagram depicting the complete treatment process carried out in the present study is shown in Fig. 2.3.

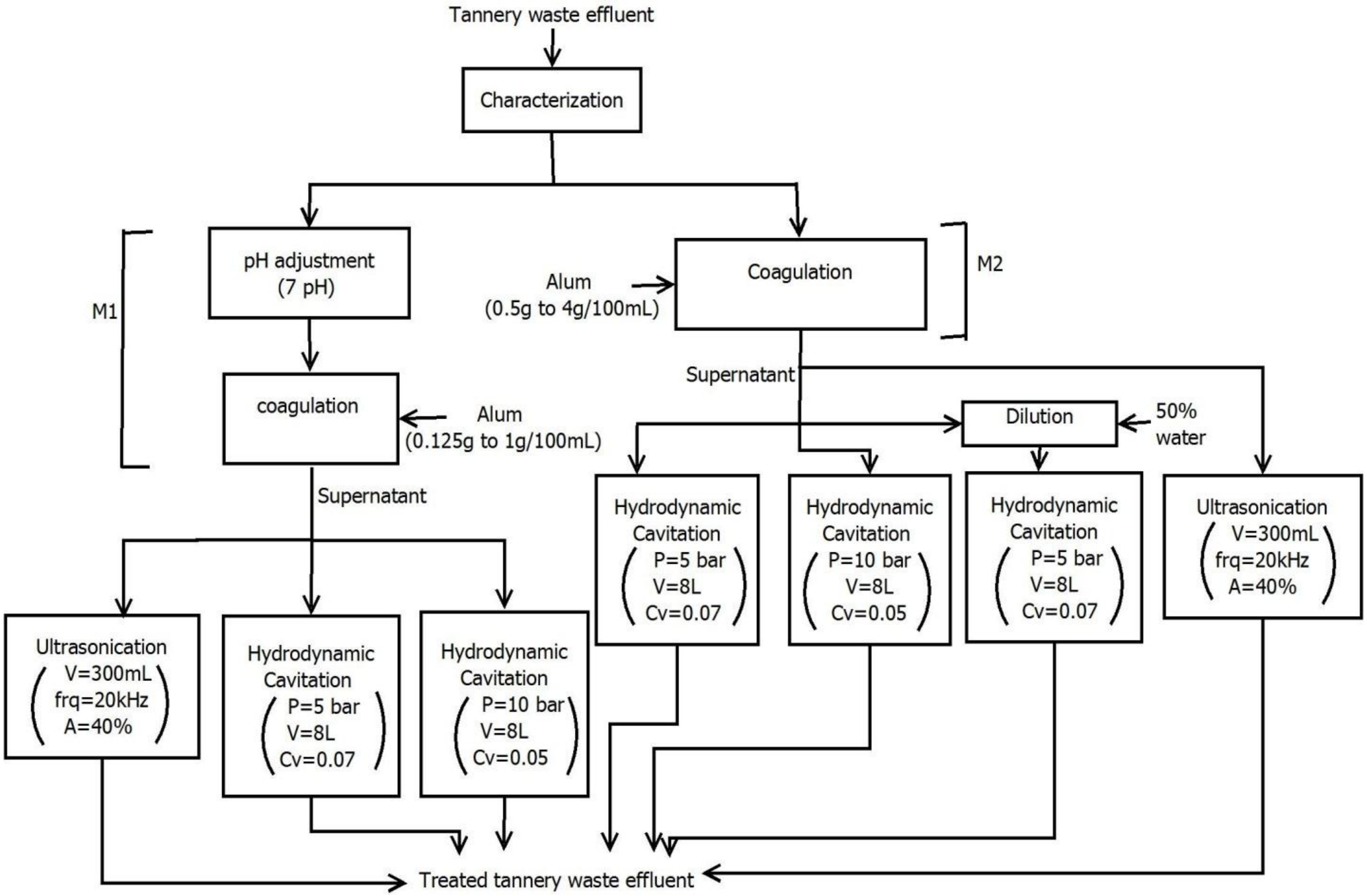


Fig. 2.3 A block diagram of pretreatment methodology of TWE

2.2.4.1 Pretreatment with Coagulation

A block diagram of the pretreatment methodology of TWE used in the present study is given in Fig. 2.3. Two different coagulation methodologies were followed for pretreatment as mentioned below:

Methodology 1 (M1): In this methodology, initially the solution pH of TWE was adjusted from pH of 12 to pH of 7.0 using 12.18 M HCl with continuous stirring. Thereafter, alum doses were varied from 0.125 g to 1.0 g per 100 mL of TWE to study the effect of alum doses on COD and TSS removal. The solution was mixed with the coagulant in a rotary flask shaker for a time period of 15 min at 200 rpm and then allowed to settle the colloidal and particulate matter for 90 min. The obtained supernatant after 90 min of settling was subjected to further treatment by HC and US and analyzed for COD, BOD, TDS, TSS, etc.

Methodology 2 (M2): In this methodology, TWE was pretreated with alum doses without pH adjustment. The well mixed tannery effluent was coagulated in 250 mL Teflon bottles in batch mode by treating with alum doses varying from 0.5 to 4.0 g per 100 mL of TWE. The remaining steps were same as described in M1 in which 100 mL solution was mixed with the coagulant in a rotary flask shaker for a time period of 15 min at 200 rpm and then allowed to settle the colloidal and particulate matter for 90 min. The obtained supernatant after 90 min of settling was subjected to further treatment by HC and US and analyzed for COD, BOD, TDS, TSS, etc.

The supernatant obtained from the CTWE sample was further subjected to HC and US and analyzed for COD, BOD, TOC, TDS, TSS, etc.

2.2.4.2 CTWE treatment using Hydrodynamic cavitation

The supernatant obtained after coagulation was further treated in the slit venturi based HC reactor. All the experiments related to HC were carried out using 8 L of CTWE obtained from M1 and M2 at the optimized process conditions. Initially, the cavitation experiments were conducted at two different operating inlet pressures i.e. 5 and 10 bars. The inlet pressure conditions for the slit venturi was chosen based on the studies reported by (Rajoriya et al., 2017a) on the HC reactor for degradation of a textile dye. Their cavitation studies were conducted on the same HC reactor for various configurations of cavitation devices and reported on the performance of the slit venturi for the optimized cavitation conditions such as inlet pressure and cavitation number for obtaining the highest cavitational intensity, which was taken as basis for performing the cavitation phenomena in our experimental studies. Padoley et al., (2012) also reported that 5 bar pressure in HC was sufficient enough to produce significant number of cavities using venturi as the cavitating device for the degradation of the organic contaminant. However, in order to check the degradation of organic contaminants at high pressure using HC, experiment was also performed at 10 bar pressures. Further, the effect of dilution on the treatment of CTWE was studied with 50% dilution at an optimum inlet pressure of 5 bar. The process temperature was kept constant at 30 ± 2^{o}C by circulating cooling water through the jacket around the process tank. Total treatment time was 120 min and samples were taken at regular time intervals to further analyze for pH, COD, TOC, TSS, BOD, TOC, and TDS.

2.2.4.3 CTWE treatment using Ultrasonication

The obtained supernatant solutions from both methodologies were also subjected to US operated at a frequency of 20 kHz and 40% amplitude in a batch mode with a nominal power of 750 W. In all these experiments, the probe tip was immersed 2.5 cm below the free surface of CTWE solution. 300 mL of CTWE sample was subjected to US with 25s on and 5s off cycle. The temperature (30±2°C) was maintained by cooling water circulation through the jacket surrounding the batch reactor. Samples were taken at fixed intervals of time for further analysis.

2.2.5 Analytical methods

A pH meter (Thermo scientific, USA) was used to determine the pH of the solution throughout the experiments. TOC content of tannery effluents was measured using TOC analyzer (GE InnovOx). BOD and COD of samples were determined as per the standard APHA methods (*APHA, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington DC, 1998.*, 1998). The conductivity and TDS were measured using ion meter (Thermo scientific, USA). Total solids (TS) and TSS of the samples were determined by drying the tannery effluent at 104°C in an oven (Make: DAIHAN Scientific Co. Ltd.). Turbidity was measured using turbidity meter (Spectra lab NT-4000). All experiments were repeated twice and reported values are the average of two runs. The experimental errors were found to be within 3% of the reported average values.

2.3 Results and discussion

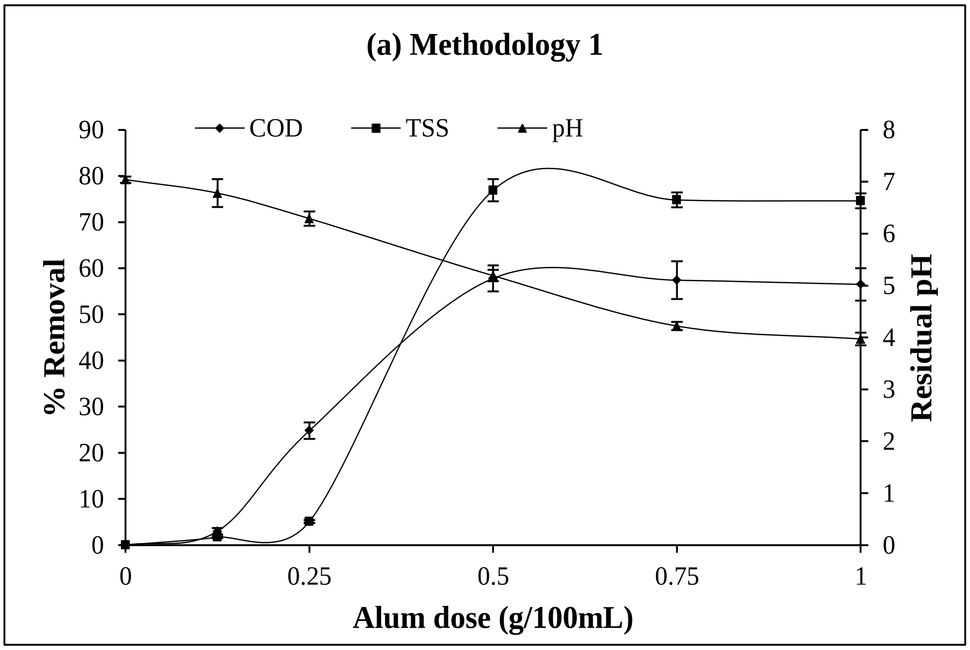
2.3.1 Treatment of TWE using coagulation

The nature of the organic and inorganic matter present in TWE and its characteristic properties such as charge, functionality, size, hydrophobicity etc., play an important role in the quantity of coagulant required for effective precipitation. The organic content of TWE is a mixture of both aliphatic and aromatic compounds present in suspended, colloidal and dissolved forms in the aqueous medium carrying high level of negative charge due to the presence of ionic groups such as carboxylic and phenolic groups. Alum which is amphoteric in nature, when used as the coagulant, hydrolyses in the aqueous medium to form charged ionized particles depending upon the pH of the solution. Hydrolysis of aluminum ions is represented as a sequential replacement of the water molecules by hydroxyl ions, or progressive deprotonation reactions (George et al., 2009) and is represented as

$$Al^{3+} \leftrightarrow Al(OH)^{2+} \leftrightarrow Al(OH)_2^{+} \leftrightarrow Al(OH)_3^{0} \leftrightarrow Al(OH)_4^{-}$$

Acidic pH favors formation of the positively charged ions whereas alkaline pH favors the formation of negatively charged $Al(OH)_4^-$ ions in the alkaline medium. Separation of the organic matter by coagulation process is achieved by a combination of charge neutralization, entrapment into the larger flocs and their precipitation (Parthasarathy et al., 2016a). Some fraction of the organic matter may also be removed by adsorption or complexation with coagulant metal ions into insoluble particulate aggregates. However, these charge driven mechanisms are considered to be completed at the optimized pH conditions achieved for maximum precipitation. Therefore the solution pH of the tannery effluent varied during the coagulation process and was primarily dependent on the dosage and initial pH of TWE effluent (Gomes et al., 2015).

The effect of coagulant doses was studied based on removal efficiencies of COD and TSS and the optimum dosage of the coagulant was found for maximum removal. Fig. 2.4 presents the effect of alum doses on COD and TSS removal for M1 and M2. In the case of method M1, initially HCl was added to reduce the pH of the TWE from pH 12 to pH 7, and further it was treated with alum for coagulation with further pH reduction to pH 4.5. The maximum of 72.4% COD and 77% TSS removal was obtained with an optimized alum dose of 0.5g/100mL at pH 4.5 using method M1. In case of method M2, alum addition caused two effects i.e. coagulation of the suspended particles as well as reducing the solution pH from initial value of pH 12 to around pH 4.5. Hence the amount of alum required for M2 was higher in comparison to M1. Moreover, for M2, maximum of 68% COD and 82.4% TSS removal was obtained at pH 4.5, with an optimized alum dose of 2 g per 100mL. The solution pH decreased only up to around pH 4 with further increase in alum doses for both cases as shown in Fig. 2.4. The optimum alum dose for M1 was 0.5 g/100 mL and for M2 was 2 g/100 mL at the pH of 4.5 which caused the maximum destabilization of the suspended matter present in TWE for both the methodologies. These destabilized particles formed clumps and settled down in the form of precipitates.



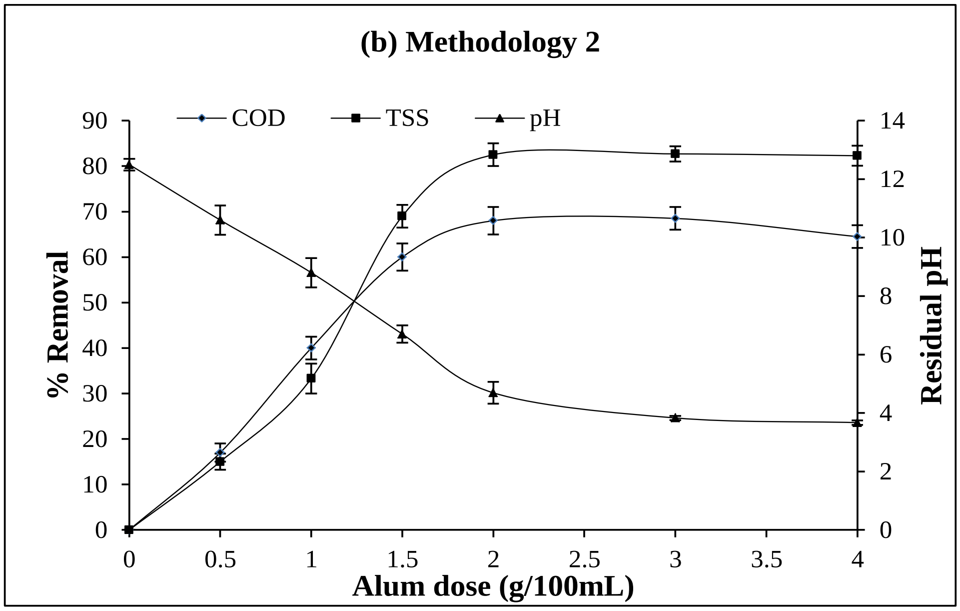


Fig. 2.4 Effect of alum doses on COD and TSS removal and residual pH (a) using M1 (b) using M2

The optimum pH for the TWE effluent at which coagulation was effective was observed to be pH 4.5, where maximum precipitation occurred. This primarily depends upon the nature of the pollutants, initial pH, turbidity of TWE as well as the dosage of alum coagulant. Maximum destabilization of suspended particles took place at pH 4.5, as zeta potential measurements for the TWE sample given in Fig. 2.5 also indicate minimum potential at this pH. Therefore, maximum removal of the suspended particles at the optimum pH of 4.5, caused the increase in the removal of COD and TSS. However, some fraction of the organic carbon present in TWE could not be destabilized by increasing the alum dosage beyond the optimum conditions. This indicated the presence of TWE components which are recalcitrant to removal by coagulation. The percentage removal of COD and TSS increased with an increase in alum doses up to an optimum value and thereafter slightly decreased or no significant reduction was observed. Therefore, all the remaining experiments were performed over the pH range of 4.0 to 5.0 only. It can be clearly seen that M1 is a better choice if compared in terms of TSS and COD reduction per amount of alum used.

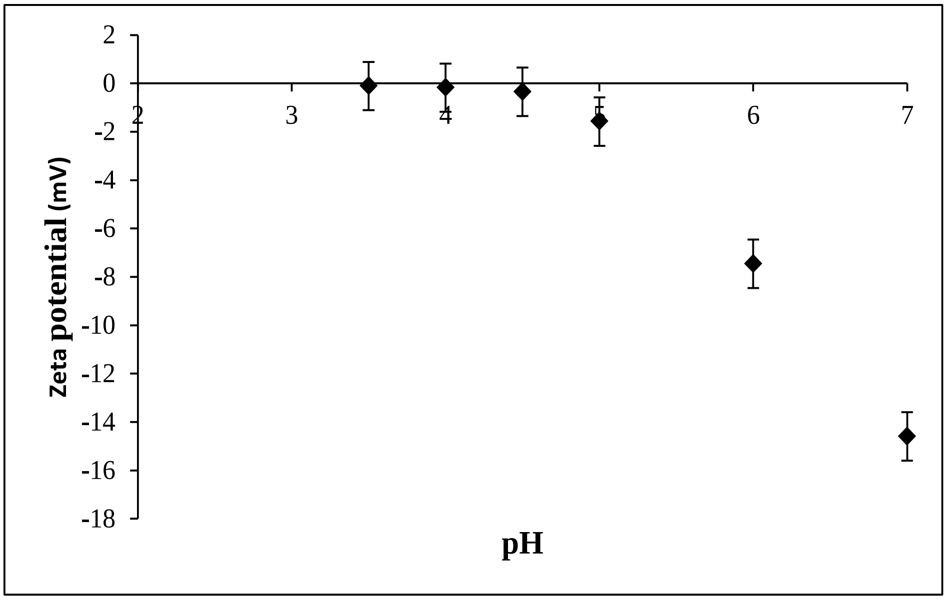
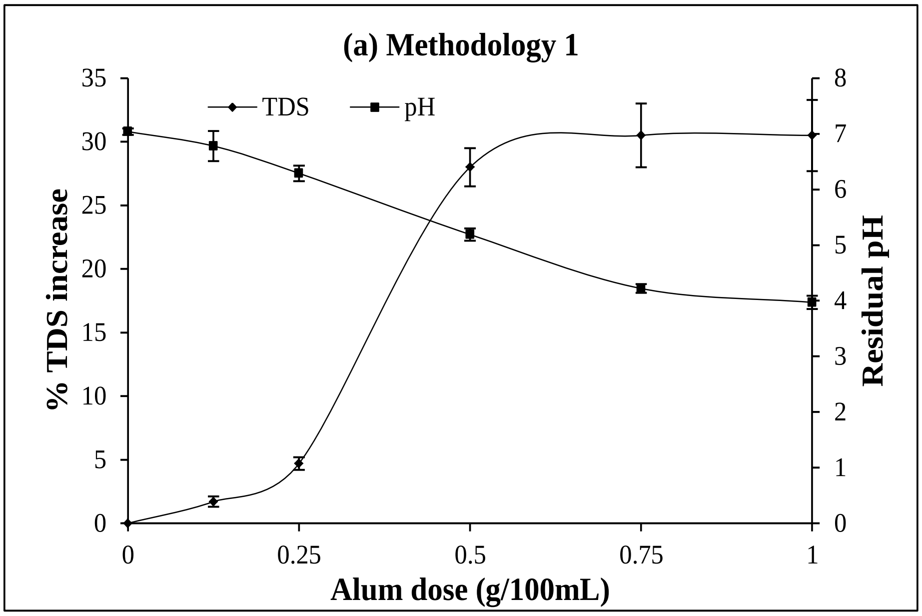


Fig. 2.5 Effect of coagulation pH on zeta potential

The effect of alum doses on TDS of TWE using both methodologies are shown in Fig. 2.6. It was observed that %TDS increased with increase in alum doses for both cases. The increase in % TDS was observed at 48.6% and at 28% for the two methodologies M2 and M1 under the optimized alum doses. It is well known that TDS amount of any industrial wastewater increases with the addition of chemicals/coagulants (Metcalf & Eddy, 2003), which is the major disadvantage associated with physico-chemical treatment processes.

The TOC values, turbidity and conductivity of the coagulated TWE obtained from M1 and M2 are presented in Table 2.3, The TOC values of the raw samples were in the range of 3512 to 3868 mg/L (Table 2.1) whereas the TOC values of the coagulated TWE ranged in the values 3211 to 3554.mg/L as mentioned in Table 2.3. There has been only a marginal reduction in TOC after coagulation which can be attributed to the fact that it was primary the settling of maximum inorganic content in comparison to the organic component present in TWE through coagulation process. The TWE was rich in suspended matter and it was observed that, after coagulation, the reduction in TSS was around 50% whereas there was little reduction in the TDS value. This indicates that coagulation is effective only in the removal of suspended matter and not in the dissolved organics, and the same has been reflected in the TOC values correspondingly. Moreover, the TOC measurements account only for the dissolved TOC because during the TOC measurements the samples are subjected to filtration through a 0.45micron membrane and therefore the TOC values account only for the fraction of the dissolved organic matter which was not separated by coagulation. Therefore, as the reduction in TOC by coagulation was minimal, the CTWE in the present study was further pretreated using advanced physical phenomenon such as HC and US.



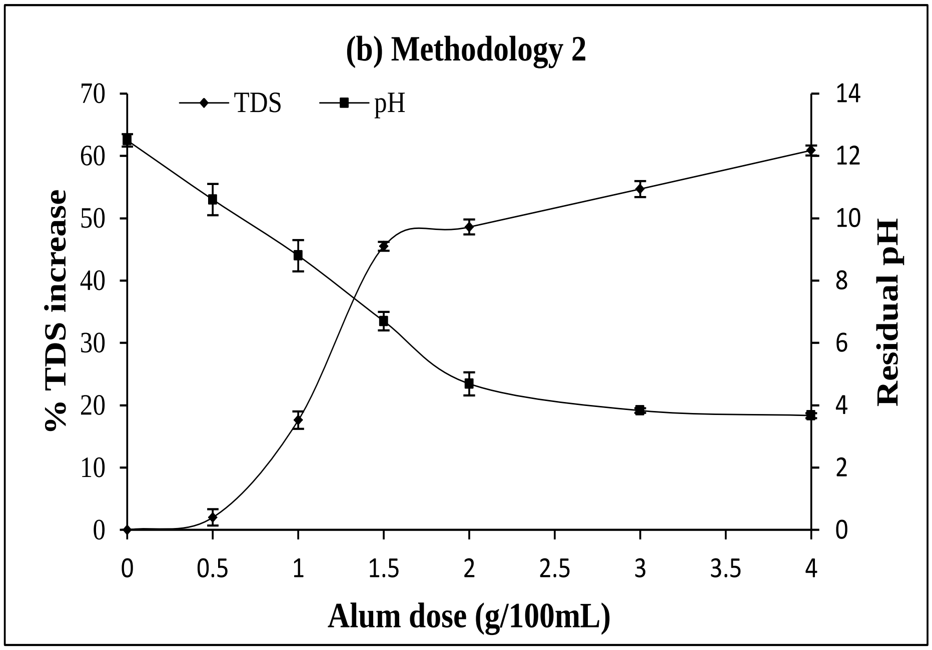


Fig. 2.6 Effect of alum doses on % TDS increase (a) using M1 (b) using M2

2.3.2 Treatment of coagulated TWE (CTWE) using hydrodynamic cavitation (HC)

2.3.2.1 Effect of inlet pressure and cavitation number

In HC, an important factor is the cavitation number which is used to characterize the cavitating conditions inside the cavitating device i.e. the slit venturi (Rajoriya et al., 2016). Cavitation number (C_v) is defined as the ratio of the pressure drop between the throat and extreme downstream section of the cavitating device to the kinetic head at the throat. It is given by following Eq. (1):

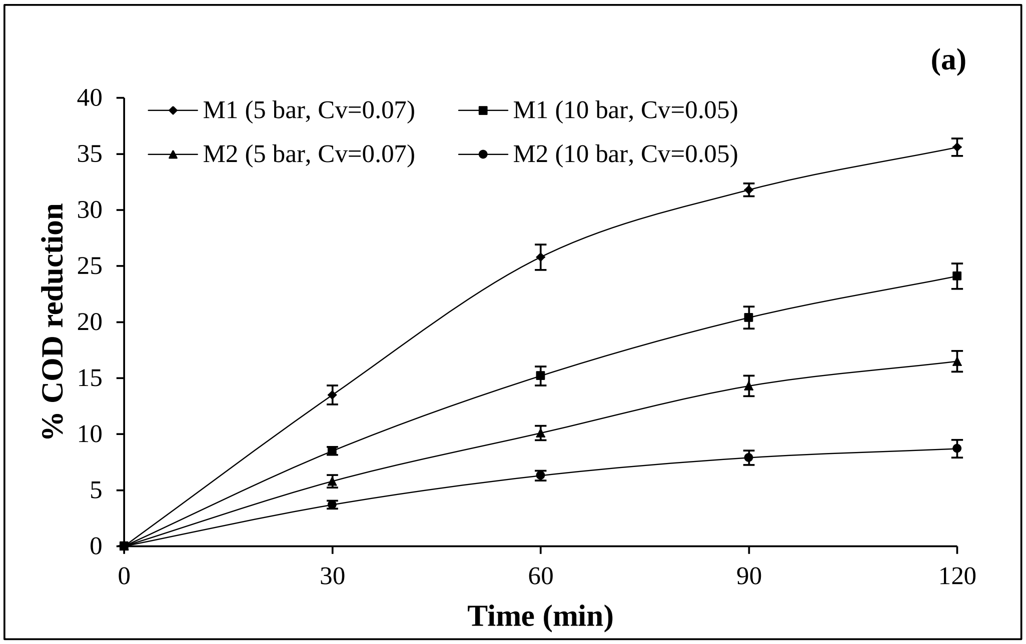
$$C_v = (P_2 - P_v)/(\frac{1}{2})\rho v^2 \qquad (1)$$

Where, P_2 is fully recovered downstream pressure, P_v is the vapor pressure of the liquid, ρ is the density of liquid and v is the velocity at the throat of the cavitating device. C_v is calculated by knowing the main line flow rate and area of slit venturi opening. As the inlet pressure increases, velocity at the throat of the cavitating device also increases which subsequently reduces the cavitation number. Sample calculations for cavitation number at their corresponding operating inlet pressure are given in Appendix A (page no. 191).

In order to examine the effect of inlet pressure on the treatment of CTWE, in terms of reduction in COD, TOC, TSS, TDS, conductivity and turbidity, experiments were conducted at two different inlet pressures i.e. 5 and 10 bar and the results are presented in Table 2.3. In case of CTWE obtained from M1, higher reduction of 35.6% and 43.9% was obtained for the COD and TOC respectively as compared to the reduction of 16.5% and 18.2% obtained for COD and TOC respectively for CTWE obtained from M2 within 120 min at 5 bar pressures and C_v of 0.07. Similarly % reduction of 24.2% and 26.2% was obtained for the COD and TOC respectively for CTWE from M1 compared to reduction of 8.7% and 6.1% obtained for COD and TOC respectively for CTWE obtained from M2 within 120 min at higher 10 bar pressure and C_v of 0.05. The reduction in COD and TOC was found to be higher for M1 than M2 for lower pressure at 5 bar and C_v=0.07 when compared to pressure of 10 bar and C_v=0.05 for the same cavitation time of 120 min. It was observed from Fig. 2.7 that, lower operating inlet pressure of 5 bar favored the HC process than the higher pressure of 10 bar for obtaining the maximum TOC and COD reduction for CTWE samples obtained from M1 and M2.

Table 2.3 Effect of operating inlet pressure on COD, TOC, TSS, TDS, conductivity, and turbidity of CTWE

Type of CTWE	**Pressures (bar)**		**Parameters**					
			COD (mg/L)	TOC (mg/L)	TSS (mg/L)	TDS (mg/L)	Conductivity (mS/cm)	Turbidity (NTU)
CTWE obtained from M1	5	Initial	8320	3554	13970	31250	63.7	1952
		Final	5360	1994	9340	27540	56.2	788
		% reduction	35.6	43.9	33.2	11.9	11.8	59.7
	10	Initial	8400	3418	14050	31470	64.2	2058
		Final	6370	2523	11430	29874	61.3	1540
		% reduction	24.2	26.2	18.6	5.1	4.5	24.8
CTWE obtained from M2	5	Initial	6720	3279	7800	29480	60.8	821
		Final	5610	2683	7550	27810	57.4	806
		% reduction	16.5	18.2	3.2	5.6	5.5	1.8
	10	Initial	6400	3211	7680	29140	59.7	643
		Final	5840	3016	7490	28460	58.4	639
		% reduction	8.7	6.1	2.4	2.3	2.1	No reduction



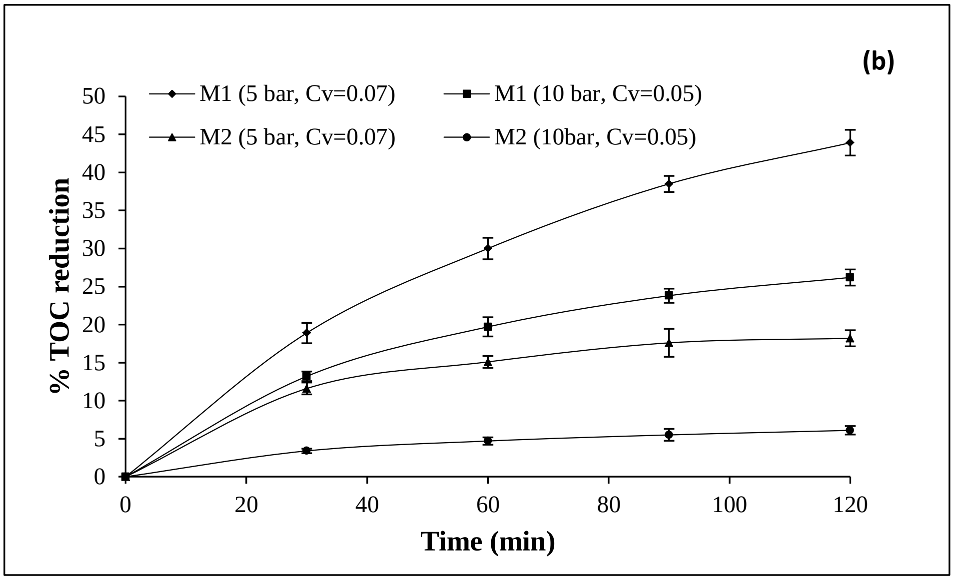


Fig. 2.7 Effect of operating inlet pressure on (a) COD reduction (b) TOC reduction, for both methodologies

Lower reduction efficiencies obtained at the higher inlet pressure may be attributed to the choked cavitating conditions. At these conditions, the entire downstream side of the cavitating device is completely filled with large number of vaporous cavities (i.e. cavity cloud formation occurs) which coalesce to form a larger bubble thus also reducing the cavitational intensity due to partial collapse of cavities/micro-bubbles (Padoley et al., 2012; Rajoriya et al., 2016). It was noted here that higher pressure conditions (10 bar) did not yield a significant effect on the reduction in COD or enhancement in BI values. Therefore, the remaining experiments were carried out at 5 bar operating pressure. Similar effects were observed by (Rajoriya et al., 2017a) using the same cavitating device for the degradation of rhodamine 6G dye, wherein maximum degradation efficiency was attained at 5 bar inlet pressure for the HC reactor.

Coagulation was not effective in reducing the TOC values of CTWE for both M1 and M2, whereas reduction in both COD and TOC was observed when the coagulated samples were subjected to HC treatment. This may be attributed to the oxidation of the dissolved organic molecules by the OH radicals generated during cavitation (Parthasarathy et al., 2016b). HC also affects the other physicochemical characteristic parameters, such as the TSS, TDS, conductivity and turbidity of the CTWE. Maximum of 33.2% TSS and 11.9% TDS were reduced at the optimized inlet pressure of 5 bar in case of CTWE obtained through M1. It can also be seen from Table 2.3 that in case of CTWE from M2, there was no significant reduction i.e. only 2 to 5% for all parameters such as TSS, TDS, conductivity and turbidity. On comparing the obtained data for CTWE using M1 and M2, higher reduction efficiencies were achieved in case of CTWE obtained using M1 as compared to that obtained using M2. This may be attributed to the fact that CTWE from M1 was high in suspended organic matter (higher TSS) and therefore presence of suspended particles acted as nucleation sites for cavitation which resulted into more cavity formation and subsequent generation of more $^{\bullet}$OH radicals. Moreover, the addition of acid (HCl) in case of M1 may have initiated the acidogenesis of the organic matter and therefore enhanced the treatment efficiency under the cavitating conditions. the extreme conditions of cavitation favor the dissociation of HCl in to $^{\bullet}$H and $^{\bullet}$Cl under the effect of HC and $^{\bullet}$Cl can combine itself to form a stronger oxidative reagent as Cl_2. The Cl_2 may combine with H_2O and form HOCl which is capable of oxidizing the organic pollutants present in wastewater. The following reactions (Eqs. (2)-(6)) can occur during the process of HC in case of the effluent treated with HCl for maintaining its pH (Rajoriya et al., 2016):

$$H_2O \xrightarrow{HC} H^{\bullet} + HO^{\bullet} \quad (2)$$

$$HO^{\bullet} + HO^{\bullet} \rightarrow H_2O_2 \quad (3)$$

$$HCl \xrightarrow{HC} H^{\bullet} + Cl^{\bullet} \quad (4)$$

$$Cl^{\bullet} + Cl^{\bullet} \rightarrow Cl_2 \quad (5)$$

$$Cl_2 + H_2O \rightarrow HOCl + HCl \quad (6)$$

It is observed that CTWE from M1 was more suitable to be used for HC for effective reduction in the COD, TOC and TSS values at lower pressure conditions and C_v of 0.07.

2.3.2.2 Effect of dilution

As the reduction in COD and TOC was lower in case of CTWE from M2 and TDS was the main hindering parameter, it was further subjected to HC treatment after 50% dilution (%.V/V).The effect of dilution was studied at an optimum inlet pressure of 5 bar, C_v=0.7 and the obtained results are depicted in Fig. 2.8 and Table 2.4. It was observed from Fig.

2.8 that there was a considerable increase in the percentage reduction in TOC and COD on diluting the original sample. Table 2.4 presents that almost 53% COD and 45% TOC reduction was obtained with 50% dilution, whereas only16.5% COD and 18.2% TOC reduction was observed with undiluted sample. It is also worth noting here that dilution was effective in HC treatment by causing the dispersion and degradation of the suspended matter and almost 15% reduction in TSS, conductivity and turbidity was obtained, compared to only 3 to 5% reduction without dilution. The effect of dilution on the effluent also increases the total quantum of TOC and COD of CTWE. Table 2.4 presents that the maximum quantum of TOC and COD reduction for the 8L volume treated using HC was observed at 1023 mg/L and 1880 mg/L respectively with 50% diluted sample, whereas, it was only 576 mg/L of TOC and 1110 mg/L of COD reduction with undiluted sample. It can be seen that dilution on the CTWE gives not only higher percentage reduction in TOC and COD but also enhances the total quantum of TOC and COD reduction. This enhanced reduction due to dilution can be attributed to the availability of more $^{\bullet}$OH radicals due to the splitting of the OH ions caused by HC process. The excess free hydroxyl radicals are capable of oxidizing and degrading the suspended organic matter under conditions of high pressure and temperature within the hot spots generated in the cavitating device. The reactions that take place during cavitation of diluted samples are given in Eqs. (2) and (3).

Therefore, dilution of CTWE can be a better option for the effective pretreatment of CTWE using HC. Similar trends have been reported in literature for the treatment of industrial wastewater (Chakinala et al., 2008). Chakinala et al. (2008) investigated the effect of dilution on the industrial wastewater in terms of COD and TOC reduction. They reported that the extent of COD reduction in 150 min was 42%, 61%, and 73% for dilution ratios of 10, 20, and 50 respectively.

Table 2.4 Effect of dilution on COD, TOC, TSS, TDS, conductivity, and turbidity of CTWE obtained after M2

Parameters	**HC, no dilution**			**HC, 50% dilution**		
	Initial	**Final**	**% reduction**	**Initial**	**Final**	**% reduction**
COD (mg/L)	6720	5610	16.5	3400	1520	53.3

TOC (mg/L)	3279	2683	18.2	2295	1272	44.6
TSS (mg/L)	7800	7550	3.2	2400	2050	14.5
TDS (mg/L)	29480	27980	5.6	14860	14530	2.2
Conductivity (mS/cm)	60.8	57.4	5.5	29.2	25.22	13.6
Turbidity (NTU)	821	806	1.8	352	298	15.3

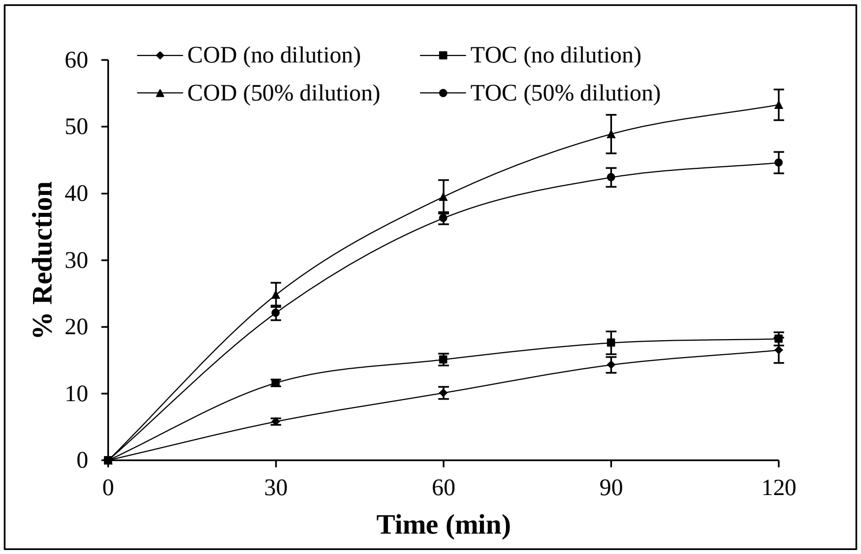


Fig. 2.8 Effect of dilution on COD and TOC reduction

2.3.2.3 Effect of HC on biodegradability index

Biodegradability index (BI) can be defined as a ratio of BOD to COD. BI is a measure of extent to which wastewater is vulnerable to biodegradation (Padoley et al., 2012). BI values in the range of 0.3 to 0.4 are indicative of good biodegradability of any wastewater and is considered to be the ideal values. If BI <0.3, waste effluent cannot be treated biologically (Metcalf & Eddy, 2003). Wastewater with a BI value ≥0.3 is amenable to biological process under aerobic conditions, whereas with a BI ≥0.4 is amenable to biological process under anaerobic conditions (Metcalf & Eddy, 2003; Padoley et al., 2012). The biodegradability of wastewater can be enhanced to a certain range using HC treatment by breaking complex molecules into short chain molecules which can easily be degraded by biological methods. Therefore in this study, the BI was considered as the deciding factor for the treatability of the HC treated effluent by conventional biological techniques.

The process conditions of HC treatment such as cavitation time and inlet pressure were chosen such that the HC treated CTWE had a BI value in the range of 0.3 to 0.4 for the samples obtained via M1, M2 or after dilution. The BI value of influent samples treated using HC is given in Table 2.5. These different samples corresponding to M1, M2, and 50% dilution were subjected to HC at an optimum inlet pressure of 5 bar and named as CTWE1, CTWE2, and CTWE3 respectively. It has been observed that BI increased to 0.57, 0.45 and 0.51 for the samples CTWE1, CTWE2 and CTWE3 respectively after subjecting to HC for 120 minutes at the optimized inlet pressure of 5 bar. HC pretreatment enhances the BI of tannery wastewater which is due to the breakage of bio-refractory pollutants into simpler molecules which are amenable to biodegradation. It can also be observed from Table 2.5 that the pretreatment of HC could lead to lesser increment in BI value for either undiluted (CTWE2) or diluted (CTWE3) wastewater than CTWE1. The maximum BI enhancement for CTWE1 was found from 0.34 to 0.57 using HC pretreatment in 120 min, indicating the effectiveness of methodology M1 over M2.

Table 2.5 Effect of HC pretreatment on Biodegradability index of different coagulated effluent samples

Type of effluent	Time (min)	BOD (mg/L)	COD (mg/L)	BI (BOD:COD)
CTWE 1	0	2840	8320	0.34
	120	3080	5360	0.57
CTWE 2	0	2580	6720	0.38
	120	2520	5610	0.45
CTWE 3	0	1210	3400	0.35
	120	780	1520	0.51

From the observed results, it is clearly shown that coagulation followed by HC pretreatment has capability to enhance the BI of wastewater and it can further be treated with subsequent biological treatment methods under anaerobic conditions on an industrial level.

2.3.3 Treatment of coagulated TWE (CTWE) using ultrasonication (US)

The effect of US process in order to cause the reduction in COD as well as enhancement in BI of the CTWE obtained from both M1 and M2 were also studied. The main reaction mechanism for radical generation during sonication of wastewater is expressed as Eqs (2) and (3). Fig. 2.9 and Table 2.6 present the % reduction in COD when samples of M1 and M2 were subjected to US. It can be seen from Table 2.6, that 50.45% COD reduction was obtained in 120 min for CTWE obtained from M1 along with BI enhancement from 0.12 to 0.27 whereas 52.38% COD reduction was obtained for CTWE obtained from M2 with BI enhancement from 0.16 to 0.38. In order to further increase the BI, sonication was given for another 30 minutes and BI increased from 0.27 to 0.29 for CTWE from M1 along with 53% reduction in COD, whereas BI increased from 0.38 to 0.41 along with 56% reduction in COD for CTWE from M2. It was observed that sonication beyond 120 minutes only marginally changed the BI value. More treatment time was required in case of US compared to HC in order to get the required BI value. Hence it can be concluded that ultrasonically treated CTWE can be subjected to conventional biological treatment processes under anaerobic conditions. Table 2.6 presents the effect of US on TSS, TDS, conductivity, and turbidity of the CTWE samples from M1 and M2 for 120 minutes of sonication. It was observed that US had marginal effect on reduction of TDS and TSS. Almost 11.6 % and 6.8 % reduction in TDS was attained for CTWE samples from M1 and M2 respectively, whereas TSS reduction was 9.7 % and 12.2 % in case of M1 and M2 respectively.

Table 2.6 Effect of US on COD, BOD, BI, TDS, TSS, conductivity, and turbidity of CTWE

Parameters	**CTWE obtained from M1**			**CTWE obtained from M2**		
	Initial	**Final**	**% reduction**	**Initial**	**Final**	**% reduction**
COD (mg/L)	8720	4320	50.45	6720	3200	52.38
BOD (mg/L)	1046	1187	--	1075	1225	--
BI	0.12	0.27	--	0.16	0.38	--
TDS (mg/L)	26760	23640	11.6	24350	22690	6.8
TSS (mg/L)	4090	3690	9.7	3830	3360	12.2
Conductivity (mS/cm)	47.3	43.6	7.8	46.2	43.3	6.2
Turbidity (NTU)	1356	1288	5.0	910	885	2.7

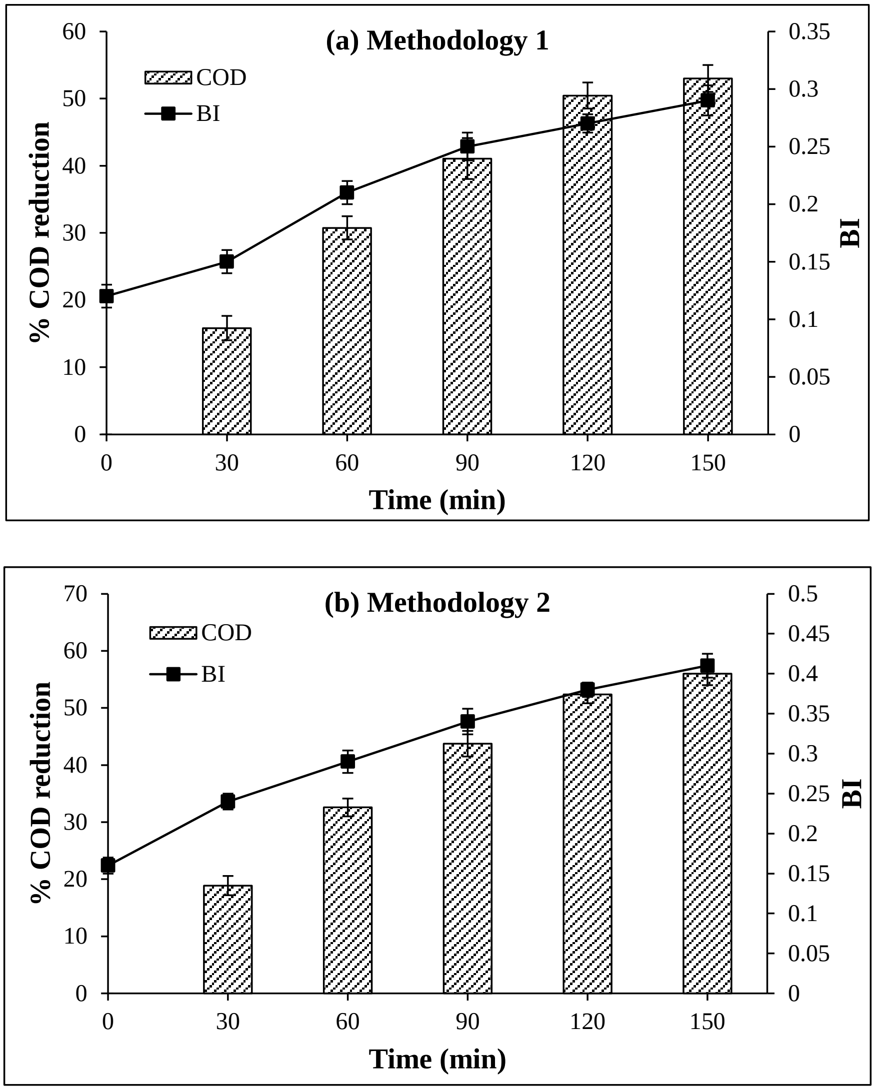


Fig. 2.9 Effect of US on the biodegradability of CTWE (a) using M1 (b) using M2

2.3.4 Characteristics of final treated TWE using coagulation followed by HC/ US

The untreated TWE having the initial COD in the range of 10560-21000 mg/L and BOD in the range of 1100-2960, these parameters attain a value of BI in the range of 0.09 to 0.14. The results obtained for the physico-chemical parameters of TWE before and after pretreatment with HC and US are summarized in Table 2.7. Maximum amount of COD and TSS reduction was almost 75% (15640 mg/L) and 73.4% (25860 mg/L) respectively for TWE of M1 and 70% (13190 mg/L) and 75.8% (23750 mg/L) respectively for TWE of M2 using coagulation followed by HC. Similarly, maximum amount of COD and TSS reduction was almost 63.5% (7520 mg/L) and 68.2% (7940 mg/L) respectively for TWE of M1 and 69.6% (7360 mg/L) and 69% (7500 mg/L) respectively for TWE of M2 using coagulation followed by US. Biodegradability index was enhanced in 120 min of treatment time from 0.14 to 0.57 and 0.10 to 0.38 using coagulation followed by HC and US respectively. It has been observed that coagulation alone is not sufficient to enhance the BI to ≥0.4 which is the necessary condition for AD, whereas when the coagulated samples were subjected to HC, the BI value increased to 0.57 and 0.45 for M1 and M2 respectively. This clearly indicates that HC is more effective than US in enhancing the BI value when combined with coagulation for pretreatment.

Table 2.7 Comparison of untreated and treated TWE characteristics

Parameters		**Coagulation followed by HC**		**Coagulation followed by US**	
		M1	**M2**	**M1**	**M2**
pH	Untreated	12.5	12.5	12.4	12.26
	Coagulated	4.86	4.18	4.32	4.08
	Treated	5.04	4.25	4.56	4.18
TSS (mg/L)	Untreated	35200	31300	11630	10860
	Coagulated	13970	7800	4090	3830
	Treated	9340	7550	3690	3360
COD (mg/L)	Untreated	21000	18800	11840	10560
	Coagulated	8320	6720	8720	6720
	Treated	5360	5610	4320	3200
BOD (mg/L)	Untreated	2960	2660	1040	1050
	Coagulated	2840	2580	1046	1075
	Treated	3080	2520	1187	1225
BI	Untreated	0.14	0.14	0.09	0.10
	Coagulated	0.34	0.38	0.12	0.16
	Treated	0.57	0.45	0.27	0.38

2.3.5 Comparison of energy efficiency in HC and US

Energy efficiency evaluations of HC and US have been done based on the net chemical effects (the amount of COD degraded (mg) per unit energy delivered in to the system (J)). The sample calculation of energy efficiency for HC and US is given in Appendix A (page no. 187). The total treatment time was taken 120 min for both processes to evaluate the energy efficiency. The energy efficiency obtained for both the processes are summarized in Table 2.8. In case of HC, the main energy consumption was by the pump which is used to recirculate the waste effluent through the cavitating device whereas in the case of US, the main energy consumption was by the ultrasound generator used for introducing ultrasonic waves into the solution. It can be observed that the energy required per unit volume was higher in case of US than that required for HC. The total quantum of COD reduction achieved using coagulation followed by HC (CFHC) was found to be higher than that obtained using coagulation followed by US (CFUS). The net energy efficiency for CFHC using coagulation methodology M1 and M2 was 1.494×10^{-3} (mg/J) and 0.56×10^{-3} (mg/J) respectively whereas energy efficiency for CFUS using M1 and M2 was 0.244×10^{-3} (mg/J) and 0.195×10^{-3} (mg/J) respectively. This clearly indicates that the energy efficiency obtained using CFHC was higher than that obtained for CFUS. Comparison of the energy efficiency showed that CFHC was found to be almost six folds more energy efficient as compared to CFUS in treating the CTWE obtained from M1. Hence, CFHC can be considered as more energy efficient approach for the treatment of TWE and other similar waste effluent on an industrial level.

Table 2.8 Energy efficiency evaluation for CTWE using HC and US

Type of effluent	**Process**	**% COD reduction**	**Total amount of COD reduced (mg/L)**	**Energy required/volume (J/L × 10^{-6})**	**Energy efficiency (mg/J × 10^{3})**
CTWE obtained from M1	**HC**	35.57	2960	1.98	1.494
	US	50.45	4400	18.00	0.244
CTWE obtained from M2	**HC**	16.51	1110	1.98	0.560
	US	52.38	3520	18.00	0.195

2.3.6 Cost estimation for TWE using coagulation followed by HC and US

Cost estimation is based upon the amount of COD reduced in association with amount of chemical and energy (kWh) consumed for the COD reduction. In case of HC reactor, the high power pump is major energy consuming and cost determining factor, whereas power required for ultrasonic processor is the cost determining factor for ultrasonication. Methodology 1 (M1) followed by HC caused reduction of COD from 21000 to 5360 mg/L with a treatment cost of 0.0026 Rs/mg of COD reduced as seen in Table 2.9.

Whereas, the application of US provided total reduction of COD from 11840 to 4320 mg/L and resulted in overall treatment cost 0.002 Rs/mg of COD reduced which is slightly less than the treatment cost of HC. However, the volume of TWE treated in HC is higher than the US process; the cost of treatment in US (52.66 Rs/L) was almost 11 folds higher in comparison to HC (5.00 Rs/L). Similar results were also observed in case of Methodology 2 (M2) followed by HC and US. The treatment cost for US (52.63 Rs/L) was also found to be almost 11 folds higher in comparison to HC (5.08 Rs/L). Calculation for cost estimation is given in Appendix A.

Table 2.9 Cost estimation for CTWE using HC and US

Process		Total amount of COD reduced (mg/L)	Energy required for the reduction of one mg of COD (kWh/mg)	Cost of the treatment for the reduction of one mg of COD (Rs/mg)	Cost of the treatment for treating the one liter of TWE (Rs/L)
Coagulation through M1	**HC**	15640	0.00028	0.0026	5.00
	US	7520	0.00023	0.002	52.66
Coagulation through M2	**HC**	13190	0.00033	0.003	5.08
	US	7360	0.00024	0.0021	52.63

2.4 Summary of the chapter

The effect of coagulation coupled with cavitation as a pretreatment strategy was investigated for TWE for achieving maximum COD and TSS reduction and also to increase its biodegradability. It was observed that coagulation being a highly pH dependent process, pH adjustment was needed prior or to alum (coagulant) treatment. It was observed that as the residual pH of treated tannery wastewater approached around 4.5, maximum COD and TSS reduction was attained. To further improve COD reduction along with waste mineralization, the coagulated TWE was further subjected to HC and US and the findings are summarized as follows.

- Coagulation followed by cavitation process was effective for the pretreatment of TWE. The coagulation efficiency was maximum at pH around 4.5 and the optimum alum dose was 0.5 g/100mL and 2 g/100mL for methodology M1 and methodology M2 respectively.
- In case of HC treatment, lower operating inlet pressure of 5 bar yielded higher COD and TOC reduction for the pretreatment of CTWE as compared to higher operating inlet pressure (10 bar).
- Maximum reduction of 35.6% and 43.9% was obtained for the COD and TOC respectively for CTWE obtained from M1 whereas maximum reduction of 16.5% and 18.2% obtained for COD and TOC respectively for CTWE obtained from M2 at 5 bar in 120 minutes.
- Dilution (50% dilution) of the CTWE prior to HC treatment was found to be very effective in reduction of the COD and TOC of the tannery effluent. It enhanced the reduction in COD and TOC to 53% and 45% respectively for CTWE obtained from M2.
- In case of US treatment, 50.45% COD reduction was obtained in 120 minutes for CTWE obtained from M1 whereas 52.38% COD reduction was obtained in 120 minutes for CTWE obtained from M2.
- The maximum biodegradability index enhanced from 0.14 to 0.57 (in 120 minutes) and 0.10 to 0.41 (in 150 minutes) with pretreatment using combination of coagulation followed by HC and US respectively and it indicates that the pretreated tannery effluent can be treated in a subsequent AD unit.
- HC was found to be more effective than US in enhancing the BI value and therefore has potential to scale up and can be fitted in the existing CETP units.
- HC was found more energy efficient treatment technique as compared to US. In case of CTWE obtained from M1, energy efficiency of HC and US was 1.494×10^{-3} mg/J and 0.244×10^{-3} mg/J respectively whereas in case of CTWE obtained from M2 energy efficiency of HC and US was 0.56×10^{-3} mg/J and 0.195×10^{-3} mg/J respectively.

- Coagulation followed by HC for the pretreatment of TWE was found to be more cost efficient in terms of treating the unit volume of TWE i.e., almost 11 times higher as compared to coagulation followed by US.

Overall, present study indicates that coagulation followed by cavitation process i.e. HC and US could be applied as pretreatment tools in enhancing the biodegradability index of tannery wastewater for an anaerobic biological treatment approach, However HC was found to be more effective in terms of energy and cost efficiency. The use of US and HC in combination with various advanced oxidation reagents have been investigated for the treatment of TWE and presented in subsequent chapters 3 & 4.

CHAPTER 3

Treatment of TWE using hybrid technique of Ultrasonication (US) combined with advanced oxidation reagents (using Hydrogen Peroxide/Fenton's Reagent/Sodium Hypochlorite/Ozone)

3.1 Introduction:

Recent literature reports that US is capable of degrading recalcitrant matter such as organic dyes (Priya and Madras, 2006; Wang et al., 2011; Zhang et al., 2007), phenolic compounds (Liu et al., 2009), pesticides (Wang et al., 2007, 2006), aqueous carbon tetrachloride (Francony and Pctrier, 1996), benzene compounds (Nanzai et al., 2009), herbicides (Bahena et al., 2008), polycyclic aromatic hydrocarbons (David, 2009) and chloro-aromatic compounds etc. (Ku et al., 2005; Lim et al., 2008). Its application in combination with advanced oxidizing agents has shown promising results for the treatment of wastewater and is capable of increasing the biodegradability along with the reduction of toxicity. It has been reported that US alone was not too 11efficient to break down the bio-refractory pollutants, whereas US in combination with advance oxidation reagents were found to be effective to degrade organic pollutant present in the waste effluent. US based hybrid processes provided enhanced generation of hydroxyl radicals which resulted in efficient degradation of organic pollutants when compared to individual treatment processes.

This study was aimed to evaluate the effectiveness of US in combination with various advanced oxidation reagents so as to investigate the effect of combined treatment on the treatment of TWE. Various factors that affect the process efficiency include pollutant characteristics; hydroxyl radical's production mechanism, nature of the hybrid combination and interaction of techniques with pollutant molecules. In this hybrid method, various oxidation agents such as hydrogen peroxide, Fenton reagent, sodium hypochlorite and ozone were studied for the treatment of TWE and also in combination with conventional treatment technique i.e. coagulation which has not been reported earlier. The process efficiency of this integrated approach was evaluated in terms of maximum COD reduction of TWE and the effect of various process parameters such as coagulant dosages, ultrasonic amplitude, concentration of oxidizing agents etc. on the COD reduction of TWE.

3.2 Material and Method:

3.2.1 Tannery wastewater

Collection was done as discussed in section 2.2.2 and the physico-chemical characteristics of TWE sample used in present study are shown in Table 3.1. The TWE was stored in a deep freezer at -17°C so as to prevent any change in the initial physico-chemical characteristics. Prior to experimental studies, TWE was allowed to attain room temperature (30°C approximately) and mixed thoroughly and analyzed for its physico-chemical characteristics.

Table 3.1 TWE characteristics

Parameter	Raw TWE
pH	7.5-8.14
COD (mg/L)	8160-8760
TS (mg/L)	18280-19420
TDS (mg/L)	11030-11970
BOD (mg/L)	2200-2800
BI	0.27-0.32

3.2.2 Experimental set-up

The schematic representation of US reactor set-up used in this study is shown in Fig. 3.1. US was conducted for the pretreatment of TWE at 20 kHz using ultrasonic horn (VCX 750, Sonics, USA). As shown in schematic representation, an ultrasound generator is connected with ultrasonic transducer which converts the electrical energy to vibrational energy. The tip of the ultrasonic horn is kept immersed in the sample and the amplitude is regulated with the help of ultrasound generator. The temperature of the sample was maintained during the US by cooling water circulation through the jacket surrounding the batch reactor. In case of Ozonation process the ozone was generated using ozonator and introduced at the bottom of the US reactor through sparger. In case of US coupled with advanced oxidizing agents such as Fenton, hydrogen peroxide and sodium hypochlorite, the respective reagents were introduced from the top of the batch reactor.

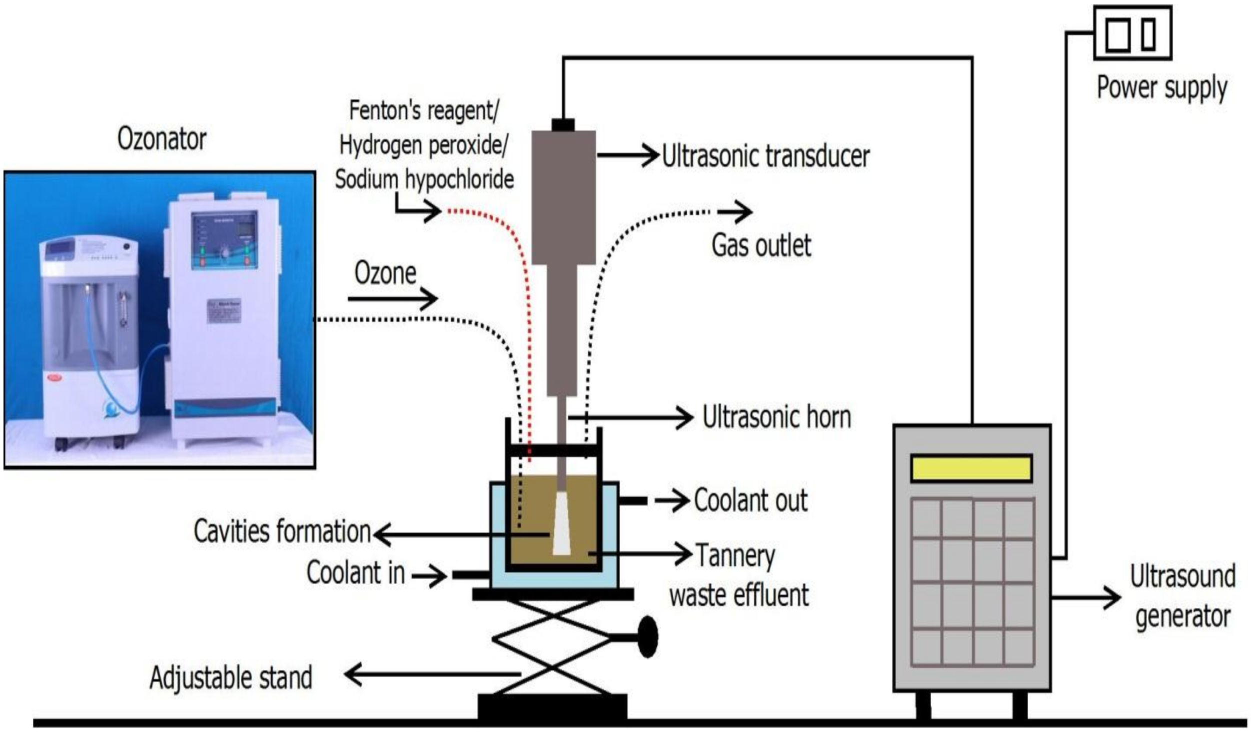


Fig. 3.1 Schematic representation of ultrasonic reactor set-up

3.2.3 Analytical methods and instruments

The pH of the sample was measured using pH meter (Thermo scientific, USA). BOD and COD of samples were determined as per the standard APHA methods (*APHA, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington DC, 1998.*, 1998). The conductivity and TDS was measured using ion meter (Thermo scientific, USA). TSS was determined by subjecting the TWE samples to filtration and drying whereas the TS of the samples were determined by direct drying, both at 104 °C in an oven (Make: DAIHAN Scientific Co. Ltd.) as per APHA methods. All experiments were repeated twice and reported values are the average of two runs.

3.2.4 Chemicals

All the chemicals used in this study were purchased from M/s Loba Chemie Pvt. Ltd., India, and were of analytical grade (AR). Alum ($Al_2(SO_4)_3.18H_2O$) (98%) and aluminum chloride ($AlCl_3$) (99%) were used as the coagulant. Chemicals such as potassium dichromate (99.5%), concentrated sulfuric acid (98%), silver sulfate (99%), mercuric sulfate (98%), ferrous ammonium sulfate (99%) and ferroin indicator (0.025 M) were used for COD analysis. BOD analysis was carried out using sodium thiosulfate (99.5%), sodium hydroxide (98%), sodium iodide (99.5%), manganous sulfate (99%), starch, potassium dihydrogen phosphate (99.5%), dipotassium hydrogen orthophosphate (99%), disodium hydrogen phosphate (99%), ammonium chloride (99.8%), calcium chloride (99%), magnesium sulfate (99.5%) and ferric chloride (99%). Hydrogen peroxide solution (30% w/w), ferrous sulfate ($FeSO_4.7H_2O$) (99%) and sodium hypochlorite solution (4-6% w/v) were used as the oxidizing agents. Double distilled water was used for the sample dilution studies.

3.2.5 Treatment Methodology:

The methodologies adopted for the treatment of TWE is presented in Fig. 3.2, in which the various hybrid treatment methods are drawn as a flowchart for the combination of coagulation, US, and the advanced oxidizing reagents. Strategy ‘A’ follows treatment of TWE by US combined with advanced oxidizing reagents, whereas strategy ‘B’ follows pretreatment of TWE by coagulation followed by US combined with advanced oxidizing reagents.

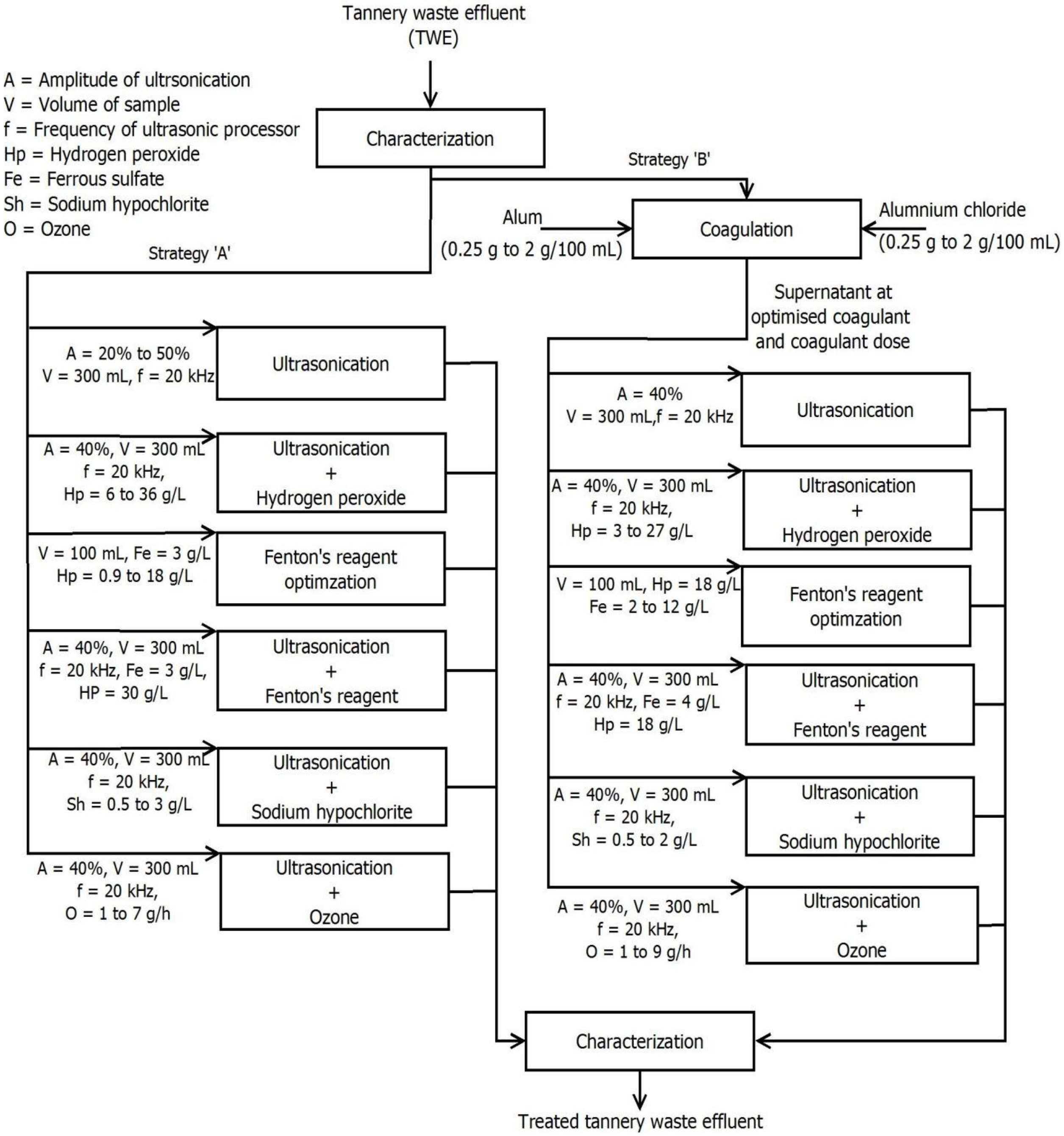


Fig. 3.2 Treatment methodology used in present study

3.2.5.1 Coagulation of raw TWE:

In order to reduce organic load and to make the treatment process more efficient, coagulation of TWE was carried out with two coagulants alum ($Al_2(SO_4)_3.18H_2O$) and aluminum chloride ($AlCl_3$) separately without any prior pH adjustment. The effect of coagulant dosage on COD and TSS removal was studied by varying the dosage of alum ($Al_2(SO_4)_3.18H_2O$) and aluminum chloride feed from 0.25 to 2.0 g per 100 mL into the TWE, shaken in a rotary flask shaker at 200 rpm for 15 minutes and allowed to settle down over a period of 60 minutes. The supernatant (CTWE) was collected and analyzed for its COD, TSS and TDS based on which the optimum dosage was selected for further studies in treatment of TWE by US and in combination with other oxidizing agents.

3.2.5.2 Treatment of raw TWE & CTWE using Ultrasonication process:

Raw TWE and CTWE (supernatant from coagulation process) was subjected to US at a frequency of 20 kHz and amplitude varying from 20 to 50 % in a batch mode with a nominal power of 750 W and analyzed to obtain the optimum amplitude for maximum COD reduction. In the US experiments, the probe tip was immersed 2.5 cm below the free surface of 300 mL sample and subjected to US with 59 s on and 10 s off cycle. The temperature of the samples (30 ± 2 °C) was maintained by cooling water circulation through the jacket surrounding the batch reactor and samples were taken at fixed intervals of time for further analysis.

3.2.5.3 Treatment with advanced oxidizing agents:

In order to enhance the treatment efficiency of TWE and CTWE, the US process was carried out in combination with various oxidizing agents such as Fenton's reagent, O_3, H_2O_2, and sodium hypochlorite and studied for their synergistic effects. The effect of H_2O_2 was studied by varying H_2O_2 dosage from 6 g/L to 36 g/L for TWE sample and 3 g/L to 27 g/L for CTWE sample and subjected to US. To further intensify the reduction of organic pollutants in TWE, Fenton's reagent was used in which the ferrous ion reacts with H_2O_2 generating extra hydroxyl radicals for increasing the degradation rates. Fenton’s oxidation process was carried out for both TWE and CTWE samples to optimize the dosage of Fenton’s reagent and further combined with US by loading Fenton’s reagent from the top of the US reactor. O_3 for TWE treatment was generated using a O_3 generator (high voltage corona discharge ozonator, maximum O_3 rate: 10 g/h, make: Eltech Engineers, India) and introduced at the bottom of the US reactor in to the solutions. Effect of varying feed rate of O_3 (1 to 7 g/h) during US + O_3 process was studied and for determining synergetic effects. Sodium hypochlorite was also added as an oxidizing agent in combination with US and its effect on degradation process was studied, by varying dosage from 0.5 g/L to 3 g/L for TWE sample and 0.5 g/L to 2 g/L for CTWE samples respectively.

3.3 Result and discussion

3.3.1 Pre-treatment of TWE using Coagulation

The removal mechanism of organic matter using coagulation involves the neutralization of charged particles and integration of impurities in an amorphous hydroxide precipitate and hydrolyzed products. The dosage of coagulant required for effective precipitation depends upon the characteristics of TWE such as pH, organic matter concentration, ionic strength, functionality and hydrophobicity etc. Aluminum salts i.e. alum ($Al_2(SO_4)_3.18H_2O$) and aluminum chloride ($AlCl_3$) was used as coagulant and effect of coagulant dosages was studied on the basis of efficacy of the treatment i.e. COD and TSS removal from the TWE. Due to the amphoteric nature of aluminum salts, the aluminum ions behave differently in both acidic as well as basic medium, the basic reaction mechanism governing aluminum ion behavior in acidic or basic medium is as follows;

$$In\ acid: Al(OH)_3(s) + 6H_3O^+(aq) \leftrightarrow Al^{3+}(aq) + 6H_2O \qquad (1)$$

$$In\ base: Al(OH)_3(s) + OH^-(aq) \leftrightarrow Al(OH)_4^-(aq) \qquad (2)$$

Table 3.2 represents the % COD and % TSS reduction and % TDS increase as well as corresponding pH and conductivity of the treated TWE solution for alum and aluminum chloride dosage varying from 0.25 to 2 g/100 mL. Coagulation is a pH dependent process and therefore the optimized pH is to be identified for maximum precipitation. Fig. 3.3 presents the effect of varying dosage of alum and aluminum chloride on % removal of COD and TSS of TWE samples and the corresponding residual pH. It was observed that as the alum dosage varied from 0.25 g to 2 g for 100 mL of TWE sample, residual pH of sample decreases continuously from pH 8.03 to pH of 4.01. With the increase in alum dosage, % COD and % TSS removal increases until the optimum alum dosage of 1.5 g/100 mL and further decreases producing an adverse effect on treatment strategy.

Maximum of 52.01 % COD and 69.79 % TSS removal was achieved at the alum dosage of 1.5 g/100 mL of TWE sample and the residual pH of sample reached a pH of 4.45. Similar pattern was observed for COD removal, TSS removal and residual pH in case of aluminum chloride as shown in Fig. 3.3 with optimum dosage of aluminum chloride at 1.5 g/100 mL. For dosage of 1.5 g/100 mL of aluminum chloride maximum of 46.31% COD and 55.70% TSS removal was obtained with corresponding residual pH of 4.11. The organic and inorganic matter present in TWE that cannot be destabilized beyond the optimum coagulant dosage may be attributed to its refractory nature.

Table 3.2 Effect of coagulant dosage on COD, pH, TSS, TDS and conductivity

Parameters		**COD (mg/L)**	**% COD reduction**	**pH**	**TSS (mg/L)**	**% TSS removal**	**TDS (mg/L)**	**Conductivity (mS/cm)**
Coagulant dosage	**Initial**	8420	-	8.17	7450	-	11780	24.14
0.25 g	Alum	7120	15.43	8.03	6450	13.42	11960	24.46
	Aluminum Chloride	7550	10.33	8.14	6700	10.06	12120	24.63
0.5 g	Alum	6240	25.89	7.65	5200	30.20	12310	24.87
	Aluminum Chloride	6480	23.04	7.21	5850	21.47	12450	25.6
1.0 g	Alum	4480	46.79	6.56	3150	57.71	12640	25.34
	Aluminum Chloride	5120	39.19	4.76	3650	51.00	13570	27.71
1.5 g	Alum	4040	52.01	4.45	2250	69.79	13080	25.76
	Aluminum Chloride	4520	46.31	4.11	3300	55.70	14490	30.4
2.0 g	Alum	4220	49.88	4.01	2400	67.78	13230	25.92
	Aluminum Chloride	4680	44.41	3.94	3550	52.34	15340	33.63

Addition of external coagulants cause an increase in TDS of the TWE solution (Saxena et al., 2018a). And as given in Table 3.2, it was observed that the TDS increased by 11% and 23% TDS at the optimum dosage of alum and aluminum chloride respectively which is a major drawback of this treatment strategy.

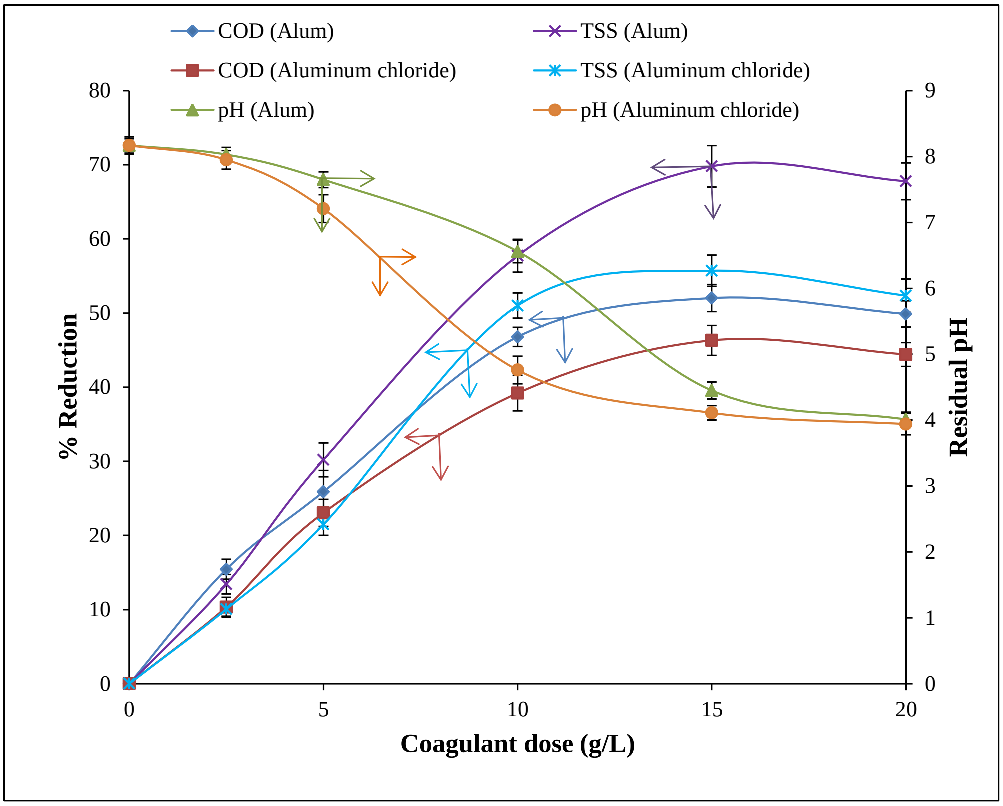


Fig. 3.3 Effect of coagulant dosage on % removal of COD and TSS and residual pH

It was also observed from Fig. 3.3 that with increase in dosage of both coagulants from 0.5 g/100 mL to 1.5 g/100 mL a sudden drop in solution pH was observed with less reduction in COD in case of aluminum chloride, whereas in case of alum solution pH was gradually decreased with high reduction in COD. The optimum pH for coagulation process using aluminum chloride and alum with maximum reduction in COD was pH 4.11 and pH 4.45 respectively. To identify the appropriate coagulant, Fig. 3.4 presents a comparison between alum and aluminum chloride on the basis of quantum of COD and TSS removal and corresponding increase in TDS in TWE at their optimum dosage of 1.5 g/100 mL. Even with similar dosage of both coagulants the effectiveness to treat TWE sample was different. Alum was more effective as, higher removal in COD and TSS with lesser increase in TDS amount was obtained compared to aluminum chloride and therefore alum was used as coagulant for further treatment studies.

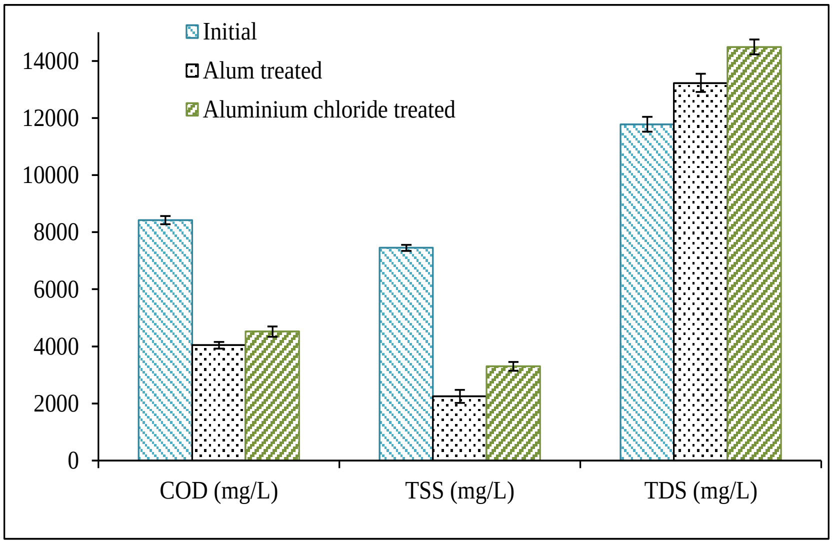


Fig. 3.4 Comparison between alum and aluminum chloride based on COD, TSS and TDS at optimized dosage of both coagulants

3.3.2 Effect of amplitude of ultrasonication:

Effectiveness of US to disintegrate the organic matter is dependent on the amplitude chosen for the sonication process. Therefore in order to examine the effect of amplitude on the COD reduction, the raw TWE was subjected to US at different amplitudes and frequency of 20 kHz for 2 hr. and Fig. 3.5 presents the effect of amplitude variation on COD reduction. As the amplitude increased from 20% to 50%, reduction in COD increased up to 40% whereas further increase in amplitude beyond 40% % reduction in COD decreased. Maximum COD reduction of 20.3% was observed at 40% amplitude with a quantum of 1740 mg/L COD as shown in Table 3.3. Rate kinetics was applied to represents the COD reduction behavior in terms of rate and order and it was observed that pseudo first order rate kinetics was fitted well for the COD reduction at different amplitude of US. It was observed that as the amplitude of US increased from 20% to 40%, the rate constant of COD reduction increased from 0.0002 to 0.0021 min^{-1} respectively. Further as the amplitude increased from 40% to 50% COD reduction rate constant decreased to 0.001 min^{-1}.

The coagulated CTWE sample was also subjected to US at 40% of amplitude and compared to US of TWE and presented in Fig. 3.5 and Table 3.3. It was observed that COD of CTWE reduced from its initial value of 4560 mg/L to 3480 mg/L in 2 hr. of US and pseudo first order rate kinetics fitted well with the rate constant estimated at 0.0024 min^{-1}, which was higher than the rate constant for COD reduction of TWE at 40% amplitude. The pH of the sample slightly increased from its initial value after the US of both TWE and CTWE samples. The TDS and conductivity of TWE sample decreased with increase in amplitude from 20% to 40% and further increase in amplitude from 40% to 50% resulted in decrease in reduction of TDS and conductivity. The quantum of TDS and conductivity reduction was higher in ultrasonically treated CTWE sample as compared to ultrasonically treated TWE sample. The TDS of ultrasonically treated CTWE sample decreased from 12630 mg/L to 11410 mg/L whereas in case of ultrasonically treated TWE sample, TDS was decreased from 11950 mg/L to 11430 mg/L for the same amplitude of 40%. The less reduction in TDS of TWE may be due to the turbidity or interaction of the suspended particles in TWE sample, which may be converted into their dissolved forms as residual TDS under the effect of US, whereas for CTWE sample lesser interactions were present as the suspended particles were already removed by coagulation.

Table 3.3 Effect of ultrasonic amplitude on pH, COD, TDS and conductivity of TWE and comparison with CTWE treated at 40% optimized amplitude

Parameters		**TWE**				**CTWE**
		20%	30%	40%	50%	40%
pH	Initial	7.63	7.63	7.55	7.54	4.26
	Final	7.72	8.03	7.84	7.78	4.39
COD (mg/L)	Initial	8160	8640	8560	8280	4560
	% reduction	2.5	18.8	20.3	10.1	23.7
	Quantum	200	1620	1740	840	1080
	Rate constant (min^{-1})	0.0002	0.0019	0.0021	0.001	0.0024
	R^2	0.961	0.965	0.9622	0.9506	0.9921
TDS (mg/L)	Initial	11930	11970	11950	11970	12630
	Final	11900	11520	11430	11610	11410
Conductivity (mS/cm)	Initial	24.33	24.46	24.40	24.49	25.89
	Final	24.24	23.51	23.34	23.83	22.67

(Experimental conditions; Sample Volume 300 mL, Treatment time 120 minutes)

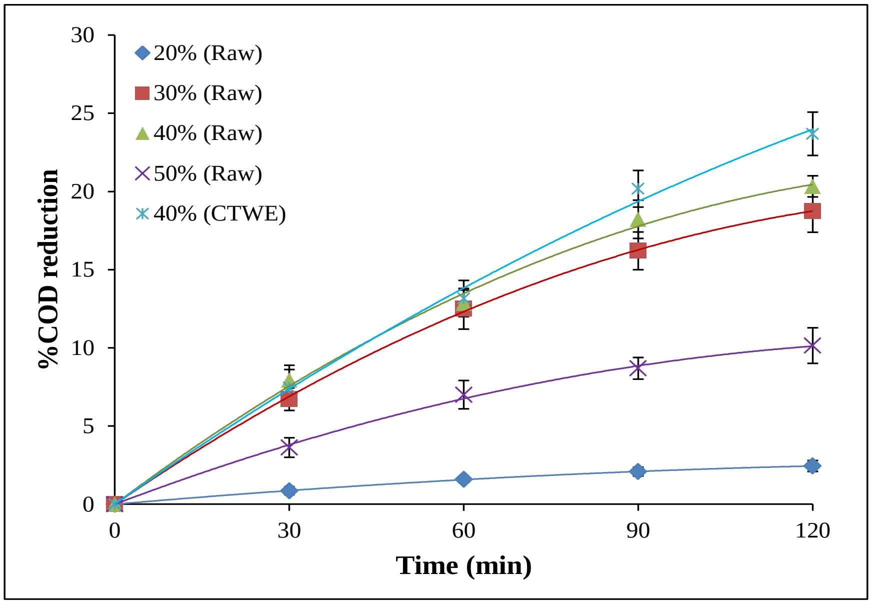


Fig. 3.5 Effect of ultrasonic amplitude on % COD reduction of TWE and comparison with CTWE treated at 40% amplitude

3.3.3 Hybrid treatment of TWE and CTWE using US + H_2O_2:

H_2O_2 is an active oxidizing agent which is easily dissociated in presence of cavitational conditions and produces hydroxyl radicals (Raut-jadhav et al., 2013). Under the hot spot conditions of ultrsonication process, H_2O_2 readily undergoes sonolysis and dissociates into hydroxyl radicals (Pang et al., 2011). These extra generated hydroxyl radicals participate in the degradation of organic pollutants presents in TWE sample. Therefore in order to accelerate the ultrasonic degradation of organic molecules present in TWE, H_2O_2 was added at the time of US as an external oxidizing agent. Varying dosages of H_2O_2 from 6 g/L to 36 g/L were externally added and US was performed at the optimized amplitude of 40% for treating 300 mL of TWE sample over a period of 120 minutes. The effect of combined treatment on COD, pH, TDS and conductivity is presented in Table 3.4. It was observed that even though there is considerable decrease in TDS and conductivity of TWE samples, addition of external H_2O_2 did not enhance the degradation of organic pollutants presents in TWE, but only acted as a scavenger for hydroxyl radicals produced during the US. The addition of H_2O_2 in raw TWE did not attribute to enhance the reduction capacity of US in order to degrade the organic molecules. It was observed that with increase in H_2O_2 amount in TWE, no COD reduction was observed which attributed to the scavenging of hydroxyl radicals at increased concentrations of H_2O_2.

Table 3.4 Effect of US + various dosages of H_2O_2 on COD, pH, TDS, and conductivity of raw TWE

Parameters		**US alone**	**US + H_2O_2 dosage (mg/L)**					
			6 g/L	9 g/L	12 g/L	18 g/L	24 g/L	36 g/L
COD (mg/L)	Initial	8560	8280	8220	8760	8460	8520	8480
	Final	6820	7220	7340	8040	8180	8440	8440
	% reduction	20.3	12.8	10.7	8.2	3.3	0.9	0.4
pH	Initial	7.55	7.56	7.48	7.44	7.73	7.82	7.67
	Final	7.8	7.48	7.39	7.39	7.42	7.56	7.44
TDS (mg/L)	Initial	11970	11390	11320	11410	11030	11150	11290
	Final	11430	11080	11110	11090	10430	10420	10730
Conductivity (mS/cm)	Initial	24.46	23.21	23.11	23.17	22.49	22.66	23.01
	Final	23.34	22.61	22.83	22.6	21.3	21.32	21.75

(**Experimental conditions**: Sample Volume 300 mL, Treatment time 120 minutes, US amplitude 40%)

The same experiments were conducted for the treatment of CTWE with H_2O_2 dosage varying from 3 g/L to 27 g/L, which was externally added prior to US to the 300 mL of CTWE sample and US was performed at the optimized amplitude of 40% for 120 minutes. Fig. 3.6 depicts the reduction in COD with respect to time for the varying dosages of H_2O_2 and Table 3.5 presents the effect of various dosages of H_2O_2 on COD, pH, TDS and conductivity. It was observed that % reduction in COD increased from 28.51% to a maximum of 36.82% with an increase in H_2O_2 dosages from 3 g/L to 18 g/L and thereafter it decreased to 34.54% at higher H_2O_2 dosage of 27 g/L. However excess dosage of H_2O_2 from the optimum value resulted in scavenging of hydroxyl radicals (Pang et al., 2011), which lead to decrease in overall reduction rate of organic molecules present in sample. It was observed from Table 3.5 that reduction in TDS decreased with increase in H_2O_2 dosage so as conductivity, which may be due to the solubility of H_2O_2 in the treated samples.

Table 3.5 Effect of US + various dosage of H_2O_2 on COD, pH, TDS, and conductivity of CTWE

Parameters		**US alone**	**CTWE followed by US + H_2O_2**			
			3 g/L	9 g/L	18 g/L	27 g/L
COD (mg/L)	Initial	4560	4560	4560	4400	4400
	Final	3480	3260	3120	2780	2880
	% reduction	23.68	28.51	31.57	36.82	34.54
pH	Initial	4.26	4.26	4.26	4.34	4.34
	Final	4.39	4.30	4.19	4.03	3.85
TDS (mg/L)	Initial	12630	12630	12630	12510	12510
	Final	11410	12350	12420	12320	12370
Conductivity (mS/cm)	Initial	25.89	25.89	25.89	25.76	25.76
	Final	22.67	25.25	25.32	25.15	25.40

(**Experimental conditions**: Sample Volume 300 mL, Treatment time 120 minutes, US amplitude 40%)

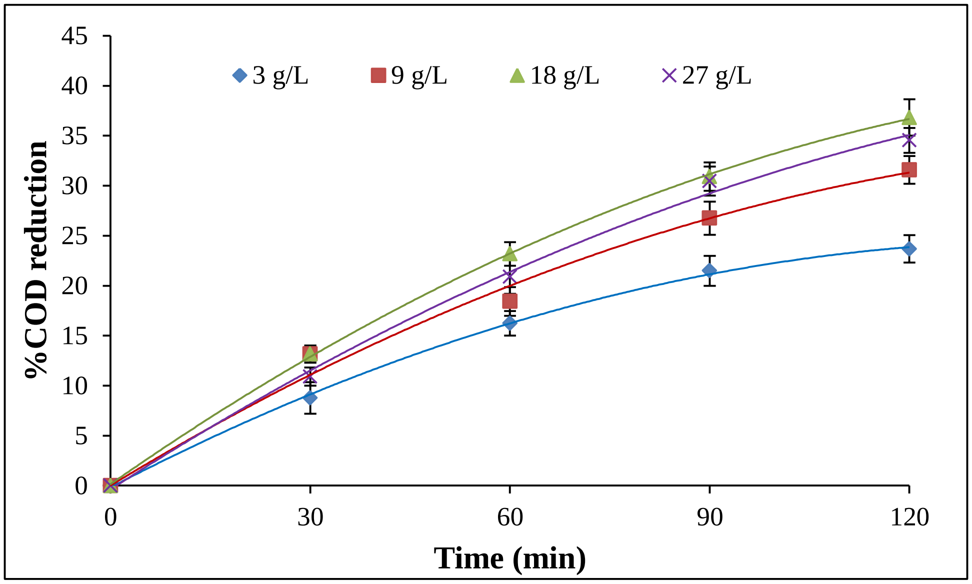


Fig. 3.6 Effect of US + various dosage of H_2O_2 on COD reduction of CTWE

The synergetic coefficient "$\gamma_{US+H_2O_2}$" was also estimated for the combined process of US with H_2O_2 for the treatment of CTWE using Eq.3. The first order rate constant of COD reduction at optimized conditions was 0.004 min^{-1} for combined process of US + H_2O_2 and 0.0024 min^{-1} for US only. The addition of H_2O_2 dosage doesn't reduce the

COD of CTWE therefore first order rate constant for COD reduction for only H_2O_2 was taken as zero.

$$\text{Synergetic coefficient } \gamma_{US+H_2O_2} = \frac{k_{(US+H_2O_2)}}{k_{US}+k_{H_2O_2}} \qquad (3)$$

$$\gamma_{US+H_2O_2} = \frac{0.004}{0.0024+0.0} = 1.67$$

The value of synergetic coefficient "$\gamma_{US+H_2O_2}$" estimated at a value of 1.67 shows the synergetic effect of the combined process in comparison to the efficiency of the individual processes.

3.3.4 Hybrid treatment of TWE and CTWE using US + Fenton's reagent:

In the Fenton process, reaction between ferrous ion (Fe^{+2}) and H_2O_2 produces hydroxyl radicals and ferric ions which further reacts with H_2O_2 to produce more highly reactive oxy-hydroxyl radicals. With an optimum concentration of ferrous ion and H_2O_2, production of hydroxyl radicals could be maximized. Therefore initially the Fenton reagent dosage was optimized by fixing the ferrous dosage at 3 g/L and varying the H_2O_2 dosage from 0.9 g/L to 18 g/L. Fenton reagent dosage was varied in terms of weight ratio of Fe^{2+}: H_2O_2 [W:W] from 1:0.3 to 1:6. The effect of various Fenton dosages on COD, pH, TDS and conductivity is shown in Fig. 3.7 and Table 3.6. It was observed from the data that reduction in COD increased with increase in weight ratio of Fenton reagent dosage from 1:0.3 to 1:3 and maximum reduction 26.58% in COD was obtained for the weight ratio of 1:3. Further increase in Fenton reagent ratio to 1:3 caused a decrease in % reduction of COD 19.26%, which may be due to the excess dosage of H_2O_2 that may cause scavenging of hydroxyl radicals. Therefore the optimized weight ratio 1:3 of Fenton dosage and optimized amplitude 40% of US was used to treat 300 mL of raw TWE, however it was observed that the hybrid treatment process of US and Fenton reagent was not effective in the treatment of raw TWE as the % COD reduction was low at 11.08 %, when compared to the individual treatment process, which had 20.32% and 26.58% reduction in COD for US alone and Fenton respectively at their optimized conditions. The decrease in degradation of organic molecules present in raw TWE may be due to the scavenging of hydroxyl radicals generated during both the process, as well as may be due to the negative interaction between the processes.

Table 3.6 Effect of various Fenton dosages on COD, pH, TDS, and conductivity of TWE and comparison with US + optimized Fenton dosage

Parameters	**Fenton, Fe^{2+} : H_2O_2[W:W]**						**US + Fenton, Fe^{2+} : H_2O_2[W:W]**	
	Initial	1:0.3	1:1.5	1:3	1:4.5	1:6	Initial	1:3
COD (mg/L)	8200	6840	6240	6020	6480	6620	8480	7540
% COD reduction	-	19.88	23.90	26.58	20.97	19.26	-	11.08
pH	7.52	7.36	7.24	7.11	7.01	6.81	7.65	7.54
TDS (mg/L)	11130	11200	11320	11430	11660	11830	11020	10880
Conductivity (mS/cm)	22.7	22.87	22.94	23.11	23.37	23.88	22.40	22.19

(**Experimental conditions: Fenton:** Sample volume = 100 mL, Fe^{2+}= 0.3 g/ 100 mL (3 g/L), H_2O_2= 0.9g/L to 18g/L, treatment time = 120 minutes, **US + Fenton:** Sample volume = 300 mL, $FeSO4.7H_2O$= 3 g/L, H_2O_2= 9 g/L, treatment time = 120 minutes)

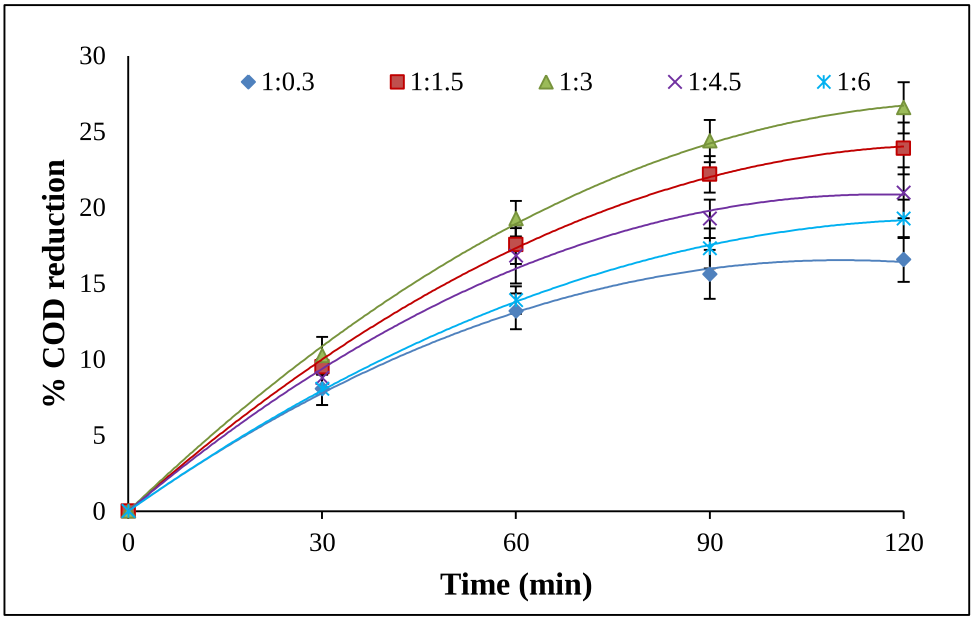


Fig. 3.7 Effect of various Fenton dosages on % COD reduction of TWE

Fenton reagent dosage was also optimized for the treatment of CTWE by fixing the H_2O_2 dosage (18 g/L) as optimized in US + H_2O_2 treatment process and varying the ferrous ion dosage ferrous sulfate from 2 g/L to 12 g/L. 100 mL of CTWE was treated for maximum of 120 minutes and Table 3.7 presents the data of % reduction in COD, pH, TDS and conductivity of CTWE. Fig.3.8 depicts the % reduction in COD of CTWE at different dosages of Fenton reagent in 120 minutes. It was observed from Table 3.7 that % COD reduction increased from 34% to 47% as the ferrous sulfate dosages increased from 0.2 g/100 mL to 0.4 g/100 mL and on further increase from 0.4 g/100 mL to 1.2 g/100 mL % COD reduction decreased to 25.5%. Maximum 47% COD reduction was obtained at optimized dosage 0.4 g/100 mL of ferrous sulfate with an equivalent weight ratio of 1:4.5 with H_2O_2 (Fe^{2+}: H_2O_2 [W: W]). The decrease in COD reduction may be due to the scavenging of hydroxyl radicals at higher dosage of ferrous sulfate than the optimum dosage. The pH of the solution also decreased with increase in ferrous sulfate dosage, whereas TDS and conductivity remained almost constant. After optimizing the Fenton reagent dosage, CTWE was subjected to hybrid US + Fenton process. 300 mL of CTWE was subjected to 40% amplitude of US and Fenton reagent (0.4 g/100 mL Fe^{2+} and 1.8 g/100 mL H_2O_2) was added for 120 minutes. The combined effect of the hybrid treatment process on COD, pH, TDS and conductivity is presented in Table 3.7. It was observed that the hybrid process exhibited the synergistic effect on degradation of organic pollutants present in CTWE, because after 120 minutes of treatment, 67% reduction in COD was observed with slight reduction in pH and marginal increase in TDS and conductivity were observed. The gradually reduction in pH may be due to the production of organic acids from the disintegration of organic molecules during the treatment process (Saxena et al., 2018b) whereas with increase in weight ratio of Fenton reagent H_2O_2 dosage increased which leads to increase in TDS and conductivity of the treated sample. As a whole total 82.7% reduction in COD was observed from initial COD of TWE with a quantum of 7060 mg/L.

The hybrid treatment was not effective for the treatment of TWE whereas it effectively exhibited the synergetic effect in case of CTWE with higher degradation rate of organic molecules. This may be because in case of TWE the presence of suspended particles higher organic load hindered the reaction of hydroxyl radicals in degradation reactions. The efficacy of hybrid process combining US with Fenton for the treatment of CTWE was estimated in terms of synergetic coefficient, estimated as per Eq (4). The first order rate constant for combined process at optimized conditions was 0.0096 min^{-1} whereas 0.0056 min^{-1} for only Fenton process and 0.0024 min^{-1} for only US.

$$\text{Synergetic coefficient } \gamma_{\mathrm{US+Fenton}} = \frac{k_{(\mathrm{US+Fenton})}}{k_{\mathrm{US}}+k_{\mathrm{Fenton}}} \quad (4)$$

$$\gamma_{\mathrm{US+Fenton}} = \frac{0.0096}{0.0024+0.0056} = 1.2$$

The value of synergetic coefficient $\gamma_{\mathrm{US+Fenton}}$ was 1.2, which denotes that the hybrid process combining US with Fenton process was more efficient than the individual processes for the treatment of CTWE.

Table 3.7 Effect of various Fenton dosages on COD, pH, TDS, and conductivity of CTWE and comparison with US + optimized Fenton dosage

Parameters	**Fenton, Fe^{2+}: H_2O_2[W:W]**						**US + Fenton, Fe^{2+}: H_2O_2[W:W]**	
	Initial	1:9	1:6	1:4.5	1:3	1:1.5	Initial	1:4.5
COD (mg/L)	4000	2640	2320	2120	2460	2980	4480	1480
% COD reduction	--	34	42	47	38.5	25.5	-	66.96
pH	4.21	3.90	3.73	3.41	3.15	2.95	4.33	3.84
TDS (mg/L)	12140	12230	12280	12450	12630	12760	12540	12410
Conductivity (mS/cm)	24.73	24.88	25.02	25.26	25.57	26.05	25.71	25.47

(**Experimental conditions; Fenton:** Sample Volume 100 mL, Treatment time 120 minutes, Fe^{2+}= 0.2 g/ 100 mL to 1.2 g/ 100 mL (2 g/L to 12 g/L), H_2O_2= 18 g/L, **US + Fenton:** Sample Volume 300 mL, Treatment time 120 minutes, Fe^{2+}= 4 g/L, H_2O_2= 18 g/L)

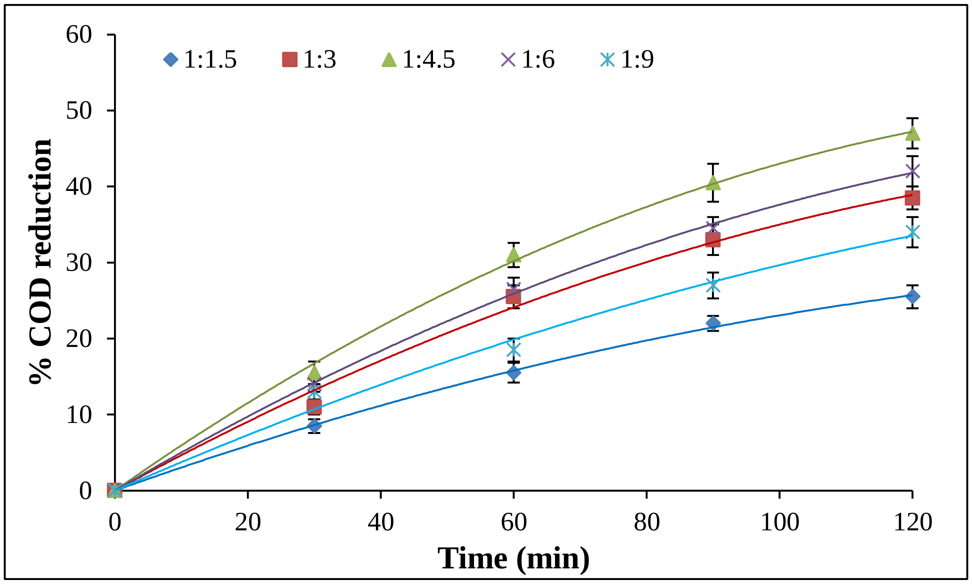


Fig. 3.8 Effect of various Fenton dosages on COD reduction of CTWE

3.3.5 Hybrid treatment of TWE and CTWE using US + Sodium hypochlorite:

The combined oxidation capacity of US with sodium hypochlorite was studied using varying dosages of sodium hypochlorite and with optimized ultrasonic conditions. The combined treatment was applied to 300 mL of TWE sample for 120 minutes with US amplitude of 40% and dosages of sodium hypochlorite varying from 0.05 g/100 mL to 0.3 g/100 mL, and the results are presented in Table 3.8. It was observed that % reduction in COD slightly increased with increase in sodium hypochlorite dosage from 0.05 g/100 mL to 0.2 g/100 mL, and any further increase in dosage beyond 0.2 g/100 mL to 0.3 g/100 mL it decreased the % COD reduction. Maximum 26.30 % COD reduction was obtained at optimized dosage of 0.2 g/100 mL with optimized condition of US in 120 minutes. The increase in degradation of organic pollutants may be attributed to enhance production of hydroxyl radicals in presence of sodium hypochlorite and also the generation of hypochlorous acid (HOCl) which also an oxidizing agent. The reaction of formation of hypochlorous acid due to addition of sodium hypochlorite in effluent sample may follow as Eq. 5;

$$NaOCl + H_2O \rightarrow HOCl + NaOH \qquad (5)$$

Table 3.8 Combined effect of US + NaOCl on COD, pH, TDS and conductivity of TWE

Parameters		**US alone**	**US + NaOCl dosages**			
			0.5 g/L	1 g/L	2 g/L	3 g/L
COD (mg/L)	Initial	8560	8440	8440	8440	8440
	Final	6820	6640	6480	6220	6340
	% reduction	20.32	21.33	23.22	26.30	24.88
pH	Initial	7.55	7.50	7.50	7.50	7.50
	Final	7.8	7.56	7.64	7.73	7.82
TDS (mg/L)	Initial	11970	11840	11840	11840	11840
	Final	11430	12520	13180	14570	15950
Conductivity (mS/cm)	Initial	24.46	23.82	23.82	23.82	23.82
	Final	24.04	24.46	26.96	29.63	32.4

(**Experimental conditions:** US amplitude = 40%, Sample Volume = 300 mL, Treatment time = 120 minutes)

The observed decrease in degradation of organic pollutants at higher dosage can be attributed to the saturation of sample with hypochlorite ions and scavenging of hydroxyl radicals. The same was repeated to treat 300 mL of CTWE with different dosage of sodium hypochlorite within the range of 0.05 g/100 mL to 0.2 g/100 mL of CTWE and 40% amplitude of US for 120 minutes. Table 3.9 presents the % COD, pH, TDS and conductivity of CTWE after 120 minutes of treatment and Fig. 3.9 presents the effect of combined treatment on % COD reduction with respect to time. It was investigated that reduction in COD increased with increase in dosage from 0.05 g/100 mL to 0.15 g/100 mL of sodium hypochlorite and became saturated with further increase in sodium hypochlorite dosage to 0.2 g/100 mL. Maximum 35.94% COD reduction was observed at 0.15 g/100 mL of CTWE. It was observed in both cases that pH, TDS and conductivity increased with increase in sodium hypochlorite dosages. The increase in pH may be due to the presence of caustic soda in sodium hypochlorite which leads to increase in pH however the pH of solution may also depend upon how much hypochlorous acid was formed. It was reported that addition of chemicals in any aqueous solution resulted in increase in TDS of that solution, simultaneous increase in the conductivity was observed (Saxena et al., 2018a). The quantum of COD reduction in combined treatment at optimized conditions was higher in the case of TWE than the treatment of CTWE which may be because the initial COD of TWE was higher in concentration than the initial COD of CTWE. This indicates the effectiveness of sodium hypochlorite to handle higher organic load than other AOP's.

Table 3.9 Combined effect of US + NaOCl on COD, pH, TDS and conductivity of CTWE

Parameters	**US + NaOCl dosages**				
	Initial	**0.5 g/L**	**1 g/L**	**1.5 g/L**	**2 g/L**
COD (mg/L)	4340	3120	2940	2780	2800
% COD reduction	--	28.1	32.3	**35.94**	35.48
pH	4.34	4.37	4.42	4.55	4.68
TDS (mg/L)	12720	12840	12870	13060	13110
Conductivity (mS/cm)	26.66	26.82	27.17	27.48	27.73

(**Experimental conditions:** US amplitude = 40%, Sample Volume = 300 mL, Treatment time = 120 minutes)

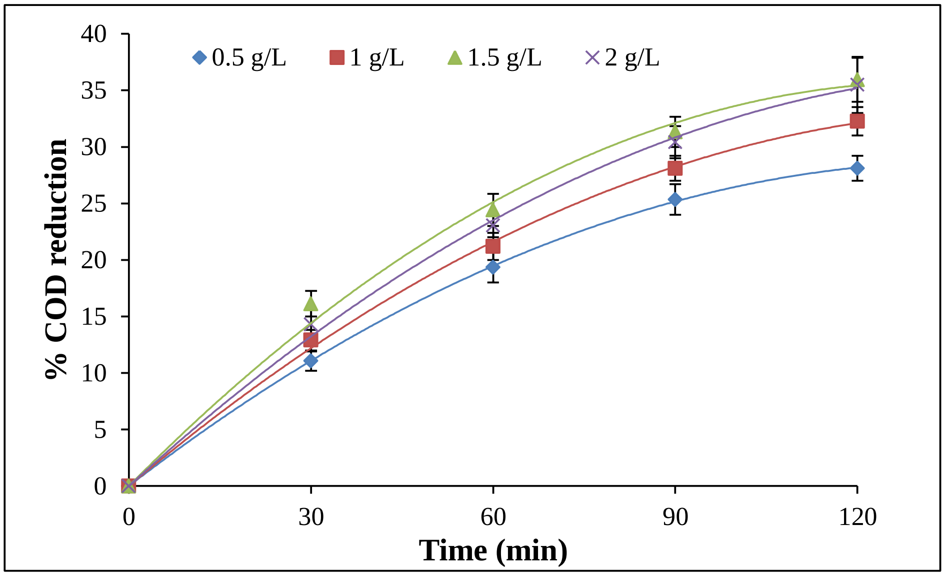


Fig. 3.9 Combined effect of US + various NaOCl dosages on COD reduction of CTWE

The synergetic coefficient "$\gamma_{US+NaOCl}$" was also estimated using first order rate constant of COD reduction for the combined process of US with NaOCl and individual US and NaOCl using Eq.6. The first order rate constant for the combined process for the treatment of CTWE and TWE at optimized conditions was 0.0041 min^{-1} and 0.0027 min^{-1} respectively, while in case of US process alone it was 0.0024 min^{-1} and 0.0021 min^{-1} for

CTWE and TWE respectively as mentioned earlier. The value of rate constant for individual NaOCl treatment process was approaching to zero due to marginal reduction in COD of CTWE and TWE by NaOCl alone therefore it was taken zero.

$$\text{Synergetic coefficient } \gamma_{\mathrm{US+NaOCl}} = \frac{k_{(\mathrm{US+NaOCl})}}{k_{US}+k_{NaOCl}} \tag{6}$$

$$\gamma_{\mathrm{US+NaOCl}} = \frac{0.0041}{0.0024+0.0} = 1.7 \ \text{(CTWE)}$$

$$\gamma_{\mathrm{US+NaOCl}} = \frac{0.0027}{0.0021+0.0} = 1.3 \ \text{(TWE)}$$

The value of synergetic coefficient "$\gamma_{\mathrm{US+\ NaOCl}}$" estimated at a value of 1.7 for CTWE and 1.3 for TWE shows the synergetic effect of combined process in comparison to the efficiency of the individual processes.

3.3.6 Hybrid treatment of TWE and CTWE using US + Ozone:

Ozone is extensively used as an oxidizing agent to degrade organic pollutants as well as inorganic pollutants. The reactivity of ozone mostly depends on the nature of pollutants present in waste effluent (Pang et al., 2011) and its higher capability to oxidize organic compounds such as unsaturated hydrocarbons, aromatic rings as well as to oxidize inorganic compounds such as sulfides etc. In ozonation process, ozone either directly reacts with organic molecules or it get dissociates into hydroxyl radicals which have higher oxidation potential than ozone. Hybrid treatment method combining the ozonation and ultrasonic irradiation can degrade the bio-refractory pollutants present in waste water with higher efficiency and higher degradation rates (Pang et al., 2011)and has the advantage of higher mass transfer rate of ozone from gas phase to liquid phase in presence of US. The effect of hybrid treatment on degradation of TWE, using US combined with ozonation was studied by ozonation of 300 mL of TWE at 40% of amplitude over a period of 120 minutes and varying the dosages of ozone from 1 g/h to 7 g/h. It was observed that % COD reduction marginally increased with increase in mass flow rate from 1 g/h to 5 g/h and thereafter remained constant at higher mass flow rate of 7 g/h. Table 3.10 presents the data of % COD reduction, pH, TDS and conductivity of TWE after 120 minutes of treatment. The maximum COD reduction of 24.11% was obtained at optimum ozone mass flow rate of 7 g/h. However, increase in ozone concentration had no significant effect on pH and TDS of TWE. The same effect of US with ozonation on CTWE was studied by applying combined treatment to treat 300 mL of CTWE for 120 minutes at different dosage of ozone varied from 1 g/h to 7 g/h (1 g/h, 3 g/h, 5g/h, and 7 g/h) with optimized US amplitude of 40%. Table 3.11 presents the data of % COD reduction, pH, TDS and conductivity of TWE after 120 minutes of treatment. It was observed that % reduction in COD as observed in Fig. 3.10, increased from 27.72 % to 36.14% with increase in ozone mass flow rate from 1 g/h to 5 g/h and thereafter further reduction in COD decreased to 34.65% at higher ozone mass flow rate of 7g/h. With increase in ozone dosage in combined treatment process of CTWE, slight reduction in pH along with marginal increase in TDS reduction was observed for treated sample of CTWE. The reduction in organic pollutants degradation in terms of COD at higher mass flow rate of ozone may be due to the recombination of hydroxyl radicals to form hydrogen peroxide and water in presence of excess hydroxyl radicals and resulted in reduction in overall degradation rate.

Table 3.10 Combined effect of US + ozone on COD, pH, TDS and conductivity of TWE

Parameters		**US alone**	**US + ozone dosage**				**Ozone**
			1 g/h	3 g/h	5 g/h	7 g/h	7 g/h
COD (mg/L)	Initial	8560	8520	8520	8460	8460	8360
	Final	6820	6760	6580	6440	6420	7400
	% reduction	20.32	20.66	22.77	23.88	24.11	11.48
pH	Initial	7.55	7.42	7.42	7.37	7.37	7.41
	Final	7.8	7.61	7.65	7.58	7.53	7.24
TDS (mg/L)	Initial	11970	11880	11880	11790	11790	11840
	Final	11430	11560	11470	11350	11360	13050
Conductivity (mS/cm)	Initial	24.46	23.73	23.73	23.64	23.64	23.81
	Final	24.04	23.47	23.36	23.40	23.43	25.36

(**Experimental conditions:** US amplitude = 40%, Sample Volume = 300 mL, Treatment time = 120 minutes)

Table 3.11 Combined effect of US + various dosage of ozone on COD, pH, TDS and conductivity of CTWE and effect of only ozone at optimized mass flow rate

Parameters	**CTWE followed by US + Ozone**					**Ozone**
	Initial	1g/h	3g/h	5g/h	7g/h	5 g/h
COD (mg/L)	4040	2920	2740	2580	2640	3460
% COD reduction	--	27.72	32.18	36.14	34.65	16.8
pH	4.31	4.19	4.15	4.06	3.98	4.16
TDS (mg/L)	12320	11600	11460	11280	11210	12930
Conductivity (mS/cm)	25.24	23.55	23.25	22.87	22.72	26.44

(**Experimental conditions:** US amplitude = 40%, Sample Volume = 300 mL, Treatment time = 120 minutes)

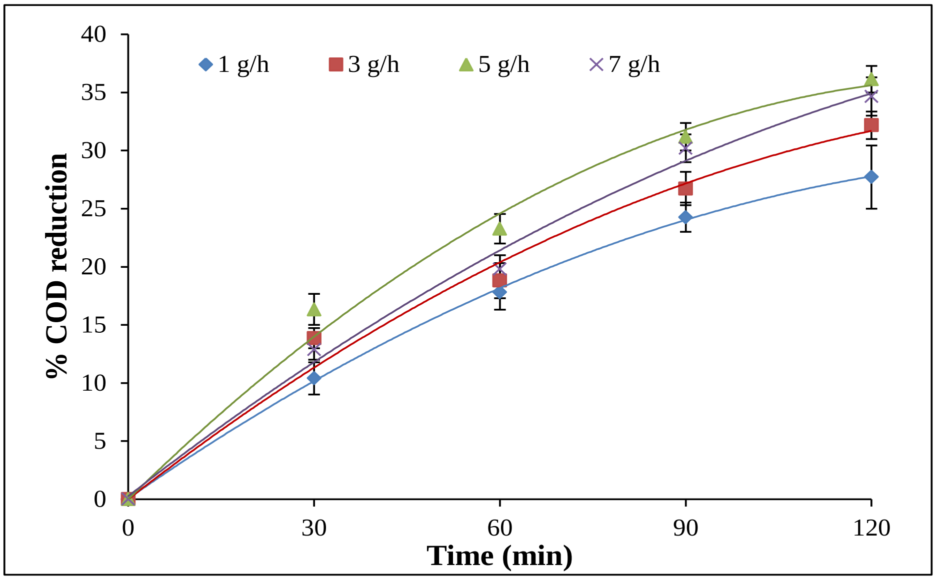


Fig. 3.10 Combined effect of US + ozone dosages on % COD reduction of CTWE

The efficacy of the hybrid treatment process comprising US with O_3 with respect to the synergistic coefficient of % reduction in COD of both TWE and CTWE was analyzed. Experiments were carried out with ozone alone for TWE at optimum mass flow rate of 7 g/h and CTWE at optimum mass flow rate of 5 g/h. The effect of ozonation on reduction in COD of both the samples were studied over a period of 120 minutes, with 30 minutes sampling intervals and analyzed for COD. It was observed in case of TWE, COD reduction was 11.48 % with first order rate constant of 0.0011 min^{-1} whereas in case of CTWE, COD reduction was 15.5% with first order rate constant of 0.0014 min^{-1}.

The synergetic coefficient for combined effect of US with ozonation was calculated for both TWE and CTWE samples according to following Eq. (7)

$$\text{Synergetic coefficient } \gamma_{\mathrm{US+O_3}} = \frac{k_{(\mathrm{US+O_3})}}{k_{\mathrm{US}}+k_{\mathrm{O_3}}} \qquad (7)$$

$$\gamma_{\mathrm{US+O_3}} = \frac{0.004}{0.0024+0.0014} = 1.05 \;\text{(CTWE)}$$

$$\gamma_{\mathrm{US+O_3}} = \frac{0.0025}{0.0021+0.0011} = 0.78 \;\text{(TWE)}$$

The synergetic coefficient “$\gamma_{\mathrm{US}+O_3}$“ of hybrid treatment of CTWE was found to be higher than TWE which indicates that the hybrid process provided marginal synergistic effect with improved degradation of the organic pollutants due to the increase in generation of hydroxyl radicals.

Table 3.12 presented the comparison of untreated and treated TWE for all treatment techniques used in this study on the basis of % COD reduction at optimized conditions. Among all the treatment strategies, maximum COD reduction of 82.67% was observed in case of coagulation followed by Fenton process at optimized conditions (Fe^{2+} = 1.2 g/300 mL, H_2O_2 = 5.4 g/300 mL) with a synergistic coefficient of 1.2.

Table 3.12 Comparison of untreated and treated TWE on the basis of % COD reduction at optimized conditions

Process	**COD**			**Optimum dose of Coagulant /oxidizing agent**	**% COD reduction**	**Synergistic coefficient**
	Initial sample	**Coagulated sample**	**Treated sample**			
US	8560	-	6820	--	20.32	--
US + Ozone	8460	-	6420	O_3 = 7 g	24.11	0.78
US + NaOCl	8440	-	6220	NaOCl = 2 g/L	26.30	1.3
US +Fenton	8480	-	7540	Fe^{2+} = 3 g/L H_2O_2 = 9	11.08	--

				g/L		
Coagulation	8420	4040	-	Alum = 15 g/L	52.01	--
Coagulation followed by US	8740	4560	3480	Alum = 15g/L	60.18	--
Coagulation followed by US + H_2O_2	8680	4400	2780	Alum = 15g/L H_2O_2 = 18 g/L	67.97	1.67
Coagulation followed by US + Fenton	8540	4480	1480	Alum = 15g/L Fe^{2+} = 4 g/L H_2O_2 = 18 g/L	82.67	1.2
Coagulation followed by US + NaOCl	8660	4340	2780	Alum = 15g/L NaOCl = 1.5g/L	67.90	1.7
Coagulation followed by US + Ozone	8420	4040	2580	Alum = 15g/L O_3 = 5 g/h	69.36	1.05

(**Experimental conditions**; **Coagulation:** Mixing time = 15 min, Settling Time = 60 min, Sample volume = 100 mL, **US & US + AOPs:** Treatment time = 120 min, Sample volume = 300 mL, US amplitude = 40%)

3.3.7 Energy efficiency and cost estimation

Treatment cost for TWE using US, coagulation and advanced oxidation techniques mainly depends on power consumed by the ultrasonic horn and the cost of coagulants and chemicals used as oxidizing agents. In cases where ozone is used as oxidizing agent an additional operating cost due to the involvement of ozonator (power consumed) in the process. Evaluation of energy efficiency was carried out on the basis of energy required for the reduction of one mg of COD. The overall treatment time taken to evaluate energy efficiency for the US process was 120 minutes. The treatment cost along with energy efficiency calculations for the various processes is provided in Appendix B (page no. 188). The energy efficiency and cost estimations were based on the degradation of one mg of COD (kWh/mg) for US and US coupled with advanced oxidation process and is summarized in Table 3.13. Cost estimations for the chemicals consumed were calculated on the basis of commercial grade prices.

The energy required for the reduction of one mg of COD of TWE was 0.0014kWh/mg COD, and the cost involved for the treatment of one mg of COD was approximately 0.00018 USD/mg COD using US system alone. In case of US + ozone system, the energy required for reduction of one mg of COD was 0.001 kWh/mg COD and cost for the same was about 0.00013 USD/mg COD. For the system US + NaOCl, the energy required for the reduction of one mg of COD was 0.00068kWh/mg and the respective cost for the same was 0.00009 USD/mg COD. In order to evaluate the energy efficiency of cavitation reactors, cavitational yield was calculated for the treatment of TWE. Cavitational yield described as the ratio of quantum of COD reduced and power supplied to the system for treating unit volume of sample and it was observed that US + ozone and US + NaOCl processes had 291.42 mg L/kWh and 444 mg L/kWh cavitational yield respectively whereas in case of US alone it was only 216 mg L/kWh. In case of coagulation alone, energy required in terms of agitation provided by orbital shaker for the separation was 0.00006 kWh/mg COD and total cost involved for the COD reduction was 0.000007 USD/mg COD. In case of coagulation coupled with US system the energy required for the reduction of one mg of COD was 0.00033 kWh/mg COD and respective overall cost for the same was about 0.00004 USD/mg COD. For the system involving coagulation + US + H_2O_2 energy required for the reduction of one mg of COD was 0.0003 kWh/mg COD and cost for the reduction of one mg of COD was 0.00004 USD/mg COD. In case of Coagulation + US + Fenton's reagent system 0.0008 kWh/mg COD and respective cost for the same was 0.000033 USD/mg COD. For the system of coagulation + US + NaOCl the net energy required for the degradation of one mg of COD was 0.0003 kWh/mg COD and the cost for the treatment of one mg of COD was 0.00004 USD/mg COD. In coagulation + US + ozone system, energy required for the degradation of one mg of COD was 0.0004 kWh/mg COD and cost for the process was 0.00005 USD/mg COD.

Table 3.13 Energy efficiency and cost estimation

Treatment methodology	Quantum of COD reduced (mg)	Energy required for the reduction of one mg of COD (kWh/mg COD)	Cost of the treatment for the reduction of one mg of COD (Rs/mg COD)	Cost of the treatment for the reduction of one mg of COD (USD/mg COD) (USD =70.9 Rs/ INR as on 27/11/2018)	Cost of the treatment for treating the one liter of TWE (Rs/L)	Cost of the treatment for treating the one liter of TWE (USD/L)	Cavitational yield (mg×L/kWh)	Remark
US & US + AOP's								
US	1080	0.0014	0.0125	0.00018	45	0.635	216	Efficient for only small scale treatment Zero secondary waste generation Not suitable for large scale treatment
US + Ozone	2040	0.001	0.0093	0.00013	63	0.889	291.42	
US + NaOCl	2220	0.00068	0.0068	0.00009	50.46	0.711	444	
Coagulation, Coagulation + US & US + AOP's								
Coagulation	4380	0.00006	0.0005	0.000007	7.69	0.108	--	Highly efficient for small scale treatment Produces secondary waste Not suitable for large scale treatment
Coagulation + US	5260	0.00033	0.003	0.00004	52.66	0.743	--	
Coagulation + US + H_2O_2	5900	0.0003	0.0028	0.00004	54.83	0.773	--	
Coagulation + US + Fenton	7060	0.00024	0.0023	0.000033	55.2	0.779	--	
Coagulation + US + NaOCl	5880	0.0003	0.0029	0.00004	56.8	0.801	--	
Coagulation + US + Ozone	5840	0.0004	0.0036	0.00005	70.7	0.997	--	

3.4 Summary of the chapter

The combination of different advanced oxidation process coupled with US method was studied for mineralization of TWE and the key findings drawn from the present study can be summarized as follows:

- The efficacy of US as a pretreatment tool for the TWE was investigated which showed that the US amplitude had a significant effect. It was observed that 40% amplitude of US was optimum for the mineralization process.
- The hybrid treatment approaches (US + advanced oxidizing reagents) was not effective when they were applied on raw TWE, therefore coagulation of raw TWE was carried out prior to US process using two different coagulants alum and aluminum chloride separately. It was observed that alum is a better coagulant in comparison to aluminum chloride and maximum of 52.01 % COD and 69.79 % TSS removal was achieved at the optimized alum dosage of 1.5 g/100 mL of TWE with corresponding residual pH of 4.45.
- Compared to US process alone, the hybrid US processes provided higher COD reduction. However, the hybrid methods such as US combined with oxidation agents such as hydrogen peroxide / sodium hypochlorite/ozone are not suitable for treatment of raw and coagulated TWE as the %COD reduction attained for both is same around 20 to 25% only. Among all the hybrid US and AOPs combinations studied, it was observed that US and Fenton reagent was the most effective hybrid method for the treatment of coagulated TWE with the maximum increase of 30% COD reduction when compared to the other methods.
- Total 82.7% reduction in COD was observed from initial COD 8540 mg/L to 1480 mg/L of TWE by a quantum of 7060 mg/L (4060 mg/L in coagulation and 3000 mg/L in US + Fenton) using coagulation followed by US + Fenton. Maximum COD reduction was observed in case of CTWE in hybrid treatment process of US + Fenton at optimized conditions.
- Cost estimation was also carried out in terms of per unit TWE treated and it was observed that treatment costs involving US and US based hybrid oxidation

processes were very high as 45 to 70 Rs. per liter, and hence these treatment techniques were not found suitable for large scale treatment operations.

The results indicate that US in combination with other oxidizing agents could be an effective treatment approach only after reducing the organic load in TWE. As HC has a similar capability in terms of waste mineralization as US, and is more energy efficient, therefore its effectiveness as a tool for waste mineralization may be further studied as a hybrid treatment technique in combination with various oxidation agents which is presented in next chapter.

CHAPTER 4

Advanced hybrid treatment of tannery waste effluent (TWE) using hydrodynamic cavitation (HC) coupled with different oxidizing agents (hydrogen peroxide/Fenton's reagent/ ozone)

4.1 Introduction:

Earlier studies have been reported the application of cavitation process as well as pressure driven processes for the disintegration of recalcitrant molecules in waste water treatment (Rajoriya et al., 2018), oil extraction (Marousek et al., 2015, 2013), phytomass disintegration (Marousek and Kwan, 2013) etc.. Numerous laboratory scale studies (Gogate and Pandit, 2004b; Mahamuni and Pandit, 2006; Sivakumar and Pandit, 2001) have recently been reported in utilization of cavitation via the US route for the treatment of various types of wastewater. Nevertheless, the use of US for industrial scale effluent treatment plants is limited due to high equipment cost and maintenance costs involved and lower energy efficiency (Mason, 2000). Also, in our last study it was found that after reducing the organic load using coagulation, combination of US with other oxidizing agents enhanced the degradation of organic pollutants present in TWE. Therefore, the quest for the most appropriate technology for effectively treating the tannery waste water is still ongoing for the water reuse or for its safe disposal in local water bodies without causing any hazardous health threats.

HC has emerged as a new energy-efficient technology for the treatment of various bio-refractory pollutants in wastewater, either operated alone or in combination with other advanced oxidative reagents and/or processes (Rajoriya et al., 2018; Raut-Jadhav et al., 2016a). It provides an alternative approach to US utilizing the cavitational approach for wastewater treatment with more energy efficiency and may be used for large scale treatment process in a continuous mode (Saxena et al., 2018a). As the common conventional water treatment techniques are not effective in breaking down the bio-recalcitrant molecules especially present in tannery wastewater, this study presents the hybrid treatment technique of combining HC with various oxidation agents such as O_3, H_2O_2 and Fenton's reagent that may give higher degradation efficiencies yielding intensified treatments. Hybrid processes may provide better degradation efficiency as compared to the individual process due to the enhanced generation of •OH radicals in the presence of process intensifying agents, reduction in process treatment time and enhanced contact thereby maximizing the extent of mineralization. The efficiency of hybrid processes also depends on the type of pollutant, formation of hydroxyl radicals and its effective interaction with pollutant molecules. This integrated approach is also easy to be adopted into the conventional treatment processes through moderate modifications for installation into commercial practice, and therefore their process efficiencies need to be evaluated for maximum COD/TOC reduction and increase in the BI (BOD:COD) of the waste effluent.

The use of hybrid HC coupled with oxidative agents, has been reported for treatment of various dyes mostly on laboratory scale, however as per the authors knowledge no study has been yet reported for treatment of TWE. In this study, advanced treatment for reduction of COD and TOC along with increase in BI of the tannery effluent taken from an effluent treatment plant had been the main focus of the study so as to evaluate the efficiency of treatment process. The effects of various process parameters such as the fluid flow inlet pressure to the cavitational device, sample dilution ratio, concentration of various oxidative agents etc. on the BI, degradation efficiency as well as the rate kinetics were studied. The various organic components present in the raw and treated samples were also analyzed using FTIR and LCMS.

4.2 Materials and Method:

4.2.1 HC Reactor experimental setup:

The schematic representation of the HC reactor set-up used in the present study for the treatment of the tannery effluent is as shown in Fig. 4.1, manufactured by M/s Accurate Industries Mumbai. The experimental set up comprised of a closed loop circuit fitted with a slit venturi cavitating device, a high-pressure piston pump of power rating 1.1 kW and a storage tank of 20 L capacity. The storage tank was provided with the cooling jacket in order to maintain the process temperature within the temperature range (30±2°C). The discharge line from the pump was provided with two lines, i.e. the main process line and the bypass line. The process and bypass pipe lines (diameter:19 mm) were fitted with various metering devices such as flow meter, manual valves and pressure gauges. The flow rate in the main line was maintained using the bypass line as well as by regulating speed of the pump motor using a variable frequency drive. Both the mainline and bypass line discharged into the tank well below the liquid level to prevent suction of air into the liquid. The dimensions of the slit venturi cavitating device used in this study and its geometrical details have already been reported by our research group for the degradation of rhodamine 6G dye, wherein the effect of various operational parameters and design of the cavitating devices were optimized with respect to the cavitational intensity and yield (Rajoriya et al., 2017a). Therefore, the experiments were carried out using the venturi at the optimized parameters recommended in their study in order to achieve best cavitational activity.

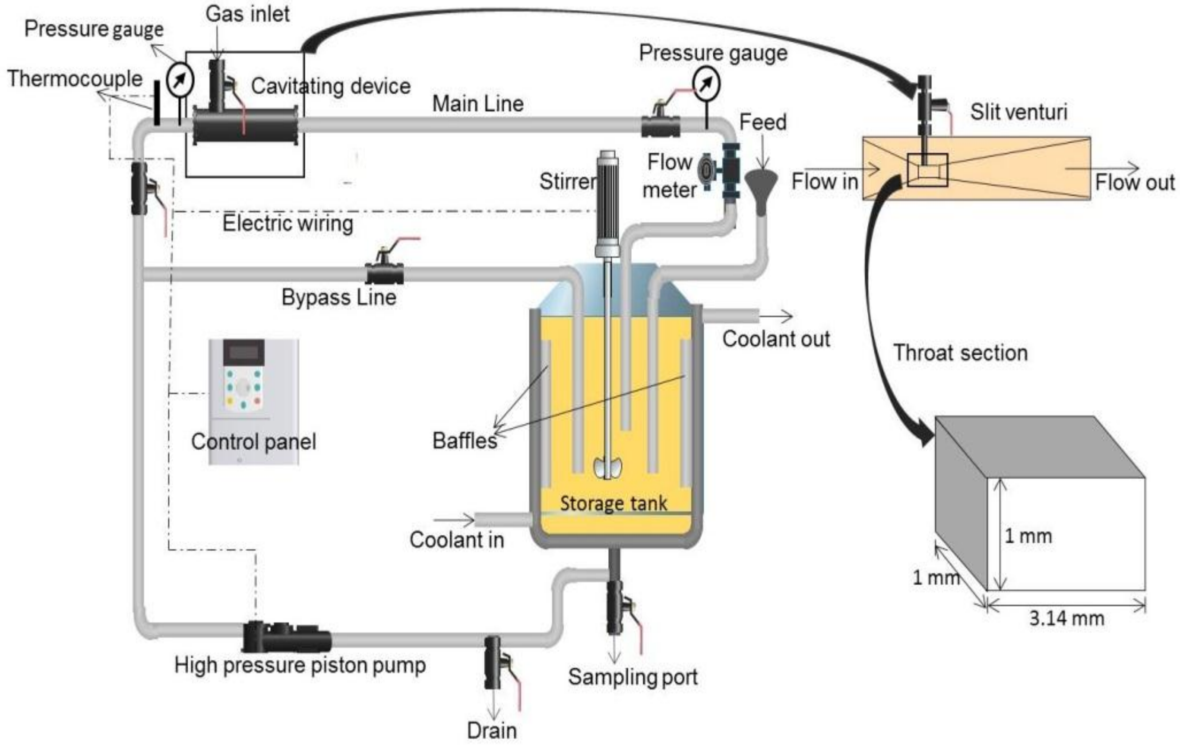


Fig. 4.1 Schematic representation of HC reactor setup.

4.2.2 Tannery waste effluent

Collection was done as discussed in section 2.2.2 and characteristics of TWE are presented in Table 4.1. The TWE required for the entire study was collected and stored in a deep freezer and allowed to achieve room temperature before performing the experimental studies using HC alone and in combination with various oxidizing agents.

Table 4.1 Characteristics of TWE

Parameter	**Range**	**Unit**
pH	7.2-7.5	--
COD	8800-10080	mg/L
TOC	2290-2583	mg/L
TDS	18850-20370	mg/L
TSS	17450-19950	mg/L
BOD	2800-3200	mg/L
Chromium	Not detectable	mg/L
BI	0.28-0.33	--

4.2.3 Chemicals:

All the chemicals used in this study were purchased from Lobachemie, India and were of analytical grade (AR). The chemicals used in COD analysis were ferrous ammonium sulfate (99%), concentrated sulfuric acid (98%), silver sulfate (99%), mercuric sulfate (98%), potassium dichromate (99.5%) and ferroin indicator (0.025 M). BOD analysis was carried out using sodium thiosulfate (99.5%), sodium hydroxide (98%), sodium iodide (99.5%), manganous sulfate (99%), starch, potassium dihydrogen phosphate (99.5%), dipotassium hydrogen orthophosphate (99%), disodium hydrogen phosphate (99%), ammonium chloride (99.8%), calcium chloride (99%), magnesium sulfate (99.5%) and ferric chloride (99%). Orthophosphoric acid (85%) and sodium peroxidisulfate (99%) were used for TOC analysis. H_2O_2 (30%, w/w) and ferrous sulfate ($FeSO_4.7H_2O$) (99%) were used as the oxidizing agents. Double distilled water prepared afresh in the laboratory was used for the sample dilution studies. Solution pH was adjusted using 1N solutions of sodium hydroxide (98%) and sulfuric acid (98%). All the chemicals were used as received from suppliers without any further purification.

4.2.4 Analytical instruments and Method of analysis:

The sample analysis for determining the COD, TOC, BOD, TS, TDS and TSS values were carried out as per the standard methods prescribed by APHA (1998). pH meter (Thermo scientific, USA) was used to determine the pH of the solution during and after the experiments. TOC content was measured using TOC analyzer (GE InnovOx). TDS were measured using ion meter (Thermo scientific, USA). An oven (Make: DAIHAN Scientific Co. Ltd.) was used for drying the tannery effluent during the TS and TSS analysis. The TSS of the TWE samples was analyzed after subjecting the samples to shaking before analysis so as to prevent any separation by settling. In order to evaluate molecular characteristics of TWE raw and treated sample, mass spectroscopy coupled with liquid chromatography (LC-MS) (make: Xevo G2-S Q-Tof, Waters, USA) using C18 column (4.6 mm×250 mm) was carried out using mixture of acetonitrile and water (1:1) as eluent. To understand bonding mechanism of various compounds, present in TWE and the effect of HC on the bonding patterns of TWE, FT-IR (Fourier Transform Infrared Spectroscopy) was conducted within the range of 400-4000 cm^{-1} and the respective spectra was recorded using Perkin Elmer UTR spectrophotometer. All experiments were repeated thrice and the reported values are the average of two runs. The experimental errors were found to be within ±3% of the reported average values.

4.3 Treatment Methodology:

TWE samples of constant volume were initially subjected to HC treatment alone in the HC reactor in order to identify the optimum operational characteristics with respect to the inlet pressure and corresponding cavitation number. 7 Liters of the TWE sample volume was treated by recirculation in the closed circuit for 120 min and process temperature was also maintained constant at 30±2°C. The inlet pressure at the venturi was varied in the range of 300 to 1000 kPa and studied for obtaining operational cavitation conditions such as flow rate, fluid velocity and cavitation number. TWE samples were drawn at regular intervals of 30 minutes and analyzed for changes in its COD and TOC which are indicative of degradation. The reaction mechanism for the dissociation of water molecules into the hydroxyl radicals and subsequent mineralization of the organic pollutants present in TWE by the hydroxyl radicals during the cavitation process is represented by Eq. (1) and (2) respectively.

$$H_2O \xrightarrow{HC} {}^{\bullet}H + {}^{\bullet}OH \quad (1)$$

$$\text{Organic pollutants} + {}^{\bullet}OH \rightarrow CO_2 + H_2O + \text{intermediate degradation products} \quad (2)$$

The TWE samples had high TDS, TSS and organic matter content and therefore dilution of the samples may affect the degradation rate. Therefore, the effect of dilution was studied by diluting the TWE samples in different proportions of 25% and 50% (v/v) using double distilled water and was further subjected to HC at the optimized pressure conditions obtained from pressure study. In order to enhance the treatment efficiency, the HC process was operated in combination with various oxidizing agents such as O_3, H_2O_2, and Fenton's reagent and evaluated for their synergistic effects. Individual advanced oxidation processes such as treating wastewater with O_3, H_2O_2 and Fenton's reagent has various limitations such as high mass transfer resistances, slow rate of mineralization etc., which can be overcome by utilizing hybrid processes such as HC in combination with these advanced techniques. O_3 required for the treatment was generated using O_3 generator (high voltage corona discharge ozonator, maximum O_3 rate: 10 g/h, make: Eltech Engineers, India) which was introduced at the throat section of the cavitating device through a nozzle. Effect of varying feed rate of O_3 during HC + O_3 process was studied in the range of 3 to 9 g/h. H_2O_2 (30% w/w) was dosed into process tank to examine the effect of combination of HC with H_2O_2 and the effects were studied for four different dosages ranging from 50 to 300 mL in 7 L (7.9 to 47.57 g/L) of TWE sample. To further intensify the reduction of organic pollutants, present in TWE, HC was further combined with Fenton's oxidation process in which the ferrous ion reacts with H_2O_2 generating extra hydroxyl radicals thereby increasing the degradation rates. Experiments combining HC with Fenton's reagent was carried out for four different loading of ferrous sulfate (i.e. 0.5 g/L, 1 g/L, 3g/L and 5 g/L) with corresponding optimized loading of H_2O_2 loaded from the top of the process tank.

4.4 Results and Discussion:

4.4.1 Effect of inlet pressure and cavitation number on HC Reactor performance:

The extent of degradation of the organic pollutants in the water medium depends on the cavitational intensity which in turn depends on the operating inlet pressure, fluid flow rate or velocity through the venturi, and therefore these parameters were initially established to maximize the efficacy of HC. The other parameter which collectively represents the effect of pressure and fluid velocity through the venturi is the cavitation number (C_v). Cavitation number quantifies the cavitational intensity of a cavitating device (Rajoriya et al., 2016) and is defined as the ratio of the pressure drop between the throat and extreme downstream section to the kinetic head at the throat, determined using Eq. (3).

$$C_v = 2\,(P_2 - P_v)/\rho v^2 \tag{3}$$

Here ρ is the density of liquid, v is the velocity of the fluid at the throat of the cavitating device, P_v is the liquid vapor pressure and P_2 is fully recovered pressure at the downstream end. The cavities are generated under the ideal condition i.e. at $C_v \leq 1$, but in many cases, cavities can get generated at $C_v>1$ due to the existence of little dissolved gases and suspended particles (Rajoriya et al., 2017b; Saharan et al., 2013). A rectangular slit venturi having a flow area of 3.14 mm^2 was used as the cavitating device and the inlet fluid pressure was varied in the range of 300 to 1000 kPa. Table 4.2 provides the data of inlet pressure with their corresponding flow rate, velocity at the throat section, cavitation number and percentage reduction of TDS, TSS, COD, BOD and TOC for 120 minutes cavitation of the TWE sample.

Table 4.2 HC characteristics and effect of HC inlet pressure on pH, COD, TOC, TDS, TSS, BOD and BI of TWE

Parameters		**HC inlet pressure**			
		300 kPa	**500 kPa**	**700 kPa**	**1000 kPa**
Flow rate (m^3/s)		1.4×10^{-4}	1.6×10^{-4}	1.7×10^{-4}	1.9×10^{-4}
Velocity (m/s)		45.86	52.55	55.74	61.48
Cavitation number (C_v)		0.092	0.070	0.062	0.051
pH	**Initial**	7.27	7.35	7.36	7.43

	Final	7.31	7.54	7.44	7.56
COD (mg/L)	**Initial**	9760	9680	10080	9820
	% reduction	2.45	14.46	13.69	4.48
	Rate constant (min^{-1})	0.0003	0.0016	0.0014	0.0005
	R^2	0.94	0.99	0.99	0.94
TOC (mg/L)	**Initial**	2365	2349	2583	2477
	% reduction	2.36	12.60	10.72	3.47
	Rate constant (min^{-1})	0.0003	0.0013	0.0012	0.0004
	R^2	0.92	0.99	0.99	0.93
TDS (mg/L)	**Initial**	19680	20370	19640	19120
	% reduction	2.38	10.01	5.90	4.60
TSS (mg/L)	**Initial**	18680	18950	19800	18740
	% reduction	12.9	34.82	24.74	22.03
COD/TOC	**Initial**	4.12	4.12	3.90	3.96
	Final	4.12	4.03	3.77	3.92
BOD (mg/L)	**Initial**	--	3200	--	--
	Final	--	3600	--	--
BI	**Initial**	--	0.33	--	--
	Final	--	0.43	--	--

It has been observed that as the pressure increases from 300 to 1000 kPa, the fluid velocity increases from 45.86 to 61.48 m/s whereas the cavitation number decreases from 0.092 to 0.051. Fig. 4.2 presents the effect of inlet pressure on the reduction in COD and TOC of the TWE with respect to the HC treatment time. The % reduction in COD and TOC increased with increase in pressure from 300 to 500 kPa and achieving a steady state in 120 minutes. It may be attributed to the fact that more cavities were generated as the pressure increased and thereby producing higher cavitational yield. However, with further increase in pressure from 500 to 1000 kPa, the % COD and TOC reduction decreased. As the inlet pressure exceeded the optimum pressure, choked cavitation, which is a condition of partial cavity collapse or inactive cavity collapse took place which reduced the cavitational intensity and led to a decrease in the extent of formation of free radicals (Saharan et al., 2014; Thanekar et al., 2018). Therefore, the optimum inlet pressure of 500 kPa was found to be most suitable for all further treatment of TWE in the HC reactor.

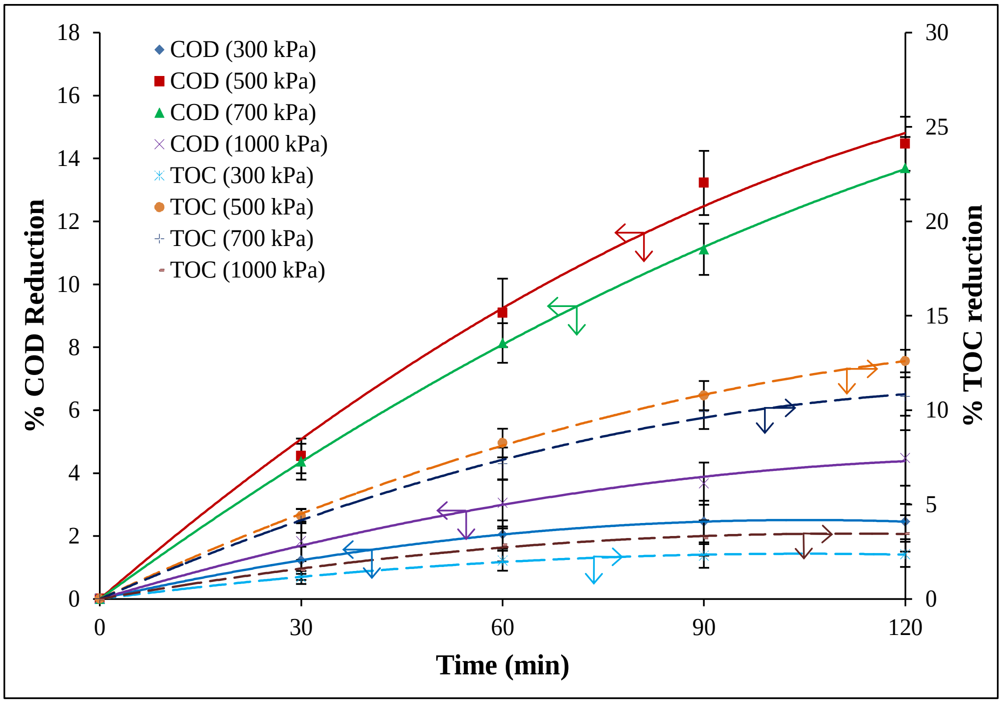


Fig. 4.2 Effect of operating inlet pressure on COD and TOC reduction (Experimental conditions: sample volume, 7L).

Table 4.2 presents that there has been an increase in the sample pH after HC treatment which is due to the generation of the hydroxyl radicals. It was observed from Table 4.2, that maximum COD and TOC reduction of 14.46% and 12.60% respectively was obtained at 500 kPa optimum pressure within 120 minutes. The reduction in TDS and TSS were also observed to be maximum at 10.01% and 34.82% at 500 kPa Pa inlet pressure. Moreover, the BOD value increased from 3200 to 3600 mg/L and the BI value changed from 0.33 to 0.43. This indicates that biodegradability of the sample has increased as the more recalcitrant organic molecules have been broken down into biologically degradable compounds.

The COD to TOC ratios remained constant around 3.9 to 4.1 for all the TWE samples before and after cavitation at all pressures. This indicates that the reduction in COD corresponds to the reduction in TOC simultaneously. The TWE degradation rate kinetics depends on the hydroxylation of TWE by the OH radicals produced during HC or by its thermal decomposition within the cavitation bubble or at the bubble–liquid interfacial region. The pseudo first order kinetic expression fitted well for COD and TOC degradation rate kinetics data at varying pressure conditions and Table 4.2 presents the corresponding rate constants. It was observed that the rate constant of COD and TOC reduction increased from 0.3×10^{-3} to 1.6×10^{-3} min^{-1} and from 0.3×10^{-3} to 1.3×10^{-3} min^{-1} with increase in pressure from 300 to 500 kPa respectively. Further as the pressure increased from 500 to 1000 kPa, the rate constant of COD and TOC reduction decreased to 0.5×10^{-3} and 0.4×10^{-3} respectively. Similar results have been reported by Rajoriya et al., (2018), for the treatment of textile dyeing industrial effluent using HC wherein they have reported that maximum of 17% TOC and 12% COD reduction was obtained at an optimum inlet pressure of 500 kPa.

4.4.2 Effect of dilution on efficacy of HC:

Under the cavitational conditions created in the HC reactor, the highly reactive hydroxyl radicals which are formed have a redox potential of 2.80 eV and target any kind of pollutant non-specifically and mineralize them completely. Moreover, the conditions of microturbulence, intense micro mixing during the implosion of the cavities and microstreaming of fluid jets in the liquid medium increase the interaction of the hydroxyl radicals with the pollutant molecules, are resulting in better utilization of the radicals for the degradation. In case of wastewaters with high organic and inorganic load present in the form of dissolved and suspended matter, dilution of the samples may alter the concentration of the hydroxyl radicals generated as well as the probability of its interaction with the pollutant molecules in the cavitational reactors, thereby affecting the overall degradation rate. Therefore, in order to understand the effect of dilution as well as effect of initial concentrations of TWE sample on the cavitational effectiveness, with respect to the degree of COD and TOC reduction and their degradation rates, samples were diluted and cavitated at the optimum inlet pressure of 500 kPa for 120 minutes. The original sample was diluted in two different proportions 25% and 50% (%V/V) using double distilled water and subjected to HC. Fig. 4.3 presents the % COD and % TOC reduction in comparison with the undiluted cavitated sample. Table 4.3 presents the effect of dilution on the %reduction of COD and TOC with respect to increase in treatment time.

Table 4.3 Effect of dilution on pH, COD, TOC, TDS, TSS, BOD and BI of TWE

Parameters		**HC + Dilution**		
		No dilution	**25% dilution**	**50% dilution**
pH	**Initial**	7.35	6.89	6.66
	Final	7.54	6.95	6.98
COD (mg/L)	**Initial**	9680	8360	5520
	% reduction	14.46	15.31	18.84
	Quantum of reduction	1400	1280	1040
	Rate constant (min^{-1})	0.0016	0.0017	0.0023
	R^2	0.999	0.948	0.970
TOC (mg/L)	**Initial**	2349	2131	1627
	% reduction	12.60	12.76	17.33
	Quantum of reduction	296	272	282
	Rate constant (min^{-1})	0.0013	0.0015	0.0020
	R^2	0.986	0.973	0.974
TDS (mg/L)	**Initial**	20370	14770	10620
	% reduction	10.01	3.52	3.67
TSS (mg/L)	**Initial**	18950	13830	9800
	% reduction	34.82	34.92	42.85
COD/TOC	**Initial**	4.12	3.92	3.39
	Final	4.03	3.81	3.33
BOD (mg/L)	**Initial**	3200	--	1400
	Final	3600	--	1600
BI	**Initial**	0.33	--	0.25
	Final	0.43	--	0.35

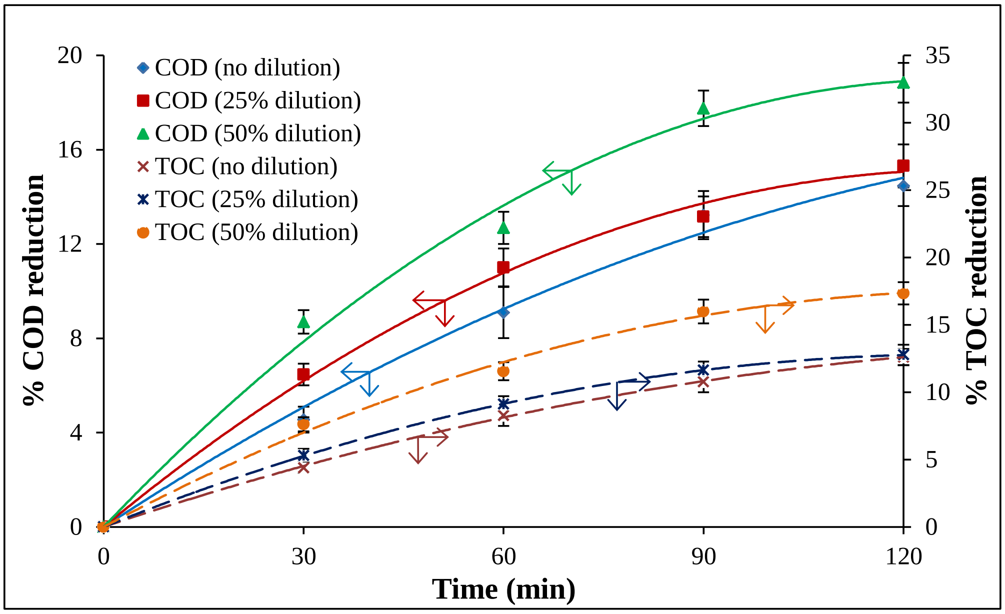


Fig. 4.3 Effect of dilution on COD and TOC reduction (Experimental conditions: sample volume, 7L; inlet pressure, 500 kPa).

Data in Table 4.3 indicates that the % dilution increased the % reduction rate of the COD and TOC reduction also increased. The degradation rate constant for COD reduction increased from 0.0016 to 0.0023 min^{-1} and for TOC reduction, it increased from 0.0013 to 0.0020 min^{-1} when sample was subjected to 50% dilution. The maximum COD and TOC reduction was 18.84% and 17.33% respectively obtained at 50% dilution which is slightly greater than the reduction obtained in undiluted sample. The TDS reduction was negligible at 3.67% whereas the TSS reduction was 42.85% which corresponded to the effect of 50% dilution of the TWE sample.

However, from the Table 4.3, it can also be observed that as the degree of dilution increased, the quantum of COD reduction was reduced by 26%, whereas the quantum of TOC reduction was reduced by 5%, which indicates that there is no significant effect of dilution on the mineralization of TWE. Therefore, it is not feasible to use dilution during the treatment of TWE using HC, as it will only increase the operational treatment costs because dilution will increase the total amount of the effluent to be treated. Moreover, the biodegradability of the TWE samples was very low on dilution, as BI values ranged from 0.25 to 0.35 only. It is also evident from the earlier literature reported by Padoley et al., (2012), Rajoriya et al., (2018) and Raut-Jadhav et al., (2016a) that dilution had no major impact on COD and TOC reduction of the wastewater using HC. Therefore, further studies were conducted without dilution of TWE at the inlet pressure of 500 kPa using HC.

4.4.3 HC in combination with advanced oxidizing agent- Ozone:

Ozone is a very powerful oxidizing agent; however, its reactivity is determined by the nature of the compounds present in wastewater. The organic compounds with specific functional groups such as aromatic rings, unsaturated hydrocarbons are oxidizable or prone to O_3 attack whereas saturated hydrocarbons, alcohols, aldehydes, ketones, carboxylic acids etc. are resistant to O_3 attack. O_3 is also capable of oxidizing inorganic compounds such as sulphides present in TWE to soluble salts and sometimes causes the precipitation of metal oxides acting as a micro-flocculant. Another process limitation is the low mass transfer rate and rate kinetics which decide whether O_3 will be able to oxidize the organic pollutant within a reasonable residence time adopted in the TWE treatment process. O_3 dissociates into oxygen having a half-life period of 8 to 15 minutes at around ambient temperature conditions, and therefore will be effective as an oxidizing agent only when there is an effective transfer from the gas to liquid phase and when it acts within the solution as a dissolved species. However, in the presence of HC, O_3 dissociates into hydroxyl radicals which have higher oxidation potential than O_3. The reactions that occur during the cavitation process in the dissociation of O_3 to form reactive oxygen that reacts with water to produce hydroxyl radicals is as given in Eq. (4) & (5).

$$O_3 \xrightarrow{HC} O_2 + O(^3P) \qquad (4)$$

$$O(^3P) + H_2O \rightarrow 2\,^{\bullet}OH \qquad (5)$$

Therefore, in order to investigate the combined effect of HC + O_3 on the treatment of TWE, different flow rates of O_3 was introduced at the throat section of the cavitating device during HC. Experiments were conducted at four different mass flow rates of O_3 i.e. 3 g/h, 5 g/h, 7 g/h and 9 g/h for 120 minutes at the optimized inlet pressure of 500 kPa. Fig. 4.4 presents the reduction in COD and TOC values at different dosage of O_3 in 120 minutes of treatment time. It was observed from Table 4.4, that the % reduction in TDS was negligible (around 6%) whereas the % reduction in TSS increased from 36.18% to a maximum of 45.21% with an increase in mass flow rate of O_3 from 3g/h to 7 g/h. The % COD reduction increased from 15.97% to a maximum value of 26.81% as O_3 dozing varied from 3 to 7g/h and thereafter decreased to 18.22% at higher O_3 dozing of 9 g/h. The recombination reactions may have taken place in the presence of formation of excess radicals to form H_2O_2 and water which reduced the overall degradation rate.

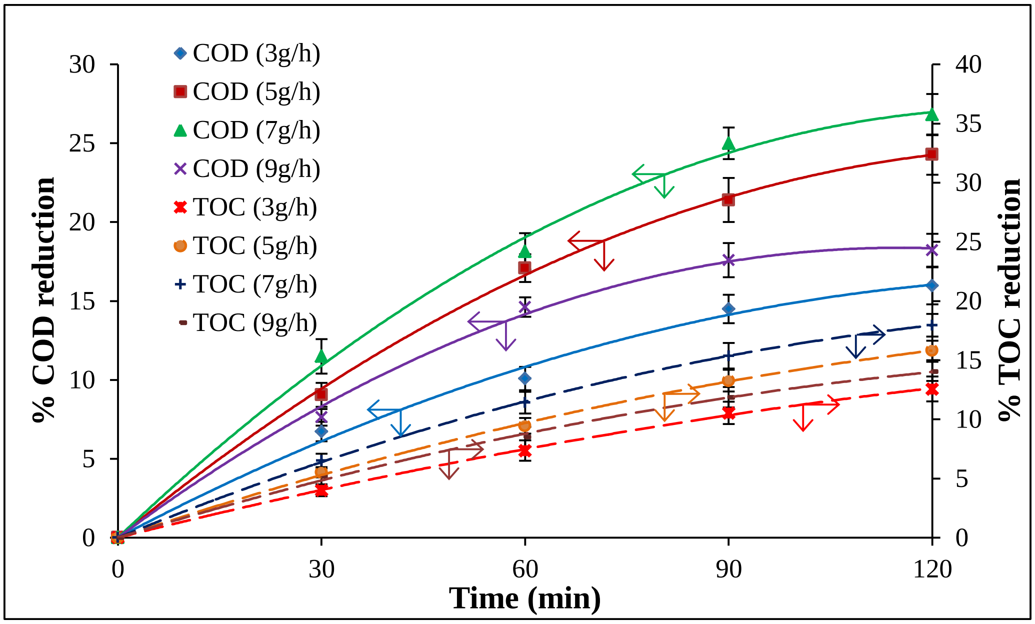


Fig. 4.4 Effect of HC + Ozone on COD and TOC reduction (Experimental conditions: sample volume, 7L; inlet pressure, 500 kPa).

Table 4.4 Effect of HC + ozone dose on pH, COD, TOC, TDS, TSS, BOD and BI of TWE

Parameters		**HC + Ozone**				
		HC only	**HC + O_3 (3g/h)**	**HC + O_3 (5g/h)**	**HC + O_3 (7g/h)**	**HC + O_3 (9g/h)**
pH	**Initial**	7.35	7.21	7.30	7.31	7.40
	Final	7.54	7.50	7.56	7.53	7.48
COD (mg/L)	**Initial**	9680	9520	9720	9920	9440
	% reduction	14.46	15.97	24.28	26.81	18.22
	Quantum of reduction	1400	1520	2360	2660	1720
	Rate constant (min^{-1})	0.0016	0.0018	0.0028	0.0033	0.0023
	R^2	0.999	0.979	0.982	0.986	0.969
TOC (mg/L)	**Initial**	2349	2324	2389	2322	2336
	% reduction	12.60	12.56	15.82	17.96	14.04
	Quantum of reduction	296	292	378	417	328
	Rate constant (min^{-1})	0.0013	0.0012	0.0015	0.0018	0.0014
	R^2	0.986	0.988	0.983	0.973	0.975
TDS (mg/L)	**Initial**	20370	20050	19830	20160	18890
	% reduction	10.01	6.88	6.60	6.10	4.60
TSS (mg/L)	**Initial**	18950	18100	19100	17450	18050

	% reduction	34.82	36.18	41.09	45.21	43.82
COD/TOC	**Initial**	4.12	4.10	4.07	4.27	4.04
	Final	4.03	3.94	3.66	3.81	3.84
BOD (mg/L)	**Initial**	3200	--	--	3200	--
	Final	3600	--	--	3100	--
BI	**Initial**	0.33	--	--	0.32	--
	Final	0.43	--	--	0.42	--

The maximum COD reduction of 26.81% and TOC reduction of 17.96% was observed with a degradation rate constant of 0.0033 min^{-1} and 0.0018 min^{-1} respectively at 7 g/h loading of O_3 with HC. The increase in BI value from 0.33 to 0.43 was found to be the same for treatment by using HC alone as well as for HC combined with O_3. This indicates favorable biodegradability of TWE by combining O_3 with HC treatment. Table 4.4 presents that there has also been a decrease in COD/TOC ratio from 4.27 to 3.81 for the TWE sample treated at 7g/h O_3 dosing which indicates considerable reduction in TOC and corresponding COD.

The synergistic coefficient with respect to COD reduction representing the efficacy of the synergistic combination of HC and O_3 treatment was also estimated. Experiments were also conducted for the treatment of samples with O_3 alone at optimum feed flow rate of O_3 at 7 g/h without HC, so as to determine the individual effect of ozonation on the COD reduction of TWE within 2 h. Raw TWE (7 L volume) was subjected to the treatment with continuous circulation through bypass line with O_3 dosing directly into the tank at the rate of 7 g/h. Samples were withdrawn at regular time intervals of 30 minutes for analyzing the COD value. It was observed that with only ozonation, the reduction in COD was 13.17 % within 2 h at a first order rate constant of 0.0013 min^{-1}. The synergetic coefficient was calculated to quantify the combined effect of HC with ozonation, according to Eq.6.

$$\text{Synergetic coefficient } \gamma_{\mathrm{HC+O_3}} = \frac{k_{(\mathrm{HC+O_3})}}{k_{\mathrm{HC}}+k_{\mathrm{O_3}}} \qquad (6)$$

$$\gamma_{\mathrm{HC+O_3}} = \frac{0.0033}{0.0016+0.0013} = 1.13$$

The value of synergetic coefficient "$\gamma_{\mathrm{HC}+O_3}$" was found to be 1.13 which indicates that the combined process exhibited favorable synergistic effect with enhanced degradation of the organic pollutants due to the increase in generation of hydroxyl radicals. Combination of HC with ozonation increased the rate kinetics due to the high micro turbulence, microstreaming and effective contact created between the oxidizing agents (i.e O_3 and hydroxyl radicals) and pollutants. Barik and Gogate, (2018), reported studies on HC combined with ozonation to achieve 97% degradation of 2,4,6-TCP which was much higher in comparison to their individual approaches. In a recent study reported by Rajoriya et al., (2017a), combination of O_3 with HC (inlet pressure: 2000 kPa, O_3 dozing :3 g/h) gave the complete decolorization of textile dye Rh6G and TOC reduction of 84% compared to only 32% decolorization and TOC reduction of 10% with HC alone.

4.4.4 HC in combination with advanced oxidizing agent- Hydrogen Peroxide:

Hydrogen peroxide (H_2O_2) is also used extensively as an additional oxidizing agent for process intensification and HC can promote its easy dissociation to produce hydroxyl radicals, thereby providing the extra $OH^\bullet$ radicals for the degradation of pollutants present in TWE. The combined hybrid process of HC in combination with H_2O_2 has been reported to have enhanced wastewater treatment ability, which can be attributed to the enhanced generation of hydroxyl radicals, enhanced contact and the elimination of mass transfer resistances as the oxidation reaction proceeds within the cavitation zone and is expected to intensify the treatment process by 5 to 20 times (Raut-Jadhav et al., 2016a).

The theoretical amount of H_2O_2 commonly used for the reduction of COD is 2.12g of H_2O_2/g of COD (Bautista et al., 2001) however it primarily depends on the nature of the organic and inorganic content present in the TWE and their specific response to H_2O_2. The COD value of raw TWE was observed to be around 9g/L and theoretically around 19 to 20 g of H_2O_2 will be required for its degradation. Batch studies conducted for the degradation of TWE effluent using H_2O_2 alone in a stirred tank mixer provided with normal stirring produced very low reduction in COD which indicated a very low dissociation of H_2O_2 into $^\bullet OH$ radicals by normal stirring and thereby low degradation efficiency. However, in order to examine the combined effect of H_2O_2 with HC, four different doses varying from 15 ml to 90 ml (i.e. equivalent to 2.38 g/L, 4.76 g/L, 9.51 g/L, 14.27 g/L) of H_2O_2 were introduced into the HC reactor prior to the cavitation process. Experiments were performed at the optimum inlet pressure of 500 kPa treating 7 liters of undiluted sample for 120 minutes. Fig. 4.5 depicts the reduction in COD and TOC with respect to time for the various H_2O_2 dosages. Table 4.5 presents the reduction in TDS, TSS, BOD, COD and TOC and their respective degradation rate constants for the various dosages.

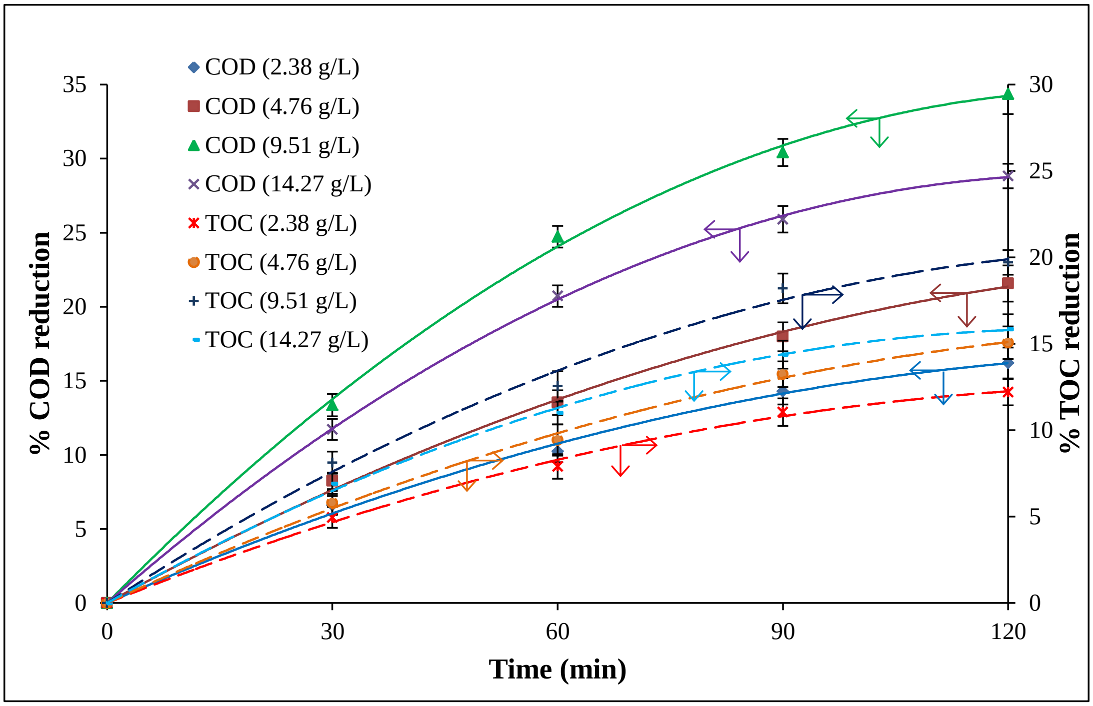


Fig. 4.5 Effect of HC + H_2O_2 on COD and TOC reduction (Experimental conditions: sample volume, 7L; inlet pressure, 500 kPa).

Table 4.5 Effect of HC + H_2O_2 dose on pH, COD, TOC, TDS, TSS, BOD and BI of TWE

Parameters		**HC + H_2O_2**				
		HC only	**HC + H_2O_2 (2.38 g/L)**	**HC + H_2O_2 (4.76 g/L)**	**HC + H_2O_2 (9.51 g/L)**	**HC + H_2O_2 (14.27 g/L)**
pH	**Initial**	7.35	7.42	7.29	7.20	7.46
	Final	7.54	7.59	7.45	7.46	7.63
COD (mg/L)	**Initial**	9680	9380	9460	9140	8880
	% reduction	14.49	16.20	21.56	34.35	28.83
	Quantum of reduction	1400	1520	2040	3140	2560
	Rate constant (min^{-1})	0.0016	0.0018	0.0023	0.0043	0.0035
	R^2	0.999	0.979	0.980	0.980	0.979
TOC	**Initial**	2349	2263	2311	2374	2290

(mg/L)	**% reduction**	12.60	12.19	15.05	19.71	15.82
	Quantum of reduction	296	276	348	468	363
	Rate constant (min^{-1})	0.0013	0.0013	0.0016	0.0023	0.0018
	R^2	0.986	0.982	0.987	0.986	0.969
TDS (mg/L)	**Initial**	20370	19930	19070	18850	18770
	% reduction	10.01	8.47	7.86	7.10	4.95
TSS (mg/L)	**Initial**	18950	19130	18930	18750	19860
	% reduction	34.82	36.01	42.63	49.60	48.34
COD/TOC	**Initial**	4.12	4.14	4.09	3.85	3.88
	Final	4.03	4.00	3.78	3.14	3.28
BOD (mg/L)	**Initial**	3200	--	--	2800	--
	Final	3600	--	--	2500	--
BI	**Initial**	0.33	--	--	0.30	--
	Final	0.43	--	--	0.41	--
H_2O_2 (g)/ COD (g)		--	1.57	2.33	3.02	5.57
H_2O_2 (g)/ TOC (g)		--	8.62	13.68	20.32	39.31

It was observed that the % reduction of TDS was decreasing with increase in H_2O_2 dosage. However, the % TSS reduction increased with increase in H_2O_2 dosing and had a maximum reduction of 49.60% for dose of 60ml (i.e. 9.51g/L). This indicates that the suspended particles are getting degraded into intermediates on reacting with H_2O_2 which are soluble and thereby increasing the TDS of the solution. The rate of reduction of COD and TOC increased with increase in H_2O_2 loading for the combined process in comparison to HC alone. Maximum reduction of 34.35% in COD and 19.71% in TOC was obtained for the H_2O_2 dose of 60 ml (i.e. 9.51 g/L) with corresponding degradation rate constants of 0.0043 min^{-1} and 0.0023 min^{-1} respectively. The process effectiveness will depend on the extent of production of hydroxyl radicals by the cavitation bubbles and the reaction of these radicals within and outside the bubbles by the various organic/ inorganic species present in the TWE sample. However, excess dosing of H_2O_2 caused the scavenging of the hydroxyl radicals and therefore the % reduction in COD and TOC decreased at the H_2O_2 dosing of 14.27 g/L. First order rate kinetics was fitted for the COD and TOC reduction and a maximum degradation rate constant of 0.0043 min^{-1} and 0.0023 min^{-1} was obtained for the % reduction in COD and TOC respectively at the optimized H_2O_2 loading for the hybrid process. Similar results have been reported on the degradation of imidacloprid by Raut-Jadhav et al., (2016a) using circular venturi HC and on the degradation of Rhodamine 6G using slit venturi by Rajoriya et al., (2017a) and for the treatment of 2,4,6- trichloro phenol (TCP) using HC + H_2O_2 by Barik and Gogate, (2018) respectively.

The synergetic coefficient "$\gamma_{HC+H_2O_2}$" was also estimated for the combined process of HC with H_2O_2 using Eq.7.

$$\text{Synergetic coefficient } \gamma_{HC+} = \frac{k_{(HC+H_2O_2)}}{k_{HC}+k_{H_2O_2}} \tag{7}$$

$$\gamma_{HC+H_2O_2} = \frac{0.0043}{0.0016+0.0} = 2.6875$$

The value of synergetic coefficient "$\gamma_{HC+\ H_2O_2}$" estimated at a value of 2.7 shows the synergetic effect of combined process in comparison to the efficiency of the individual processes.

4.4.5 Combined effect of HC and Fenton's reaction:

The advantage of combining HC with Fenton's reagent is that it produces hydroxyl radicals by the dissociation of H_2O_2 under the cavitational effects, and by the reaction between ferrous / ferric ions and H_2O_2that occurs simultaneously generating highly reactive hydroxyl and oxy-hydroxyl radicals useful for the degradation of organic molecules. When Fenton is combined with cavitation, dosage of H_2O_2 required per unit weight of COD reduction may be lower due to the generation of the highly reactive radicals by HC as well as its simultaneous uniform dispersion through effective micro-mixing and turbulence created by the cavitation bubbles within the cavitation zone.

The basic equations under the combined effect of cavitation and Fenton's reaction are reported in literature (Rajoriya et al., 2017b). The concentration of the Ferrous salt ($FeSO_4.7H_2O$) and the dosage of H_2O_2 into the HC reactor are the two deciding factors for the combined HC + Fenton process efficiency. The initial pH of the TWE was around pH 7.4±1. On addition of H_2O_2 and $FeSO_4.7H_2O$ into the TWE, the drop in pH was observed up to a pH of 6.7±1, which may be due to the production of organic acids from the fragmentation of organic molecules by the hydroxyl radicals. Whereas, when the samples were subjected to hydrodynamic cavitation, the pH of the samples again increased to a value of 7.5±1. The experiments were performed using the optimized dose of H_2O_2 (i.e. 9.51 g/L) which brought the maximum reduction of COD in the HC + H_2O_2 study and kept constant for all the ratios of $FeSO_4$ to H_2O_2. The doses of $FeSO_4.7H_2O$ were 0.5 g/L, 1 g/L, 3 g/L, 5 g/L (equivalent w/w ratio of $FeSO_4.7H_2O$ to H_2O_2 is 1:19, 1:10, 1:3, 1:2) added to 7 L of the TWE sample which was cavitated in the HC reactor at 500 kPa inlet pressure for 120 minutes. The degradation efficiency was studied in terms of reduction obtained in TDS, TSS, COD, BOD and TOC Fig. 4.6 presents the % reduction in COD and TOC values at varying doses of ferrous sulfate in 120 minutes of treatment time and presented in Table 4.6.

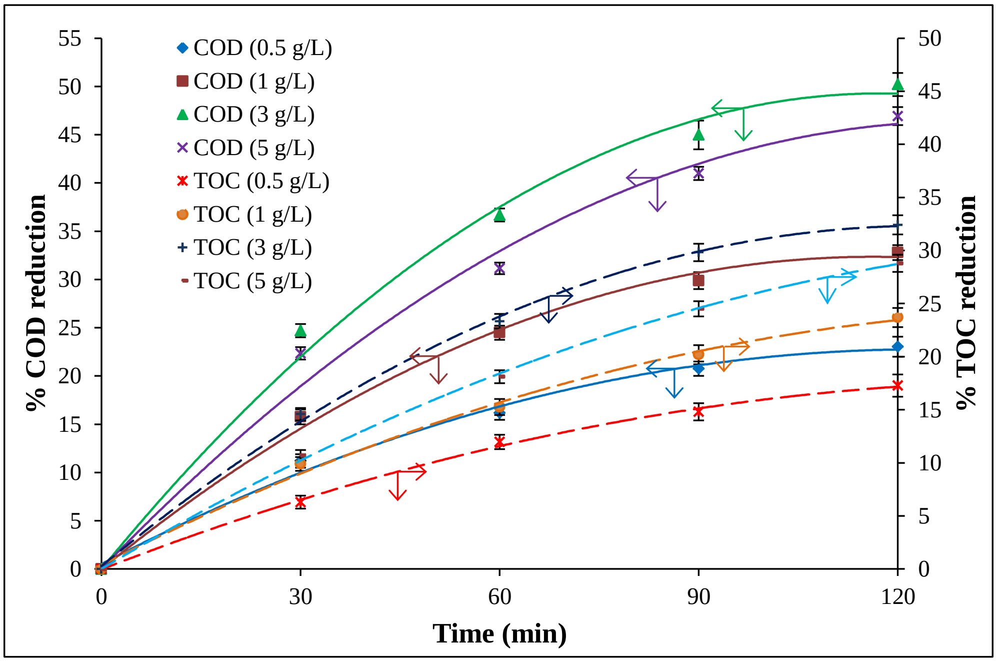


Fig. 4.6 Effect of HC + Fenton's reagent on COD and TOC reduction (Experimental conditions: sample volume, 7L; inlet pressure, 500 kPa; H_2O_2 dose, 9.51 g/L).

Table 4.6 Effect of HC + Fenton's reagent on pH, COD, TOC, TDS, TSS, BOD and BI of TWE

Parameters		**HC + Fenton's [(Ferrous dose; g/L), [$FeSO_4.7H_2O$:H_2O_2 w/w]]**				
		HC only	HC + Fenton's (0.5 g/L) [1:19]	HC + Fenton's (1.0 g/L) [1:10]	HC + Fenton's (3.0 g/L) [1:3]	HC + Fenton's (5.0 g/L) [1:2]
pH	Initial	7.35	7.40	7.40	7.31	7.31
	Final	7.54	7.47	7.53	7.45	7.39
COD (mg/L)	Initial	9680	9640	9640	9760	9760
	% reduction	14.46	23.03	32.78	50.20	46.93

	Quantum of reduction	1400	2220	3160	4900	4580
	Rate constant (min^{-1})	0.0016	0.0028	0.0043	0.0071	0.0061
	R^2	0.999	0.944	0.952	0.961	0.963
TOC (mg/L)	Initial	2389	2398	2398	2468	2468
	% reduction	12.60	17.26	23.68	32.41	28.81
	Quantum of reduction	296	414	568	800	711
	Rate constant (min^{-1})	0.0013	0.0019	0.0026	0.0042	0.0032
	R^2	0.986	0.975	0.970	0.974	0.991
TDS (mg/L)	Initial	20370	18450	18450	19180	19180
	% reduction	10.01	4.82	3.30	1.88	1.15
TSS (mg/L)	Initial	18950	17700	17700	19950	19950
	% reduction	34.82	40.96	45.48	53.88	45.86
COD/TOC	Initial	4.12	4.02	4.02	3.95	3.95
	Final	4.03	3.74	3.54	2.91	2.95
BOD (mg/L)	Initial	3200	--	--	2800	--
	Final	3600	--	--	2400	--
BI	Initial	0.33	--	--	0.28	--
	Final	0.43	--	--	0.46	--
H_2O_2 (g) /COD (g)		--	4.28	3.01	1.95	2.07
H_2O_2 (g) /TOC (g)		--	22.97	16.75	11.89	13.38

It was observed that as the loading of ferrous sulfate increased, reduction in COD and TOC also increased until the optimum loading of 3g/L i.e. for H_2O_2 /$FeSO_4.7H_2O$ ratio of 3:1. Thereafter there was a decrease in the reduction in COD and TOC which may be due to the auto scavenging of the hydroxyl radicals by ferrous ion itself at higher concentrations. The first order rate kinetics was also fitted for the reduction of COD and TOC and the data is given in Table 4.6. The maximum of 50.20% COD and 32.41% TOC reduction was observed at H_2O_2 /$FeSO_4.7H_2O$ ratio of 3:1, and with a rate constant of 0.0071 min^{-1} and 0.0042 min^{-1} respectively. Moreover, Fenton oxidation in combination with HC also increased the biodegradability of wastewater as its BOD/COD ratio increased from 0.28 to 0.46, which is an increase by 64% compared to an increase by 30% using HC alone. The improved biodegradability observed is associated with the partial oxidation of TWE effluent to give low molecular weight oxygenated compounds rather than complete mineralization to carbon dioxide.

Fenton's process alone for treatment of TWE was also conducted using the optimized doses of ferrous sulfate (3 g/L) and H_2O_2 (9.51 g/L). After 120 min, 24.52 % reduction was observed in COD with degradation rate kinetics having a first order rate constant of 0.0025 min^{-1}. The consumption of H_2O_2 (g) per g of COD and TOC for Fenton process alone was 4.14 g/g and 31.92 g/g respectively. The requirement of H_2O_2 per g of COD reduction for the hybrid process of HC + Fenton has reduced from 4.14 to 1.95 g/g. Similarly, the consumption of H_2O_2 per g of TOC reduction was reduced from 31.92 g/g to 11.89 g/g. It has been observed that application of Fenton alone is not advantageous as it requires higher dosage of H_2O_2 and ferrous sulphate which may also induce coagulation and problems of excessive sludge formation especially for complex effluents like TWE which require high oxidant dosing. Whereas in the hybrid process of Fenton combined with HC, the physical and chemical effects of cavitation created a synergistic mechanism enhancing the degradation efficiency of TWE with reduced amount of H_2O_2. The synergetic coefficient "$\gamma_{\mathrm{HC+Fenton}}$" was also estimated for the combined process of HC with Fenton's reaction using Eq.8.

$$\text{Synergetic coefficient } \gamma_{\mathrm{HC+Fenton}} = \frac{k_{(\mathrm{HC+Fenton})}}{k_{\mathrm{HC}}+k_{\mathrm{Fenton}}} \tag{8}$$

$$\gamma_{\mathrm{HC+Fenton}} = \frac{0.0071}{0.0016+0.0025} = 1.73$$

The value of synergetic coefficient $\gamma_{\mathrm{HC+Fenton}}$ was greater than 1, which indicates that the combined process is more efficient than the individual processes. Higher performance with respect to degradation efficiency has been reported with synergistic combinations of HC with Fenton for the degradation of chemicals such as dichlorvos by Joshi and Gogate, (2012), Imidacloprid by Patil et al., (2014) and Methomyl by Raut-Jadhav et al., (2016b).

4.4.6 Treated TWE characteristics based on optimized results observed in different processes

A final comparison of the effectiveness of all the hybrid techniques utilized in terms of the reduction in COD, TOC, rate of reduction, BI index of the treated TWE at their respective optimized conditions and the synergistic coefficients are presented in Table

4.7. Fig. 4.7 and 4.8 depicts the comparative studies for the reduction of COD and TOC in 120 minutes of treatment time under the effect of different pretreatment processes. It was observed that the rate of COD and TOC reduction increased in all hybrid methods in comparison to HC alone. The maximum % reduction of both COD and TOC reduction was observed for the HC + Fenton's process compared to HC+ O_3 and HC + H_2O_2 hybrid treatment methods. The BOD of treated sample was also analyzed for all the samples from the treatment method at their optimized condition. It was observed that BOD was increased in case of HC alone and HC + dilution from its initial value of 3200 - 3600 mg/L and 1400 - 1600 mg/L respectively, whereas in case of hybrid methods, BOD was decreased. Maximum BOD and COD reduction was observed in HC+ Fenton process with increase in BI from 0.28 to 0.46. Maximum TSS reduction was also observed using HC + Fenton process. It may be because of coagulative action of ferrous sulfate which caused the reduction in the TSS content of TWE. The simultaneous increase in the TDS of the samples due to the addition of ferrous salt in HC + Fenton's process may be the reason for the minor % reduction in TDS after complete treatment process. The consumption of H_2O_2 per g of COD and TOC reduction in the case of HC + H_2O_2 was 3.02 g/g and 20.32 g/g respectively at optimized conditions. Whereas in the case of HC + Fenton's process the consumption of H_2O_2 was lesser than that required for the HC + H_2O_2 process, which was at 1.95 g/g of COD and 11.89 g/g of TOC.

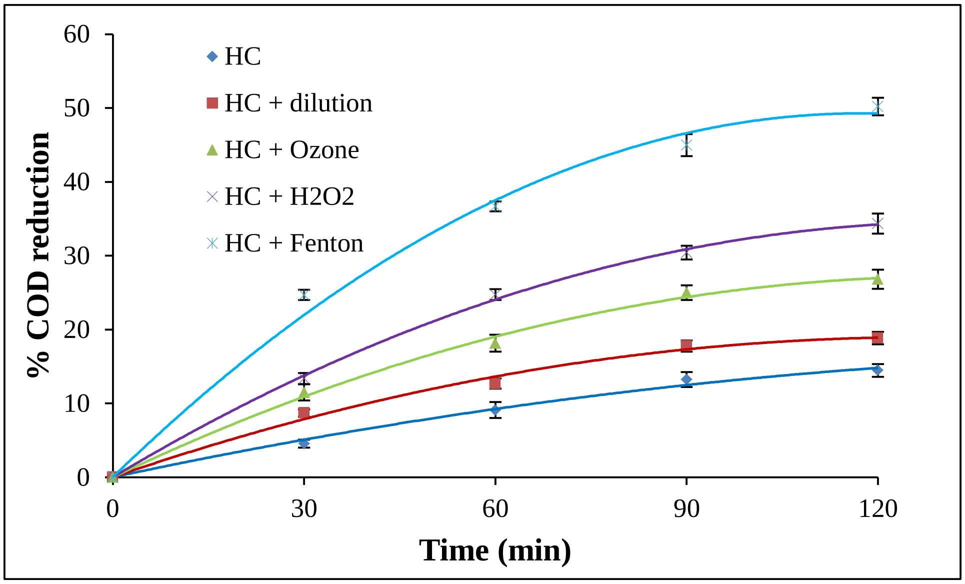


Fig. 4.7 Comparison of COD reduction at optimized condition for all treatment strategies (Optimized conditions: sample volume, 7L; inlet pressure, 500 kPa; dilution, 50%; ozone dose, 7g/h; H_2O_2 dose, 9.51 g/L; Fenton's reagent dose, 3g/L $FeSO_4.7H_2O$ and 9.51 g/L H_2O_2)

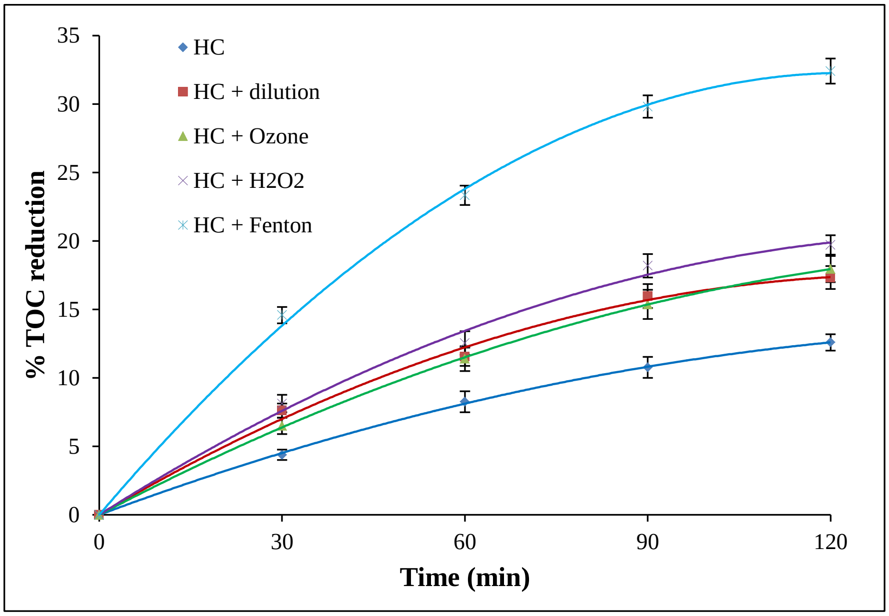


Fig. 4.8 Comparison of TOC reduction at optimized condition for all treatment strategies (Optimized conditions: sample volume, 7L; inlet pressure, 500 kPa; dilution, 50%; ozone dose, 7g/h; H_2O_2 dose, 9.51 g/L; Fenton's reagent dose, 3g/L $FeSO_4.7H_2O$ and 9.51 g/L H_2O_2).

Table 4.7 Comparison of treated TWE characteristics based on optimized results observed in different processes

Process		**HC alone**	**HC with dilution**	**HC + Ozone**	**HC + H_2O_2**	**HC + Fenton**
% COD reduction		14.46	18.84	26.81	34.35	50.20
Rate constant for COD reduction		0.0016	0.0023	0.0033	0.0043	0.0071
% TOC reduction		12.60	17.33	17.96	19.71	32.41
Rate constant for TOC reduction		0.0013	0.0020	0.0018	0.0023	0.0032
BOD/COD BI value	**Initial**	0.33	0.25	0.32	0.30	0.28
	Final	0.43	0.35	0.42	0.41	0.46
COD/TOC	**Initial**	4.12	3.39	4.27	3.85	3.95
	Final	4.03	3.33	3.81	3.14	2.91
H_2O_2 (g) /TOC (g)		---	---	---	20.32	11.89
H_2O_2 (g) / COD (g)		---	---	---	3.02	1.95
Synergetic coefficient		---	---	1.13	2.7	1.73

4.4.7 FT-IR analysis of raw and treated TWE:

FT-IR analysis was performed on raw and treated TWE to evaluate the relevant chemical bonds and functional groups of the organic compounds present. The respective wavenumber observed in different samples along with their possible functional groups are shown in Table 4.8 and a comparison of the FTIR spectrum is also presented in Fig. 4.9.

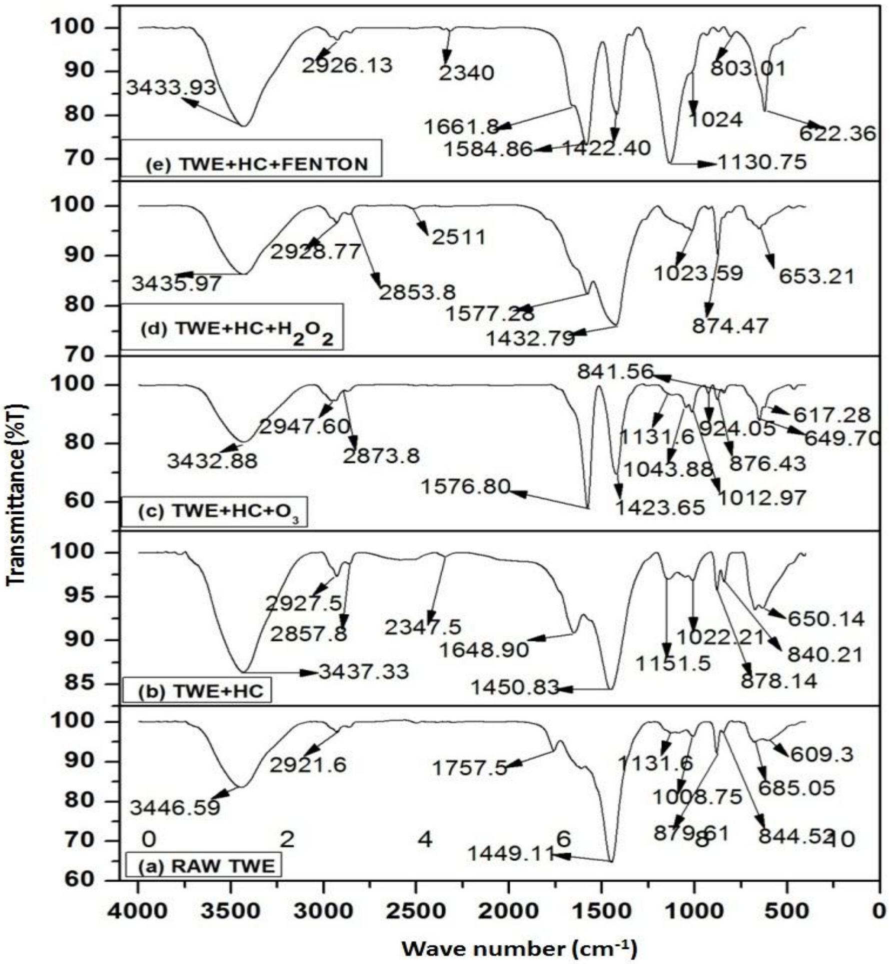


Fig. 4.9 FT-IR spectrum at optimized conditions for all treatment strategies.

As observed in the FT-IR spectra, the absorption peaks at 3446.59 to 3432.66 cm^{-1} are attributed to -OH group and O-H bond stretching vibrations, found with strong intensity and indicate the existence of alcohol and phenol derivatives in the TWE sample (Ladwani et al., 2016; Reyes and Crisosto, 2016). The peaks in the range of 2947.6 to 2853.8 cm^{-1} is attributed to stretching of C-H bond that corresponds to presence of long chain aliphatic compounds such as fatty acids, diazo compounds and surfactants that are used in leather dyeing and processing (Smidt et al., 2011). Peak of dissolved CO_2 was observed in the region of 2347.5 and 2340 cm^{-1} for HC and HC + Fenton treated samples respectively which indicate the effectiveness of hybrid processes in mineralization of the organic components (Schädle et al., 2016). The peak observed at 1757.5 cm^{-1} in case of raw TWE attributed to the presence of ketone groups which indicate presence of fatty acid molecules in raw samples. A new absorption peak which appeared in HC and HC + Fenton treated samples at 1661.8 cm^{-1} and 1648.9 cm^{-1} indicate presence of carboxylates which might be the due to the breakage/ cleavage of the cyclic compounds to straight chain carboxylic compounds (Valeika et al., 2012). The disappearance of aldehyde/ketone group and emergence of carboxyl group could be attributed to effect of $OH^{\bullet}$ on aldehyde/ketone during treatment process. The emergence of new peak in the region of 1584.86 to 1576.80 cm^{-1} for the hybrid treatment methods attributed to the N-H plane bending indicating presence of amines and amides (Reyes and Crisosto, 2016; Valeika et al., 2012). The absorption peaks in the region 1450.83 to 1422.40 cm^{-1} attributed to C-O and COO^{-}stretching indicating presence of carboxylic acids/organic acids or carbonates. The peaks in the region of 1131.6 to 924.05 cm^{-1} observed in all the samples can be attributed to C—O—C, C—O, C—O—P, C—O, alkyl organophosphorus compounds indicating presence of polysaccharides, phosphodiesters etc. (Smidt et al., 2011). Peaks in the region of 879.61 to 803.01 cm^{-1} were also observed in raw and treated samples which is attributed to C—O out of plane bending vibration, and are indicative of presence of benzene, carbonates etc. The peaks in the region 685.05 to 609.3 cm^{-1} can be attributed to S-O bending vibration which is due to the presence of sulphates (Smidt et al., 2011). The absorption at 617.28 cm−1 in case of ozonated samples indicated the O–C=O bending due to presence of carboxylic acids (Bharagava et al., 2018). Overall, the absorption spectrum of untreated and treated TWE showed the presence of some of the alcohols, phenols, fatty acids, amines, poly saccharides and aromatic compounds. The treated samples had more of dissolved carbon dioxide, low molecular compounds such as carboxylic compounds, carbonates, etc. along with those compounds observed in case of untreated sample indicative of degradation.

Table 4.8 Detected functional group with their wave number from FT-IR spectra

Vibration	**Wave number (cm^{-1})**				
	Raw TWE	**HC**	**HC + Ozone**	**HC + H_2O_2**	**HC + Fenton**
O-H stretching	3446.59	3437.33	3432.66	3435.97	3433.93
C–H stretching	2921.6	2927.75,	2947.60,	2928.77,	2926.13

		2857.8	2873.8	2853.8	
Dissolved CO_2		2347.5			2340
C=C, C=O, N—H bending C-O and COO^- stretching	1757.5, 1449.11	1648.90, 1450.83	1576.80 1423.65	1577.28 1432.79	1661.8, 1584.86 1422.40
C—O—C, C—O, C—O—P,	1131.6, 1008.75,	1151.5, 1022.21,	1131.6, 1043.88, 1012.97, 924.05,	1023.59,	1130.75, 1024
C—O out of plane bending	879.61, 844.52	878.14, 840.21	876.43, 841.56	874.47	803.01
S—O bending	685.05, 609.3	650.14	649.70, 617.28	653.25	622.36

4.4.8 LCMS analysis of raw and treated TWE:

LCMS analysis of the raw TWE, HC treated and HC+ Fenton treated samples was conducted and the nature of the organic matter as well as the probable degradation products were identified by matching their retention time and MS spectrum from standard data. The samples which had the highest % reduction in COD and TOC when treated by the three different methods were subjected to LCMS analysis to obtain their respective chromatogram and is depicted in Fig. 4.10, Fig. 4.11 and Fig. 4.12 which are provided as supplementary material. Fig. 4.10 presents the comparison of the chromatograms of raw TWE, HC treated and HC+ Fenton treated samples and significant peaks were observed at different retention time indicating presence of clusters of molecules to be present in TWE samples. The chromatograms with peaks at retention time of 0.49, 2.83, 3.89 and 5.43 min in case of raw TWE and corresponding peaks at 0.47, 2.60 and 5.36 min for HC and 0.47, 2.35, 3.79 and 5.26 min for HC+ Fenton process indicated the presence of same kind of molecules. However additional peaks of high intensity at retention time of 0.58, 1.17 and 1.61 min were found in case of HC treated samples and at retention time of 0.59, 1.18 and 8.90 min were found for HC+ Fenton treated samples that indicated the formation of new intermediates or lower mass products due to the degradation reactions. Moreover, in order to further identify the degraded molecules, MS analysis was conducted for identifying the molecular species obtained at the various retention times.

Table 4.9 and 4.10 present the list of all the probable compounds observed in the studied samples and their corresponding mass numbers obtained from their spectra. The most commonly found were Polyethylene glycols (PEG_2, PEG_4,s) and their related acidic forms such as monocarboxylated polyethylene glycols ($MCPEG_2$,$MCPEG_4$,$MCPEG_6$,$MCPEG_8$s) and dicarboxylated polyethylene glycols ($DCPEG_7$,$DCPEG_9$s) with varying number of carbon atoms in the carbon chain. Alcohol ethoxylated surfactants ($AL_{4,8}$,$Al_{3,8}$, $AL_{4,4}$,$AL_{12,4}$,$AL_{13,4}$,$AL_{14,4}$) and nonylphenol polyethoxylated surfactants ($NPEO_9$s) were present which normally has a very slow biodegradation rate (Schrank et al., 2017, 2004). Apart from these, other different group of organic pollutants identified include phenolic compounds such as nitrophenol (NP), 4-chloro-3-methylphenol and several phthalates such as diethylphthalate (DEHP) and bis (2-ethylhexylphthalate (DBP)(Castillo and Barcelo, 1999). Fig. 4.11 presents the comparison of MS spectra at retention time of 0.49 (Raw TWE), 0.47 (HC), 0.47 (HC+ Fenton). It is observed that the major peaks of $MCPEG_2$ (m/z=216.96: PI=100%, m/z=226.99: PI=40%) which had highest peak intensity (PI) in raw TWE was considerably reduced to less than 30% after HC + Fenton treatment. Similarly, major peak of Nitro BS or NPS (m/z=80.9774: PI=70%) in raw TWE was reduced to less than 30% after HC + Fenton treatment. Other prominent peaks of NPS (m/z=206.93: PI=35%), DBP (m/z=256.86:PI=30%) present in raw TWE and HC treated samples have completely disappeared in HC + Fenton indicating that it has been completely degraded forming lower intermediates. Moreover PEG_2 (m/z=101.04: PI=28%) of lower atomic mass were formed by HC from its higher forms (PEG_4). However, new peaks were also observed in MS spectra of HC treated sample as well as HC + Fenton treated samples indicating the formation of newer intermediates or low molecular mass organic compounds.

Fig. 4.12 presents the comparison of MS spectra at retention time of 5.43(RAW), 5.36(HC), 5.26 (HC +Fenton). The major peaks of DCPEG (m/z=566.45: PI=100%) which had highest intensity in raw TWE and HC treated samples was considerably reduced to 50% after HC + Fenton treatment. However, the peak intensity of DCPEG (m/z=566.45, 567.45) remained unchanged after HC treatment indicating that, only HC is not effective for degradation in case of treatment of large organic molecules. The major peak of 4-chloro-n-cresol (m/z=141.99: PI=50-90%) and 1-hydroxy-4-NPS (m/z=159.01: PI=20-30%) in raw TWE and HC treated samples was considerably reduced after HC + Fenton treatment. The peaks of NPEO and ALs (m/z=132.99: PI=30%), present in raw TWE have been reduced to less than 20% after HC and HC+ Fenton process. In case of MS spectra of HC + Fenton a significant decrease in peak intensities as well as formation of intermediates was observed with new peaks (m/z=397.83: PI=100%; m/z=397.83-418.82: PI=50-100%) indicating breakage of large molecules. Reduction in peak intensities as well as the emergence of new peaks and disappearance of the peaks present in the case of raw sample can be attributed to the degradation of the larger carbon chain molecules to smaller molecules during cavitation as well as in the hybrid process.

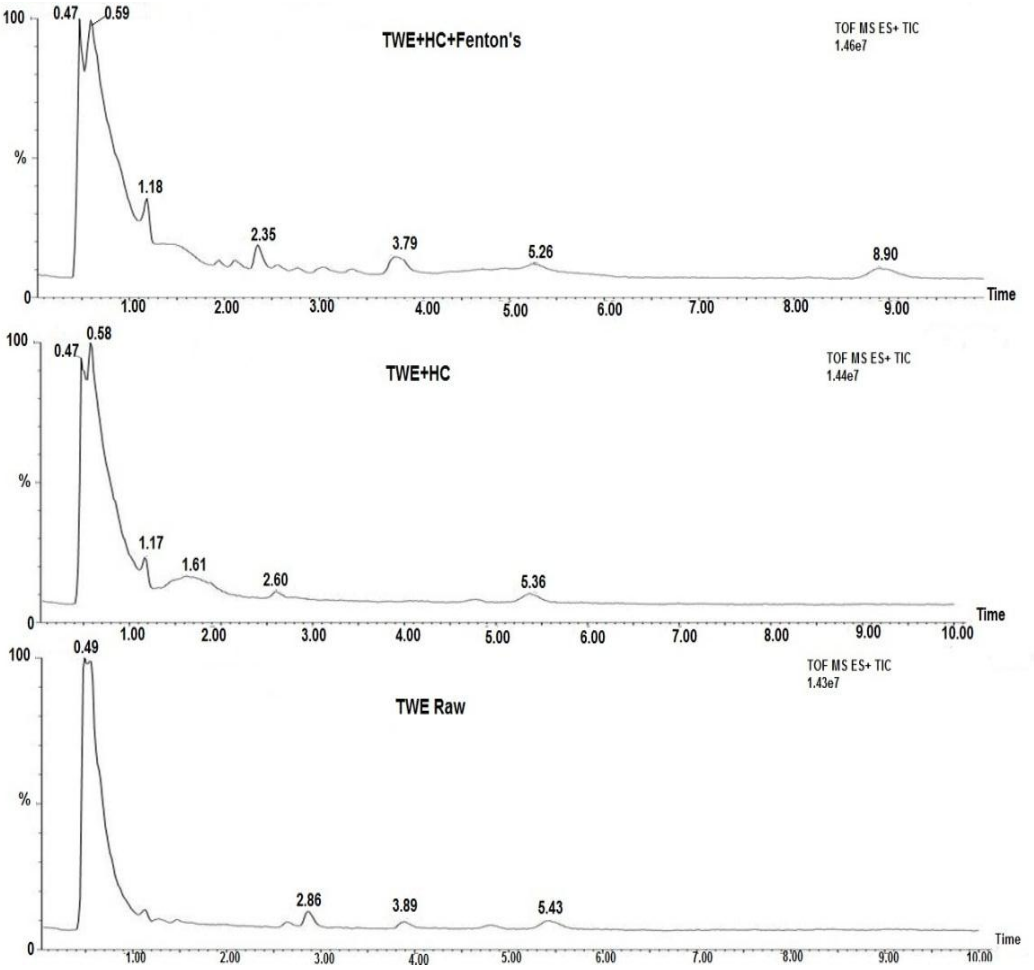


Fig. 4.10 LC-MS chromatogram of raw TWE, HC treated TWE and HC + Fenton's treated TWE sample

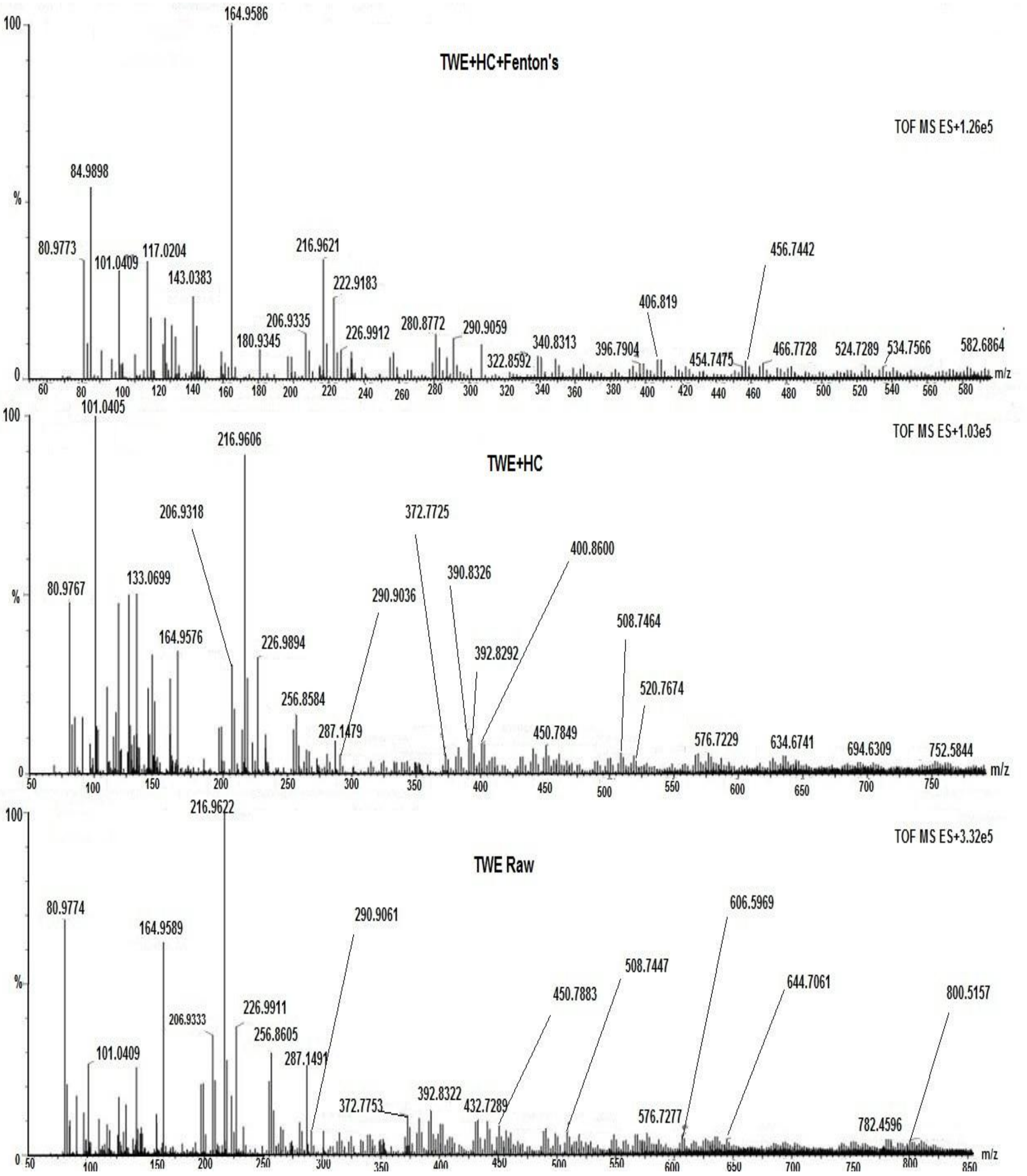


Fig. 4.11 LC-MS of raw TWE, HC treated TWE, and HC + Fenton's treated TWE for retention time 0.49, 0.47 and 0.47 respectively

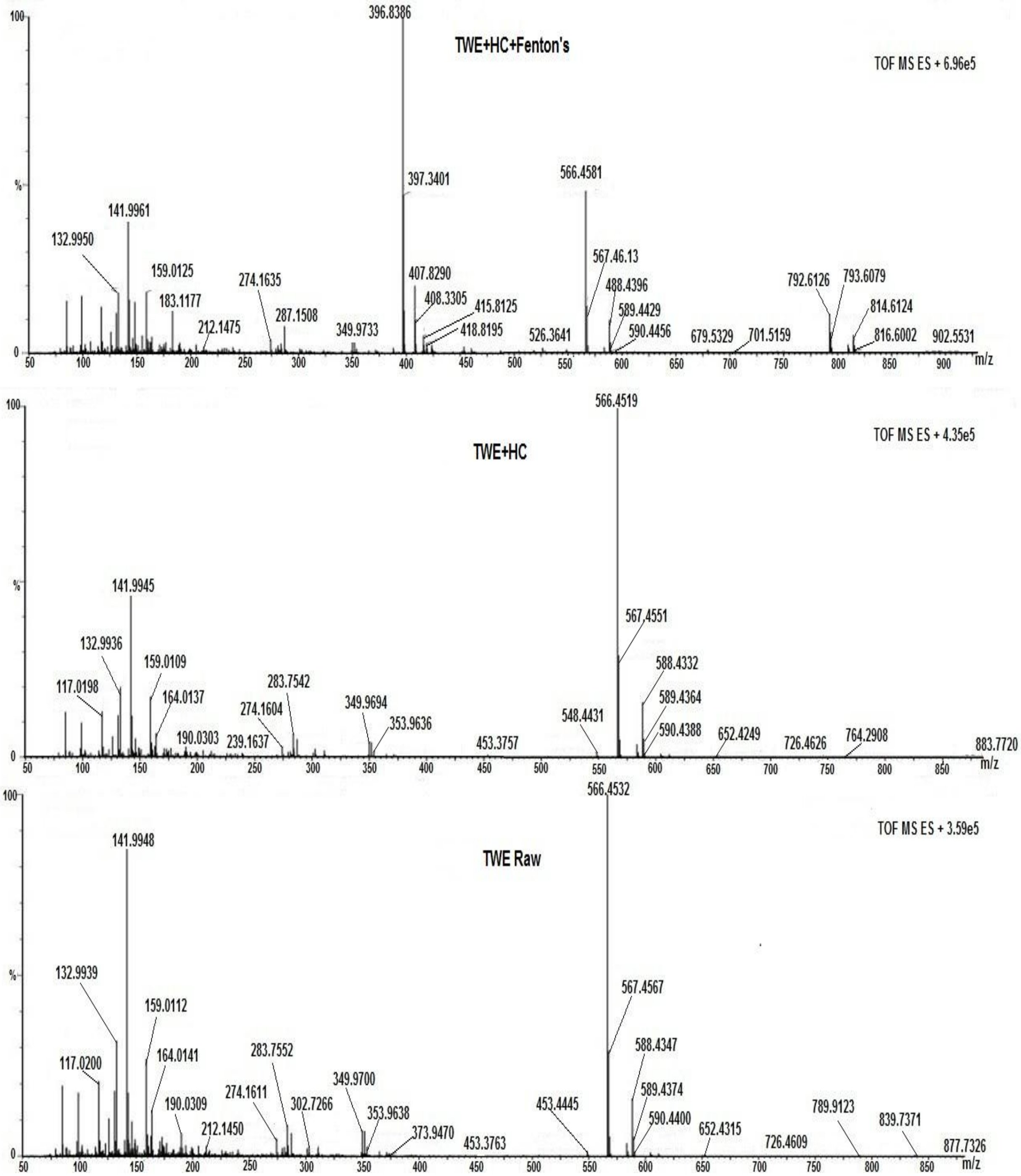


Fig. 4.12 LC-MS of raw TWE, HC treated TWE, and HC + Fenton's treated TWE for retention time 5.43, 5.36 and 5.26 respectively

Table 4.9 Identified compounds in raw TWE, HC treated TWE and HC + Fenton's treated TWE at their retention time of 0.49, 0.47, 0.47 min respectively using LC-MS

Probable Compounds	**m/z**		
	Raw TWE (0.49)	**HC (0.47)**	**HC + Fenton (0.47)**
Nitro BS, 1-amino- 7- NPS, 2 NPS	80.9774	80.9767	80.9773, 84.9898
PEG$_2$	101.0409	101.0405	101.0409
4- Chloro-m-cresol, 2-NPS, MCPEG$_2$	164.9589	164.9576	143.0383, 164.9586 , 180.9345
2-NPS	206.9333	206.9318	206.9335
MCPEG$_2$	216.9622, 226.9911	216.9606, 226.9894	216.9621, 222.9183, 226.9912
DBP	256.8605	256.8584	
NPEO$_9$, PG$_4$, MCPEG$_4$, DEHP	287.1491, 290.9061	287.1479, 290.9036	290.9059, 280.8772
PEG$_4$, MCPEG$_6$, AL$_{12,4}$			322.8592, 340.8313
MCPEG$_6$, AEO$_{10}$, AL$_{12,4}$, AL$_{13,4}$	372.7753	372.7725	
MCPEG$_8$, AL$_{3,8}$, NPE$_9$, DCPEG$_7$, AEO$_{10}$, AL$_{13,4}$, AL$_{14,4}$	392.8322, 432.7289, 450.7883	390.8326, 392.8292, 400.8600, 450.7849	396.7904, 406.8196, 454.7475, 456.7442, 466.7728
DCPEG$_9$	508.7447	508.7404, 520.7574	524.7289,534.7566
AL$_{4,8}$	576.7277, 606.5969, 644.7061	576.7229, 634.6309	582.6864
MCPEG, NPEO	782.4596, 800.5157	694.6309, 752.5844	

Table 4.10 Identified compounds in raw TWE, HC treated TWE and HC + Fenton's treated TWE at their retention time 5.43, 5.36, 5.26 min respectively using LC-MS

Probable compounds	**m/z**		
	Raw TWE (5.43)	**HC (5.36)**	**HC + Fenton (5.26)**
PEG$_2$, MCPEG$_6$, AEO$_{10}$, AL$_{3,8}$, AL$_{13,4}$, AL$_{14,4}$, NPEO$_9$	132.9939	132.9936	132.9950
4-chloro-n-cresol	141.9948	141.9945	141.9961
1-hydroxy-4-NPS	159.0112	159.0109	159.0125
MCPEG$_2$	164.0141, 190.0309, 212.1450	164.0137, 190.0303	183.1177 , 212.1475
MTBT	274.1611	274.1604	274.1635
PEG$_4$, MCPEG$_6$, AL$_{12,4}$	283.7552, 302.7286, 349.9700, 353.9638, 373.9470	283.7542, 349.9694, 353.9636	287.1508, 349.9733
PEG$_4$, MCPEG$_8$, AL$_{3,8}$, AEO$_{10}$, NPE$_9$, DCPEG$_7$			396.8386, 397.3401, 407.8290, 408.3305, 415.8125
MCPEG$_8$, DCPEG$_7$, AL$_{3,8}$, NPE$_9$, AEO$_{10}$,	453.3763	453.3757	418.8195
DCPEG$_9$, AL$_{4,8}$	548.4445, 566.4532, 567.4567, 588.4347, 589.4374, 590.4400	548.4431,566.4519, 567.4551,588.4332, 589.4364, 590.4388	526.3641, 566.4581, 567.4613, 588.4396, 589.4429, 590.4456
NPEO$_9$	652.4315	652.4249	
MCPEG, NPEO	726.4609, 789.9123, 839.7371, 877.7235	726.4626, 764.2908, 883.7720	679.5329, 701.5159, 792.6126, 793.6079, 814.6124, 816.6002, 902.5531
Note: PEG-Polyethylene glycols, MCPEG-Monocarboxylated polyethylene glycol, DCPEG-Dicarboxylated polyethylene glycol, oxoethylate, AL-Alcohol ethoxylated surfactants, NPEO-Nonyl Phenol Polyethoxylated surfactants, NP-nitrophenol, DEHP-diethylphthalate DBP -bis 2-ethylhexylphthalate, MTBT-2- (Methylthio)benzothiazole			

4.4.9 Energy efficiency and cost estimations:

The cost of the treatment in HC, HC + H_2O_2 and HC + Fenton's process, is principally the operating cost of the pump in the HC reactor setup for recirculating the TWE, operating at the optimum conditions of inlet pressure and volumetric flow rate for fully effective cavitation. In case of HC + O_3, additional energy was required by the ozonator which supplied O_3 at the throat section during the cavitation. Energy efficiency evaluations of HC and HC based oxidation methods have been done on the basis of the amount of COD degraded (in mg) per unit power delivered in to the system (kWh). The total treatment time was taken 120 min for all processes to evaluate the energy efficiency. The energy efficiency and cost estimations are provided in Appendix C (page no. 198). The energy required as well as the cost estimations for the reduction of one mg of COD (kWh/mg) for HC and hybrid HC based oxidation processes are summarized in Table 4.11. The cost estimation for the chemicals consumed was carried out on the basis of commercial grade prices. The net energy required for the reduction of one mg of COD of TWE was 0.0016 kWh/mg with HC alone. It was observed that when HC alone was used for TWE treatment, the treatment cost is 0.042 USD/L and the cost for the reduction of unit mg of COD of TWE was 0.00021 USD/mg. It was observed that for the hybrid techniques, i.e. for HC in combination with advanced oxidation processes the cost is lowered as the quantum of COD reduced is higher than using HC process alone. From Table 4.11, it can be observed that maximum energy efficiency was observed in HC + Fenton's process with maximum COD reduction. The energy requirement was minimum at 0.0004 kWh/mg of COD reduced and treatment cost at 0.00009 USD/mg of COD removed for HC + Fenton's process. Hence, HC + Fenton's process may be considered as most energy efficient approach for the treatment of TWE. In case of these HC hybrid processes, the high synergism of cavitational processes with advanced oxidation agents bring higher effectiveness in the oxidation of organic contaminants causing an increase in the effectiveness of treatment.

Table 4.11 Energy efficiency and cost estimations

Process	Quantum of COD reduction (mg)	Energy required for the reduction of one mg of COD in kWh/mg	Cost of the treatment for the reduction of one mg of COD in Rs/mg	Equivalent Cost of treatment for the reduction of one mg of COD in USD/mg (1USD=68.04INR(Rs) as on 22/05/2018)
HC	1400	0.0016	0.0141	0.00021
HC + Ozone	2660	0.0011	0.0095	0.00014
HC + Hydrogen peroxide	3140	0.0007	0.0089	0.00013
HC + Fenton's reagent	4900	0.0004	0.0061	0.00009

4.4.10 Comparison between HC and US based hybrid oxidation processes based on cavitational yield

Energy efficiency in terms of cavitational yield was also evaluated for the experimental setups on the basis of quantum of COD reduction. Cavitational yield can be described as

$$Cavitational\ yield\ = \frac{Quantum\ of\ COD\ reduced}{Power\ supplied\ to\ the\ system} \times Volume\ treated$$

$$= \frac{[COD]}{P_E \times t} \times V$$

Where, [COD] = quantum of COD reduced, P_E = power of the system (experimental setup), t = treatment time, V = volume of waste sample treated.

A comparison between HC and US based hybrid treatment approaches on the basis of cavitational yield was carried out and data are presented in Table 4.12. It was observed that in the case of HC, the cavitational yield was 4454.54 mgL/kWh which was 20 times higher than the cavitational yield of US which was 216 mgL/kWh. Further the cavitational yield of US based hybrid processes was increased due to the enhanced generation of hydroxyl radicals and maximum yield of 444 mgL/kWh was observed in the case of US + NaOCl. However, the cavitation yield of HC based hybrid processes were found to be higher than the US based hybrid processes. Among all the combinations studied, it was observed that a maximum 15590.9 mgL/kWh cavitational yield was observed in HC + Fenton system which was 3.5 times higher than the HC system alone. On the basis of cavitational yield it was observed that US and US based hybrid treatment techniques had very low cavitational yield compared to the HC and HC based hybrid methods which restrict their uses at large scale. On the other hand HC and HC based hybrid treatment techniques had high cavitational yield which is strongly advocating their uses at large scale applications

Table 4.12 Comparison between HC and US based hybrid oxidation processes based on cavitational yield

Treatment methodology	**Quantum of COD reduced (mg)**	**Power supplied to the system (kWh)**	**Volume treated (L)**	**Cavitational yield (mg×L/kWh)**
HC	1400	2.2	7	4454.54
HC + ozone	2660	2.8	7	6650.0
HC + H_2O_2	3140	2.2	7	9990.9
HC + Fenton	4900	2.2	7	15590.9
US	1080	1.5	0.3	216.0
US + ozone	2040	2.1	0.3	291.43
US + NaOCl	2220	1.5	0.3	444.0

4.5 Summary of the chapter

Hybrid methods combining HC with advanced oxidation processes such as O_3, H_2O_2 and Fenton's reagent were studied for the degradation of organic pollutants presents in TWE and evaluated for their synergistic process efficiencies. The important outcomes drawn from present study can be summarized as follows

- Treatment of TWE with HC alone at the optimum pressure of 500 kPa within 120 minutes produced a maximum reduction of 14.46% COD and 12.6% TOC. It also caused a reduction in TDS and TSS of the samples as well as an increase in BI value from 0.33 to 0.43 indicating that its biodegradability has increased due to the breaking down of the more recalcitrant organic molecules into biologically degradable compounds.
- Dilution of the samples did not enhance the HC degradation efficiency and therefore was not feasible as it only increases the operational treatment costs due to the requirement of treatment of larger volumes.

- HC when combined with ozonation exhibited favorable synergistic effect with enhanced reduction of organic pollutants due to the increase in generation of hydroxyl radicals. An increase in COD and TOC reduction was observed at 26.81% and 17.96% respectively with their degradation rate constants at 0.0033 min^{-1} and 0.0018 min^{-1} respectively at the optimum O_3 loading of 7 g/h with HC. However, the increase in BI value was found to be the same for treatment by HC alone as well as for HC combined with O_3. Higher O_3 dosing was not favorable as it reduced the degradation efficiencies due to the recombination reactions which may have taken place in presence of formation of excess hydroxyl radicals.
- HC in combination with H_2O_2 also significantly enhanced the efficiency of HC and 34.35% COD and 19.71% TOC reduction was observed in this combined treatment approach.
- However, the maximum BOD, COD, TSS reduction was observed in case of the hybrid HC+ Fenton process in which the consumption of H_2O_2 was also lesser compared to HC + H_2O_2 process at the rate of 1.95 g/g of COD and 11.89 g/g of TOC reduction. Whereas the consumption of H_2O_2 per g of COD and TOC reduction in the case of HC + H_2O_2 was 3.02 g/g and 20.32 g/g respectively at optimized conditions.
- FTIR and LCMS of untreated and treated TWE showed the presence of alcohols, phenols, fatty acids, amines, poly saccharides and aromatic compounds. The FTIR spectrum of the HC, HC+ H_2O_2 and HC + Fenton treated samples showed presence of dissolved carbon dioxide and low molecular compounds such as carboxylic compounds, carbonates, etc., whereas the LCMS spectra indicated decrease in peak intensities, as well presence of additional significant peaks in the chromatogram. This is indicative of the effectiveness of hybrid processes in mineralization of the organic components in TWE when subjected to the hybrid cavitation processes.
- Hybrid HC + Fenton shows the highest synergetic energy efficiency and cost effectiveness than HC and other hybrid processes".

The above hybrid treatment techniques of using HC in combination with three oxidation agents i.e. O_3, H_2O_2 and Fenton's reagent provided intensified treatments with higher degradation efficiencies and an increase in the BI, making the treated water more suitable for biological treatment. The high mineralization of tannery waste resulting in high BI value makes it favorable to be further used in anaerobic treatment process, which will produce methane as a byproduct to be used as an energy source for different plant processes. Therefore, hybrid HC oxidation method, considered as clean technology can be combined with AD as a pretreatment tool. The efficacy of HC pretreated TWE for production of biogas along with COD reduction by subjecting to batch AD is evaluated and presented in next chapter.

CHAPTER 5

Modeling & Simulation Studies on Batch Anaerobic Digestion (AD) of Hydrodynamically Cavitated Tannery Waste Effluent (TWE)

5.1 Introduction

Our previous study reported HC as a pretreatment strategy which enhanced the BI of TWE by breaking down the bio-refractory molecules into more biodegradable molecules. In this work, the real industrial TWE has been pretreated using the advanced HC technique followed by AD which has been studied for the first time and the primary aim was to evaluate the performance of AD using HC treated TWE as the substrate for higher biogas yield in comparison to raw TWE. Performance of anaerobic digesters of both small and larger volume was experimentally studied using raw as well as HC treated TWE and biogas generation along with COD reduction in substrate was analyzed. Effect of seed concentration and organic loading on biogas generation was studied. Mathematical models were developed differentiating the AD performance with respect to two different feeds i.e. raw and HC treated TWE and the effect of model parameters studied in the propagation of the various degradation reactions as well as for predictions of long term performance of the digester for varying feeds. The effect on the enhancement of biogas production by adding food waste to the HC treated TWE has been studied for evaluating its applicability for industrial applications.

5.2 Material and methods

5.2.1 Tannery waste water and anaerobic seed microorganisms for digestion:

The raw and HC pretreated TWE were characterized by measuring the COD, BOD, TS, VS, pH, BI etc. and the values are given in Table 5.1. TWE was stored in a deep freezer and allowed to reach ambient temperature before conducting the experimental studies. The elemental composition of the TWE sludge and HC treated TWE sludge was analyzed on dry weight basis by CHNS/O analysis using CHNS (O) analyzer (Make: Thermo Finnigan, Italy) and values are presented in Table 5.2. In the process of AD of TWE and HC treated TWE, anaerobic seed (5-20% by volume of TWE slurry) was added which was collected from the sewage treatment plant working under anaerobic conditions located at Pratap Nagar, Jaipur. It was used for the acclimatization of TWE and HC treated TWE for AD. Further in order to increase the biogas yield, AD was carried out by mixing TWE with mixed cereal based food waste collected from the Institute canteen of MNIT Jaipur. In order to keep the quality of the food waste constant throughout the experiments and to prevent its deterioration, it was initially cooked and ground using a mixer-grinder, freeze dried in a freeze dryer (-86°C) and stored in powder form in a cool dry place for further use. Its elemental composition was also analyzed for CHNS (O) and is presented in Table 5.2 along with the volatile solid content of the dried food waste sample.

Table 5.1 TWE characteristics

Parameter	**Raw TWE**	**HC treated TWE (At 5 bar for 2 hr.)**
pH	7.5-8.14	7.6-8.22
COD (mg/L)	8400-10080	7520-8320
TS (mg/L)	18850-20650	16250-18350
VS (mg/L)	4650-5250	4550-4900
BOD (mg/L)	2600-3000	3000-3600
BI	0.28-0.33	0.40-0.43

Table 5.2 CHNSO analysis of raw and HC treated TWE (dry weight basis)

Effluent	**C**	**H**	**O**	**N**	**VS**
TWE	10.259	1.528	11	0.4	VS = 5.1 g/L
HC treated TWE	10.184	1.592	9.9	0.571	VS = 4.8 g/L
Food waste (dry basis)	43.968	8.027	37.5591	3.845	0.25g/g

5.2.2 Chemicals:

All the chemicals used in the present study were purchased from Lobachemie, India. These chemicals were of analytical grade (AR) and used as received from suppliers without any further purification. The chemicals used in COD analysis were concentrated sulfuric acid (98%), ferrous ammonium sulfate (99%), silver sulfate (99%), potassium dichromate (99.5%), mercuric sulfate (98%) and ferroin indicator (0.025 M). BOD analysis was carried out using manganous sulfate (99%), sodium thiosulfate (99.5%), sodium iodide (99.5%), sodium hydroxide (98%), starch, dipotassium hydrogen orthophosphate (99%), potassium dihydrogen phosphate (99.5%), disodium hydrogen phosphate (99%), calcium chloride (99%), ammonium chloride (99.8%), ferric chloride (99%) and magnesium sulfate (99.5%). Double distilled water was used in all the analysis. Solution pH was adjusted using 1N solutions of sodium hydroxide (98%) and sulfuric acid (98%).

5.2.3 Analytical methods

The parameters such as COD, BOD, TS, VS etc. that characterize the TWE sample was carried out as per the standard APHA methods (1998). A pH meter (Thermo scientific, USA) was used to determine the pH of the solution during and after the experiments. An oven (Make: DAIHAN Scientific Co. Ltd.) was used for drying the TWE during the TS and VS analysis. All analysis was repeated twice and reported values are the average of two analytical values. VFA and alkalinity were measured using standard titration methods (Buchauer, 1998). Centrifuge (Make: REMI Equipment, India) was used to remove the suspended particulate matter present in TWE samples during the soluble chemical oxygen demand (SCOD) analysis. BOD incubator (Make: REMI Equipment, India) was used in BOD analysis and also used for maintaining the temperature during anaerobic treatment of TWE in small flasks. The amount of biogas generated during the AD was measured using water displacement method. GC (Trace 1110 Thermo scientific, India) was used for the biogas analysis, equipped with Porapak Q 80/100 mesh column using Thermal conductivity detector (TCD) and nitrogen as the carrier gas. The calibration of GC for biogas analysis was done using single point calibration with standard mixture of biogas elements (methane 60%, carbon dioxide 35%, and hydrogen sulfide 5%).

5.2.4 Experimental setup and Methodology

5.2.4.1 Pretreatment of TWE using Hydrodynamic cavitation:

In our recent reported study [S. Saxena, Saharan, and George 2018] HC was used in the pretreatment of TWE for increasing its biodegradability index (BOD: COD) at the optimized conditions of inlet pressure (5 bar) and time (120 minutes). The HC reactor setup that was used in this study has also been reported by our research group in our earlier study (Rajoriya et al., 2018; Saxena et al., 2018a). The HC reactor setup was operated in a closed loop circuit and the TWE solution was pumped through the cavitating device which was a slit venturi using high pressure piston pump from a storage tank of capacity of 20 L. 7 liters of TWE solution was pretreated at conditions of 5 bar pressure for 120 minutes while the solution temperature was maintained at 30±1°C by using a cooling jacket surrounding the reactor. The flow rate as well as the inlet pressure was maintained by regulating the pump speed using a variable frequency drive (VFD).

5.2.4.2 Anaerobic digestion and Biogas potential test:

The TWE and HC pretreated TWE samples were subjected to AD in batch reactors carried out for two different sample volumes; i.e. for smaller volume of 200 mL and larger volume of 2L. Total 12 Teflon bottles (6 bottles per sample) of 250 mL capacity were filled with 200 ml of sample mixed with anaerobic seed (10% volume) and placed in an incubator at a temperature of 37± 0.2°C. The acclimatization time for the raw and HC treated TWE was about 32-35 days and 20- 23 days respectively after which the biogas generation started. The reduction in COD, VFA content of the digested TWE samples as well as the biogas generation was monitored for more than 30 days, by regular analysis in an interval of 5 days. In order to study the scale up potential of the aforementioned study as well as the effect of seed dosage, AD was also carried out in a larger glass bio-reactor (capacity 2.5 L) with 2 L of working volume and varying the percentage of seed (5%, 10% and 20%) in the HC treated TWE feed. The schematic flow diagram of the batch AD system is presented in Fig. 5.1. The glass bioreactors were provided with the cooling jacket in order to maintain the reactor temperature at 37± 0.2°C. Three different glass bioreactors (one for each sample) were used in this study and very small amount of sample was withdrawn from the sample port in a fixed interval of 5 days for analysis of COD and VFA content.

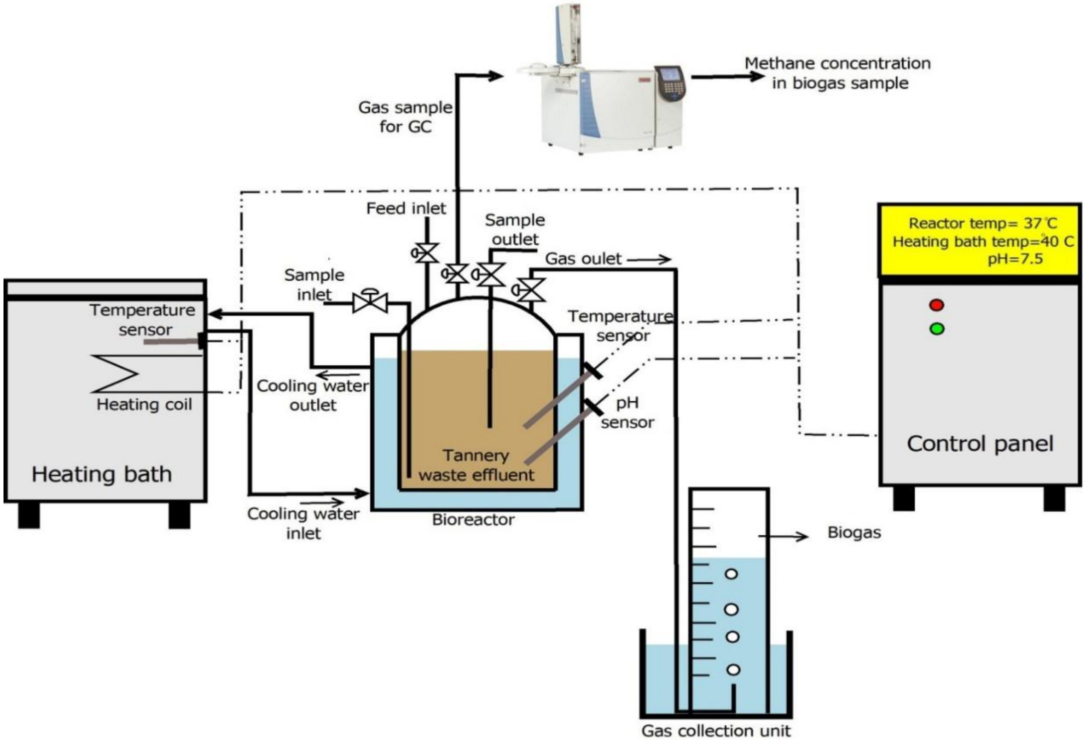


Fig. 5.1 Schematic flow diagram of batch AD system

The slow rate of degradation as well as the long acclimatization time required for the digestion of TWE was the limitation of this process. Therefore, in order to increase the biogas generation, further AD was carried out in a semi-batch mode where food waste was added at regular intervals in the bioreactor feed. The composition of feed in the bioreactors were kept same for raw TWE and HC pretreated TWE with 10% seed and AD was carried out under constant temperature of 37±0.2°C using cooling jacket. Once the biogas production started, 50 mL of sample with 10% (5 g in 50 ml) food waste was loaded in the respective bioreactors at an interval of 48 h / 24 h while maintaining a constant substrate volume. 50 mL of samples were withdrawn from the bioreactors from respective sampling port and analyzed for their SCOD, VFA and pH. The methane and carbon dioxide concentrations in the generated biogas which also contained small amounts of H_2S, H_2 and NH_3 were analyzed using GC.

5.2.5 Mathematical modeling of batch anaerobic digestion of TWE:

The mathematical model describing the basic mechanism of batch AD was developed so as to investigate the differences in the rate kinetics as well as the biogas/ methane yield during the digestion of TWE and HC treated TWE. The bacterial digestion process in AD is initiated with the hydrolysis/ dissociation of the complex biomass (organic polymers) in TWE into its simpler forms (organic monomers) that occur outside the cell by the extracellular enzymes secreted by the bacterial population and this reaction mostly follows first order kinetics represented by a hydrolysis rate constant (k). The mixed consortia of microorganisms in the TWE mixed with sewage seed consisted of five groups of bacteria namely organic monomer degrading acidogens (X_1), propionate degrading acetogens (X_2), butyrate degrading acetogens (X_3), acetoclastic methanogens (X_4), and hydrogenotrophic methanogens (X_5). Therefore, the batch AD model consisted of basically five bacterial reactions such as acidogenesis, acetogenesis, butyrate degrading acetogenesis, acetoclastic methanogenesis and hydrogenotrophic methanogenesis and the various inhibitory reactions. The schematic of the mass flow throughout the AD process i.e. the concentration of the organic polymers (S_0) which initially dissociate into organic monomers (S_1) and further through the various bacterial reactions to form the various products such as propionate (S_2), butyrate (S_3) acetate (S_4), hydrogen (S_5), carbon dioxide (S_6) and methane (S_7) as well as the path of inhibition is shown in Fig. 5.2.

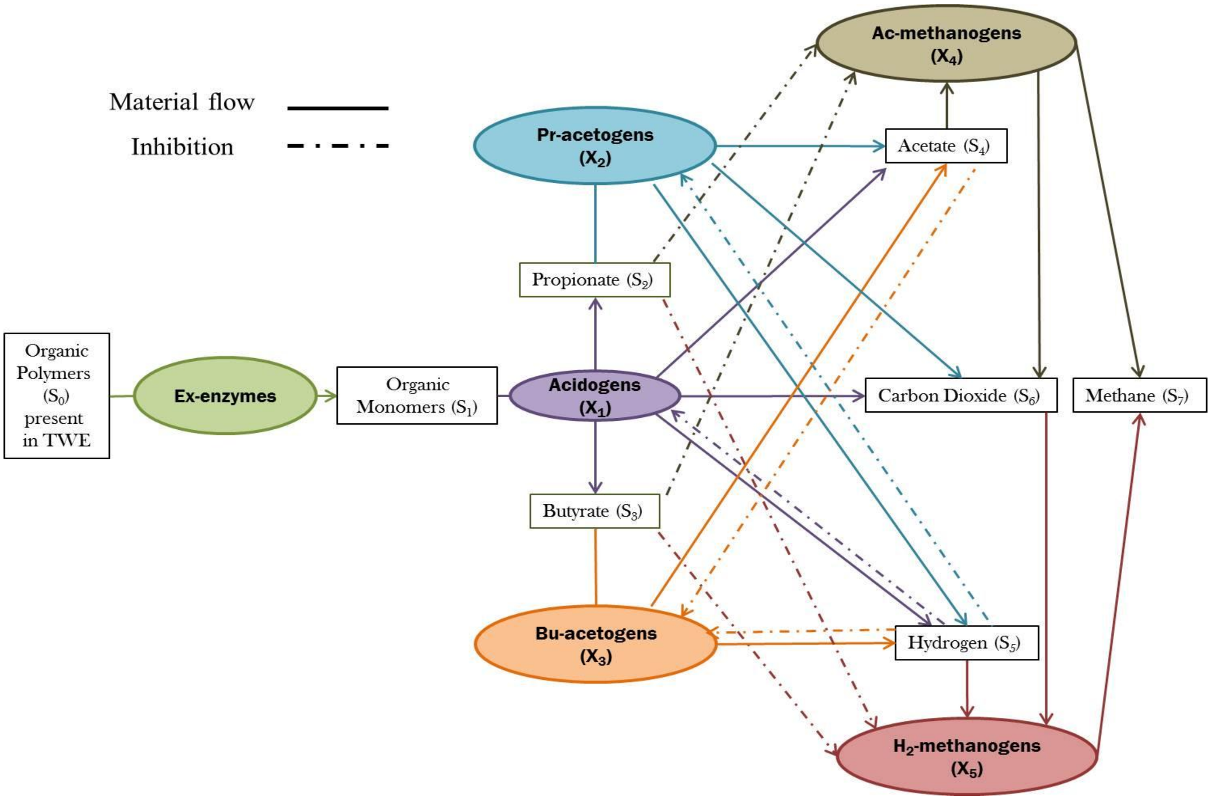


Fig. 5.2 Outline of batch AD model

The model also considered the hydrogen inhibition in acidogenic and acetogenic step, acetate inhibition in butyrate degrading step, inhibition initiated by intermediate products in the methanogenic step as well as the bacterial decay due to the longer digestion period.

5.2.5.1 Stoichiometric reaction equations and material balances

The reaction stoichiometry for all degradation reactions except for acidogenesis were taken as per the standard reactions reported for waste degradation of organic matter (Choi et al., 2003). The reaction stoichiometry for the acidogenesis reaction was determined from stoichiometric balances. The CHNS/O analysis of the dry tannery waste matter carried out for raw TWE and HC treated TWE determined the cell mass or nature of the organic monomer of TWE and HC treated TWE which was represented by $\mathbf{C_{0.855}H_{1.528}O_{0.688}N_{0.0286}}$ and $\mathbf{C_{0.849}H_{1.59}O_{0.619}N_{0.041}}$ respectively. The organic monomers dissociated into propionates($\mathbf{C_3H_6O_2}$), butyrates ($\mathbf{C_4H_8O_2}$) and acetates ($\mathbf{C_2H_4O_2}$) which form the VFA content. The stochiometric reactions for all the steps that occur in the anerobic digestion process are represented by Eq.'s 1 to12.

Acidogenesis (Raw TWE):

$$\begin{aligned}C_{0.855}H_{1.528}O_{0.688}N_{0.0286}+0.114H_2O\rightarrow 0.114C_2H_4O_2+0.064C_3H_6O_2+0.071C_4H_8O_2\\ +0.131H_2+0.152CO_2+0.0286NH_3\end{aligned} \tag{1}$$

$$C_{0.855}H_{1.528}O_{0.688}N_{0.0286}+0.1424NH_3\rightarrow 0.171C_5H_9O_3N+0.0331H_2+0.175H_2O \tag{2}$$

Acidogenesis (HC treated TWE)

$$\begin{aligned}C_{0.849}H_{1.59}O_{0.619}N_{0.041}+0.179H_2O\rightarrow 0.114C_2H_4O_2+0.064C_3H_6O_2+0.069C_4H_8O_2\\ +0.218H_2+0.152CO_2+0.041NH_3\end{aligned} \tag{3}$$

$$C_{0.849}H_{1.59}O_{0.619}N_{0.041}+0.1288NH_3\rightarrow 0.1698C_5H_9O_3N+0.1145H_2+0.1096H_2O \tag{4}$$

Propionate acetogenesis

$$C_2H_5COOH+2H_2O\rightarrow CH_3COOH+CO_2+3H_2 \tag{5}$$

$$C_2H_5COOH+0.6NH_3\rightarrow 0.6C_5H_9O_3N+H_2+0.2H_2O \tag{6}$$

Butyrate acetogenesis

$$C_3H_7COOH+2H_2O\rightarrow 2CH_3COOH+2H_2 \tag{7}$$

$$C_3H_7COOH+0.8NH_3+0.4H_2O\rightarrow 0.8C_5H_9O_3N+2H_2 \tag{8}$$

Acetoclastic methanogenesis

$$CH_3COOH\rightarrow CH_4+CO_2 \tag{9}$$

$$CH_3COOH+0.4NH_3\rightarrow 0.4C_5H_9O_3N+0.8H_2O \tag{10}$$

Hydrogenotrophic methanogenesis

$$H_2+0.25CO_2\rightarrow 0.25CH_4+0.5H_2O \tag{11}$$

$$H_2+0.5CO_2+0.1NH_3\rightarrow 0.1C_5H_9O_3N+0.7H_2O \tag{12}$$

The Monod growth kinetics model was used to represent the bacterial growth kinetics in presence of the inhibitory factor due to the presence of various inhibitory components and therefore the specific growth rate is given by Eq.13.

$$\mu_j = \frac{\mu_{m,j} \times S_i}{F(I_g) \times \left(K_{s,j} \times F(I_{g'}) + S_i\right)} \tag{13}$$

Where $K_{S,j}$ and S_i are the Monod saturation constant (mM) and substrate concentration (mM) respectively. $F(I_{g'})$ is the competitive inhibition function and only acetate inhibition in butyrate degrading step is estimated by competitive inhibition function (Denac et al., 1988), whereas $F(I_g)$ is noncompetitive inhibition function for all other inhibitions approximated by noncompetitive kinetics. Specific growth rates for different bacterial growth considered in the model are calculated using Monod kinetics according to Eq.'s 14 to 18. Material balances for the various bacterial groups (X_1 to X_5) as well as the substrates (S_0 to S_7) are represented by Eq.'s 19 to 23 and Eq.'s 24 to 33 respectively. Due to difference in the rates during AD, all the products formed are coupled to biomass yield and the substrate consumption for bacterial growth maintenance has been merged with overall biomass yield, considering first order kinetics for bacterial decay.

$$\mu_1 = \frac{\mu_{m,1} \times S_1}{K_{S,1} + S_1} \times \frac{1}{1 + \frac{S_5}{K_{1,1}}} \tag{14}$$

$$\mu_2 = \frac{\mu_{m,2} \times S_2}{K_{S,2} + S_2} \times \frac{1}{1 + \frac{S_5}{K_{1,2}}} \tag{15}$$

$$\mu_3 = \frac{\mu_{m,3} \times S_3}{K_{S,3} + (\ 1 + \frac{S_4}{K_{1,3}}\ )} \times \frac{1}{1 + \frac{S_5}{K_{1,4}}} \tag{16}$$

$$\mu_4 = \frac{\mu_{m,4} \times S_4}{K_{S,4} + S_4} \times \frac{1}{1 + \frac{S_3}{K_{1,6}}} \times \frac{1}{1 + \frac{S_4}{K_{1,5}}} \tag{17}$$

$$\mu_5 = \frac{\mu_{m,5} \times S_5 \times S_6}{(K_{S,5} + S_5)\ (K_{S.6} + \ S_6)} \times \frac{1}{1 + \frac{S_3}{K_{1,8}}} \times \frac{1}{1 + \frac{S_2}{K_{1,7}}} \tag{18}$$

Material balance equations for bacterial groups:

Acidogens (X_1):

$$\frac{dX_1}{dt} = \mu_1 X_1 - \ b_1 X_1 \tag{19}$$

Propionate degrading acidogens (X_2):

$$\frac{dX_2}{dt} = \mu_2 X_2 - b_2 X_2 \tag{20}$$

Butyrate degrading Acidogens (X_3):

$$\frac{dX_3}{dt} = \mu_3 X_3 - b_3 X_3 \tag{21}$$

Acetoclastic methanogens (X_4):

$$\frac{dX_4}{dt} = \mu_4 X_4 - b_4 X_4 \tag{22}$$

Hydrogenotrophic methanogens (X_5):

$$\frac{dX_5}{dt} = \mu_5 X_5 - b_5 X_5 \tag{23}$$

Material balance equations for substrate:

Tannery waste (S_0):

$$\frac{dS_0}{dt} = -KS_0 \tag{24}$$

Organic monomers (S1):

$$\frac{dS_1}{dt} = -\frac{\mu_1}{Y_1} X_1 + KS_0 \tag{25}$$

Propionate (S2):

$$\frac{dS_2}{dt} = 0.064(1 - f_1 Y_1)\frac{\mu_1}{Y_1} X_1 - \frac{\mu_2}{Y_2} X_2 \tag{26}$$

Butyrate (S3):

$$\frac{dS_3}{dt} = 0.069(1 - f_1 Y_1)\frac{\mu_1}{Y_1} X_1 - \frac{\mu_3}{Y_3} X_3 \quad \text{(HC treated TWE)} \tag{27}$$

$$\frac{dS_3}{dt} = 0.071(1 - f_1 Y_1)\frac{\mu_1}{Y_1} X_1 - \frac{\mu_3}{Y_3} X_3 \quad \text{(Raw TWE)} \tag{28}$$

Acetate (S4):

$$\frac{dS_4}{dt} = 0.114(\,1 - f_1Y_1)\frac{\mu_1}{Y_1}X_1 + (1 - f_2Y_2)\frac{\mu_2}{Y_2}X_2 + 2(1 - f_3Y_3)\frac{\mu_3}{Y_3}X_3 - \frac{\mu_4}{Y_4}X_4 \qquad (29)$$

Hydrogen (S5):

$$\frac{dS_5}{dt} = 0.218(\,1 - f_1Y_1)\frac{\mu_1}{Y_1}X_1 + 3(1 - f_2Y_2)\frac{\mu_2}{Y_2}X_2 + 2(1 - f_3Y_3)\frac{\mu_3}{Y_3}X_3 - \frac{\mu_5}{Y_5}X_5 \text{ (HC treatedTWE)} \qquad (30)$$

$$\frac{dS_5}{dt} = 0.131(\,1 - f_1Y_1)\frac{\mu_1}{Y_1}X_1 + 3(1 - f_2Y_2)\frac{\mu_2}{Y_2}X_2 + 2(1 - f_3Y_3)\frac{\mu_3}{Y_3}X_3 - \frac{\mu_5}{Y_5}X_5 \text{ (Raw TWE)} \qquad (31)$$

Carbon dioxide (S_6):

$$\frac{dS_6}{dt} = 0.152(\,1 - f_1Y_1)\frac{\mu_1}{Y_1}X_1 + (1 - f_2Y_2)\frac{\mu_2}{Y_2}X_2 + (1 - f_4Y_4)\frac{\mu_4}{Y_4}X_4 - 0.25(1 - f_5Y_5)\frac{\mu_5}{Y_5}X_5 - 0.5f_5\mu_5X_5 \qquad (32)$$

Methane (S_7):

$$\frac{dS_7}{dt} = (\,1 - f_4Y_4)\frac{\mu_4}{Y_4}X_4 + 0.25(1 - f_5Y_5)\frac{\mu_5}{Y_5}X_5 \qquad (33)$$

In order to carry out material balance for gas in liquid/solid phase and gaseous phase, it was assumed that both the phases are completely mixed and homogenous in nature. The gases generated and leaving solid/liquid phase into gaseous phase are in equilibrium with the former phase. The pressure exerted by mixture of gases inside the reactor is generally slightly over 1 atmosphere, which helps in venting of gas from reactor. The concentration of the gaseous products in the anaerobic process such as hydrogen, carbon dioxide and methane were determined by Eq's. 34 to 39 by performing the material balance for each gas with consideration of interphase mass transfer in both slurry and gas phases.

Material balance for each gas in both slurry and gas phase:

Hydrogen (S_8) in slurry phase:

$$\frac{dS_8}{dt} = \frac{dS_5}{dt} + K_L a_8 (S_5^e - S_8) \tag{34}$$

Hydrogen (S_9) in gas phase:

$$V_g \frac{dS_9}{dt} = -V_L K_L a_8 (S_5^e - S_8) - Q S_9 \tag{35}$$

Carbon dioxide (S_{10}) in slurry phase:

$$\frac{dS_{10}}{dt} = \frac{dS_6}{dt} + K_L a_{10} (S_6^e - S_{10}) \tag{36}$$

Carbon dioxide (S_{11}) in gas phase:

$$V_g \frac{dS_{11}}{dt} = -V_L K_L a_{10} (S_6^e - S_{10}) - Q S_{11} \tag{37}$$

Methane (S_{12}) in slurry phase:

$$\frac{dS_{12}}{dt} = \frac{dS_7}{dt} + K_L a_{12} (S_7^e - S_{12}) \tag{38}$$

Methane (S_{13}) in gas phase:

$$V_g \frac{dS_{13}}{dt} = -V_L K_L a_{12} (S_7^e - S_{12}) - Q S_{13} \tag{39}$$

5.2.5.2 Computational method for dynamic simulation and model parameters:

MATLAB R2014b was used for the development of 'AD' simulator and for performing the simulation runs by integrating the dynamic model equations, which included the material balance equations for bacterial groups, bacterial specific growth rate, decay rate, inhibitions and equations for substrates and gas concentrations. The algorithm used for performing the simulation is shown in Fig. 5.3. The 'ODE 15s' solver was used in the

‘AD’ simulator for the solution of the equations and the error minimized using an error function “fmincon” in MATLAB. The model simulation started with initial guesses for the values of growth and inhibition parameters (μ_{mi}, K_{Si}, Y_i, b_i and k) within the ranges found in literature (Kalyuzhnyi, 1997) as given in Table 5.5. Values of initial concentration for bacterial group, conversion factors, Henry’s law constants and mass transfer coefficients (Choi et al., 2003) used in model are as given in Table 5.6. Preliminary simulations were carried out using these values as given and model equations i.e. Eq’s. 19 to 39 were solved by “ODE15s” solver which is based on Runge Kutta method. The volumes of slurry (liquid/solid) phase and gas phase in bioreactors were 2 L and 0.5 L respectively. The initial conditions for all the substrates were set to zero. The optimized values of growth and inhibition parameters for both raw and HC treated TWE are shown in Table 5.7. Further the optimized values of μ_{mi}, K_{Si}, Y_i, $b_{i,}$ and k were obtained by minimizing the error between the experimental and predicted values for the output variable which is the methane production data, using “fmincon” function based on the sum of square of error method. The objective function for minimizing the error was defined as given below in Eq. 40.

$$Error = \sum_{i=1}^{n}[(CH_{4,\ experimental})_i - (CH_{4,\ predicted})_i]^2 \qquad (40)$$

To determine the most significant set of model parameters, the first order rate constant (k) for hydrolysis of the organic polymers was varied in the range of 0.00009 h^{-1} to 0.05 h^{-1} during the simulation runs and parameter values are chosen in such a way that the best possible conformity between the estimated values and experimental values were achieved. The optimized value of rate constant (k) for raw TWE and for HC treated TWE was determined to be low at 0.0001 h^{-1} and 0.0007 h^{-1} respectively in the model parameter fitting, which may be due to the recalcitrant nature of TWE and its slow biodegradability in the digestion process. Using the optimized values and various model constants, the developed simulator was also used for predicting the final concentrations of various substrates as well as the volume of the gases methane and carbon dioxide produced with respect to time for varying input feed conditions such as change in volatile solids content of the feed TWE.

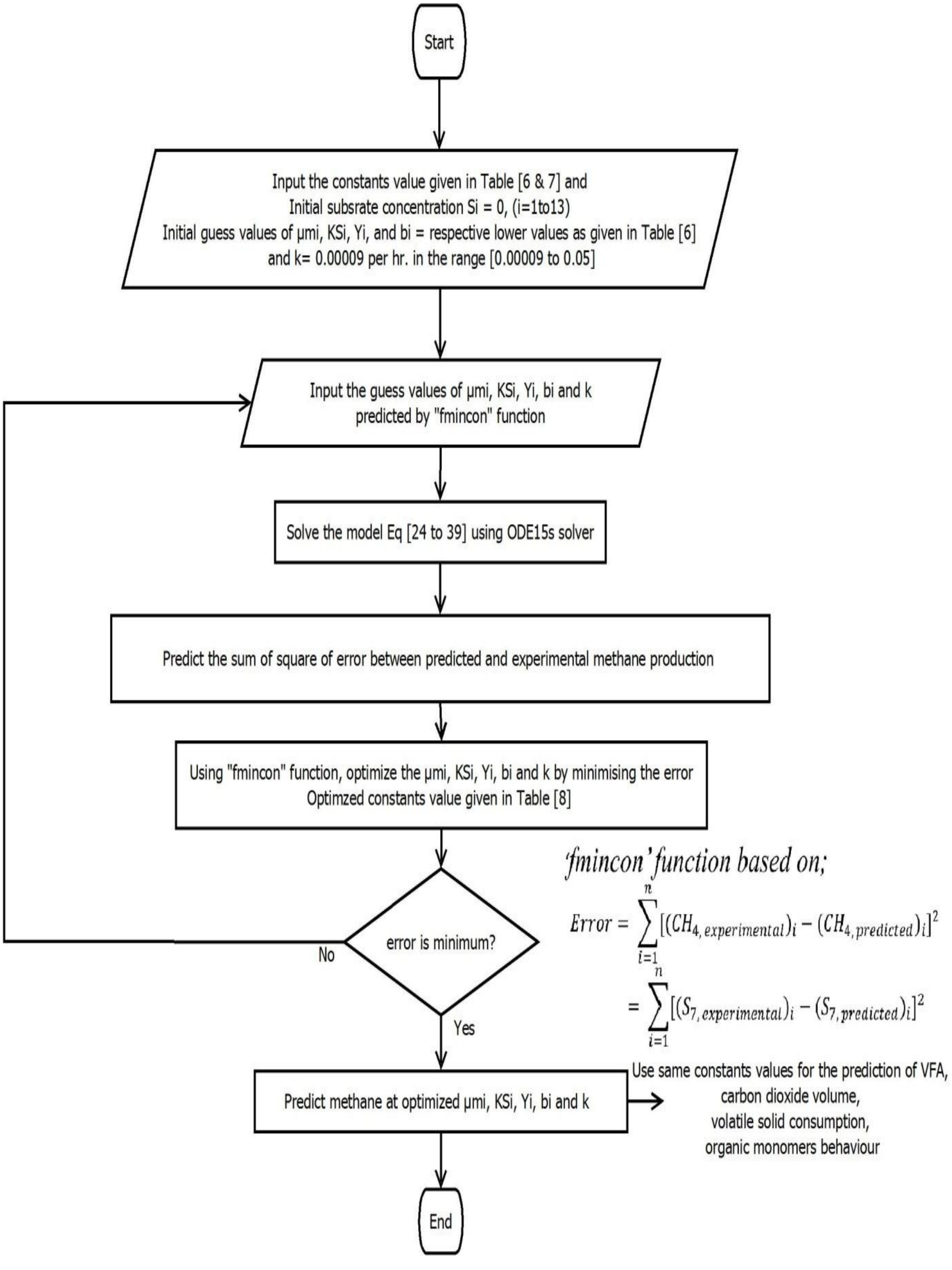


Fig. 5.3 Algorithm of 'AD' Simulator

Table 5.3 Initial range and values of growth and inhibition parameters used in model

Bacterial groups		**Acidogens (X_1)**	**Pr-acetogens (X_2)**	**Bu-acetogens (X_3)**	**Ac-methanogens (X_4)**	**H_2-methogens (X_5)**
μ_m (mM)	Lower value	0.05	0.009	0.009	0.0009	0.05
	Upper value	1.79	0.081	0.081	0.025	0.173
K_S(mM)	Lower value	0.042	0.008	0.008	0.1	0.001/0.001
	Upper value	2.778	3.125	3.125	7.81	0.008/0.01
$K_{I,H2}$ (mM)		0.0321($K_{I,1}$)	0.3205 ($K_{I,2}$)	0.0036 ($K_{I,3}$)		
$K_{I,Ac}$ (mM)				10 ($K_{I,4}$)		
$K_{I,Pr}$ (mM)					35 ($K_{I,5}$)	29 ($K_{I,7}$)
$K_{I,Bu}$ (mM)					21 ($K_{I,6}$)	16 ($K_{I,8}$)
b (h^{-1})	Lower value	0.0004	0.0001	0.0001	0.0004	0.0004
	Upper value	0.0170	0.004	0.004	0.0013	0.0042
Y (g/mM)	Lower value	0.0053	0.0045	0.0045	0.0019	0.0004
	Upper value	0.0288	0.02	0.02	0.0033	0.0025

Table 5.4 Values of initial concentration for bacterial group, conversion factors, Henry's law constants and mass transfer coefficients used in model

Specific growth rate range for the hydrolysis of organic polymers					
k (h^{-1})	0.00009 to 0.05				
Initial conditions for bacterial group					
Bacterial groups	Acidogens (X_1)	Pr-acetogens (X_2)	Bu-acetogens (X_3)	Ac-methanogens (X_4)	H_2-methogens (X_5)
Concentration (g/L)	0.0550	0.0125	0.0800	0.0440	0.0240
Conversion factors					

<table>
<tr><td>Conversion factor (g/mM)</td><td>$C_{0.855}H_{1.528}O_{0.688}N_{0.0286}$</td><td>$C_{0.849}H_{1.59}O_{0.619}N_{0.041}$</td><td>$C_2H_5COOH$</td><td>$C_3H_7COOH$</td><td>$CH_3COOH$</td><td>$H_2$</td></tr>
<tr><td>f</td><td colspan="2">10.1 (f_1)</td><td>13.5 (f_2)</td><td>11.4 (f_3)</td><td>16.7 (f_4)</td><td>500 (f_5)</td></tr>
<tr><td colspan="7">Henry’s law constant and mass transfer coefficient</td></tr>
<tr><td>Gases</td><td colspan="2">H_2</td><td colspan="2">CO_2</td><td colspan="2">CH_4</td></tr>
<tr><td>H (atm/mol fraction)</td><td colspan="2">74,000</td><td colspan="2">21,000</td><td colspan="2">48,500</td></tr>
<tr><td>S^e</td><td colspan="2">1/74,000 (S_5^e)</td><td colspan="2">1/21,000 (S_6^e)</td><td colspan="2">1/48,500 (S_7^e)</td></tr>
<tr><td>K_{La} (h^{-1})</td><td colspan="2">4.17 (K_La_8)</td><td colspan="2">4.17 (K_La_{10})</td><td colspan="2">4.17 (K_La_{12})</td></tr>
<tr><td colspan="7">Gas transfer rate from slurry to gas phase</td></tr>
<tr><td>Q (Lh^{-1})</td><td colspan="6">4.93</td></tr>
</table>

Table 5.5 Optimized values of model parameters in ‘AD’ simulators for raw TWE and HC treated TWE

Bacterial groups		**Hydrolysis constant**	**Acidogens (X_1)**	**Pr-acetogens (X_2)**	**Bu-acetogens (X_3)**	**Ac-methanogens (X_4)**	**H_2-methogens (X_5)**
k (h^{-1})	Raw	0.0001					
	HC treated	0.0007					
μ_m (mM)	Raw		0.0714	0.0450	0.0416	0.0021	0.0766
	HC treated		0.8591	0.0540	0.0407	0.0024	0.0891
K_S(mM)	Raw		2.1343	1.5665	2.0507	5.1476	0.0059/0.0074
	HC treated		1.4881	1.5340	1.6434	7.7353	0.0046/0.0049
b (h^{-1})	Raw		0.0129	0.0021	0.0009	0.0005	0.0023
	HC treated		0.0042	0.0021	0.0039	0.0013	0.0026
Y (g/mM)	Raw		0.0062	0.0118	0.0128	0.0027	0.0024
	HC treated		0.0139	0.0123	0.0152	0.0027	0.0025

5.3 Result and Discussion:

5.3.1 Elemental composition of substrate samples and theoretical biogas yield:

The potential of HC pretreated TWE as a substrate for biogas production as against raw TWE as a control was studied in 250 mL flasks under constant temperature conditions. The biogas generation started after an acclimatization period of 20 -23 days for HC pretreated TWE and 32-35 days for raw TWE. The Buswell equation (Buswell and Mueller, 1952) as given in Eq.41 was used to estimate the theoretical yield of biogas by AD of the organic material present in TWE and HC treated TWE. This equation assumes 100% decomposition of organic matter and estimates the biogas composition as well the biogas yield in liters per gram of organic matter.

$$\begin{aligned} C_cH_hO_oS_s + \left(\mathrm{c} - \frac{h}{4} - \frac{o}{2} + \frac{3}{4}\mathrm{n} + \frac{1}{2}s\right) H_2O \\ \rightarrow \left(\frac{c}{2} - \frac{h}{8} + \frac{o}{4} + \frac{3}{8}\mathrm{n} + \frac{1}{4}s\right) \mathrm{CO_2} \\ + \left(\frac{c}{2} + \frac{h}{8} - \frac{o}{4} - \frac{3}{8}\mathrm{n} - \frac{1}{4}s\right) \mathrm{CH_4} + \mathrm{nNH_3} + s\mathrm{H_2}S \qquad (41) \end{aligned}$$

The samples of TWE and HC treated TWE were subjected to CHNS/O analysis to estimate the elemental composition of samples. The elemental composition of the substrate samples is given in Table 5.2 and theoretical biogas production yield estimated from the Buswell equation is presented in Table 5.8. The experimental yield of biogas production is very less in comparison to theoretical biogas yield, which is because of the recalcitrant nature of TWE, long acclimatization period as well as the inhibitory nature of some of the reactant/ products for the proper growth of microorganism and the slow reaction kinetics. However, the experimental yield of biogas for HC treated TWE was twice the yield of raw TWE.

Table 5.6 Based on elemental composition of substrates, theoretical and experimental yield of biogas

Substrate	**Theoretical yield of biogas (L/kg)**	**Experimental yield of biogas (L/kg)**
TWE	760	17
HC treated TWE	810	36

5.3.2 Effect of HC on COD reduction of TWE and biogas generation in small scale reactor

During the AD of 200 mL of TWE samples as observed in Fig. 5.4(a), the % COD reduction and the biogas produced in HC pretreated TWE was higher in comparison to the raw TWE. It was observed that after 30 days of gas generation, 40.3 mL biogas was generated along with 21.63 % COD reduction of raw TWE whereas in case of HC pretreated TWE, 67.2 mL biogas was generated along with 44.15% COD reduction. The biogas generation was directly correlated to the COD reduction as observed from the similarity in the pattern as well as the convergence of the two graphs as shown in Fig. 5.4(a). The acclimatization time as well as the biogas generation pattern over the period of AD in the small scale bioreactor is presented in Fig. 5.4(b) which shows that the acclimatization time for HC pretreated TWE sample was lowered by 12 days and 66.7% higher yield of biogas was obtained. Moreover, the % COD reduction was increased by two times when HC treated TWE sample was subjected to AD. The reduction in acclimatization time with high COD reduction and high biogas generation in the AD of HC pretreated TWE is due to the cavitational effects which caused the conversion of the recalcitrant organic waste to more soluble biodegradable matter. During the process of cavitation, vapor cavities are generated within the liquid medium due to the pressure modulations created in the cavitating device. The isothermal expansion of these vapor cavities and their subsequent asymmetric collapse cause a huge energy release at the molecular level known as hot spots. These hot spots act as micro reactors where the temperatures reach up to 5000 K and pressure of about 1000 atm which cause the degradation of the recalcitrant organic matter and thereby increased the rate of digestion to generate more biogas. The subsequent physical effects of the intense cavity collapse in the form of high turbulence and shear also increased the rate of acidogenesis reactions, causing an increase in the volatile fatty acid contents and subsequent consumption of the volatile solid contents thereby increased the rate of biogas yield. Fig. 5.4(b) also presents that the cumulative biogas generation yield for AD over a period of 30 days was 39.5 mL/g VS in the TWE sample whereas in HC treated TWE sample it was increased to 70 mL/g VS. Moreover, it can be observed from the biogas generation pattern that biogas production rate continuously increased up to 15 days and after 15 days it decreased which was due to the pH variations in the bioreactor. As the pH value decreased to 5, from an initial value of 8, the methanogenic bacteria became inactive and ceased to produce biogas.

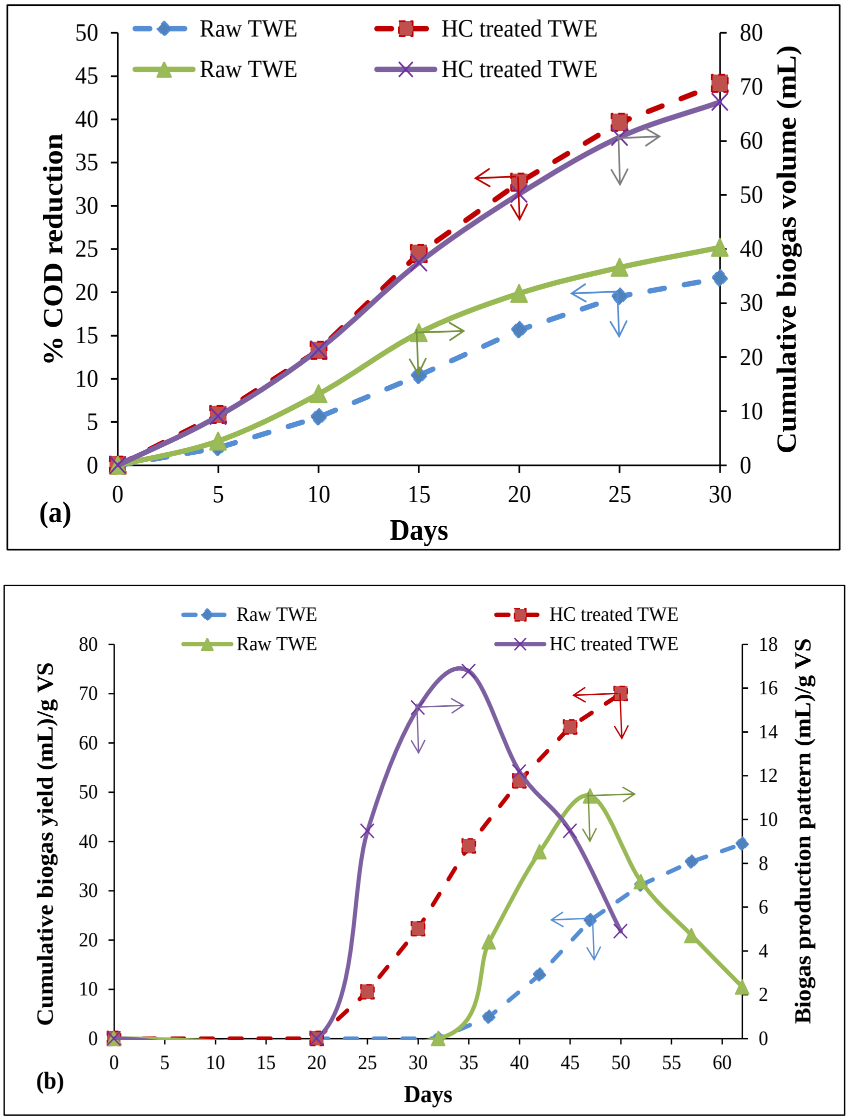


Fig. 5.4 (a) % COD reduction and (b) Cumulative biogas generation (yield and pattern) in small scale batch AD. (Working volume = 200 mL, Conditions: Raw TWE: VS = 5.1 g/L, Acclimatization period–32-35days, COD =8400 mg/L; HC treated TWE: VS = 4.8 g/L, Acclimatization period-20-23 days, COD = 7520 mg/L.)

5.3.3 Effect of dosage of sewage seed in HC treated TWE for biogas production:

Based on the results obtained from small scale (200 mL) setup, laboratory batch reactors of 2000 mL capacity were studied under similar experimental conditions to check the potential of large-scale application of AD for biogas generation and simultaneous COD reduction. The sewage seed which is rich in the anaerobic microbial population plays a vital role in biogas production. In order to examine the effect of the dosage of this sewage seed on the methane gas production and to obtain the best dosage for the HC treated TWE samples, three batch laboratory scale reactors (2 L capacity) were setup with sewage seed concentrations varied as 5%, 10% and 20 % of reactor working volume while keeping rest of the conditions same. Samples with seed biomass of volume 5%, 10% and 20% were named as Sample 1, Sample 2 and Sample 3 respectively. Fig. 5.5(a) showed that the percentage COD reduction and biogas production increased with the increase in seed dosage. Maximum 680 mL of biogas along with 45.73% reduction in COD was obtained in Sample 3, whereas 650 mL of biogas along with 43.17% reduction in COD for sample 2 and 410 mL of biogas was generated along with 31% COD reduction for Sample 1 for 30 days of treatment. It was observed that as the dose of seed increased the acclimatization time decreased. Fig. 5.5(b) presents that the acclimatization time for the Sample 1, Sample 2 and Sample 3 were 23 days, 19 days and 13 days respectively. Cumulative biogas generation yield and biogas generation pattern per day per gram of VS present in the substrate was also estimated and presented in Fig. 5.5(b). The yield of biogas production was 74.24 mL/g VS for 20% seed concentration over a period of 30 days. Fig. 5.5(b) also indicates the pattern of gas production in the three bioreactors and it can be observed that the rate of biogas generation per day increased gradually and after reaching the saturation state, it decreased in a similar manner. In sample 3 with highest sewage seed of 20%, biogas generation rate per day increased at higher rate in comparison to other samples and reached its saturation state within 25 days. Whereas it was 30 days in the case of other two samples, which can be attributed to the fact that the higher concentration of micro-organisms in Sample 3 increased the degradation rate of substrates. However, with the increase in seed biomass concentration from 10% to 20%, the TWE sample gets diluted causing an increase in sludge volume to be handled in the anaerobic digester which is undesirable, even though the %COD reduction was higher with corresponding increase in biogas production. Therefore, considering the dilution effect, 10% biomass dose was considered optimum for further studies in the 2000 mL bioreactors.

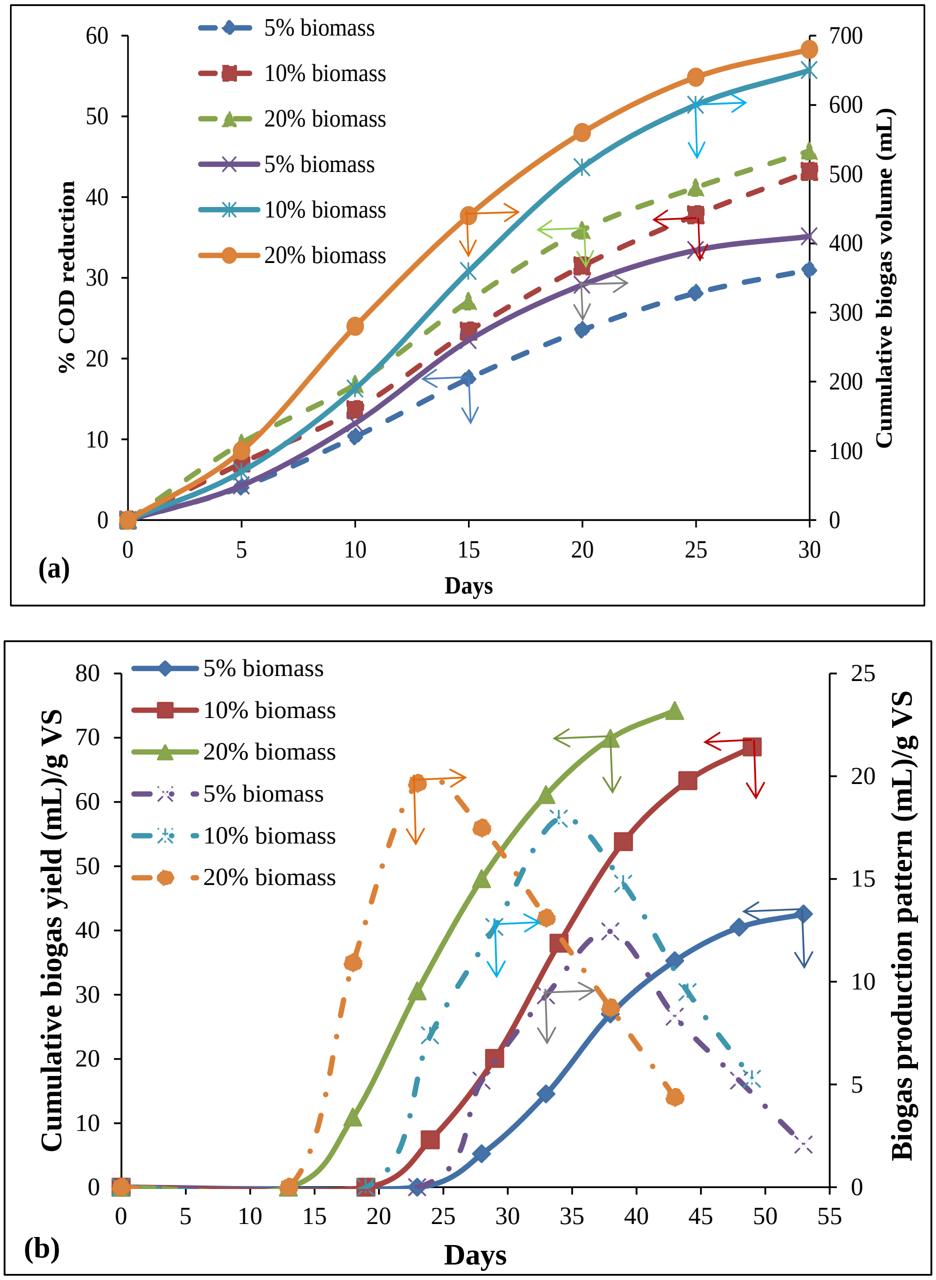


Fig. 5.5 (a) Effect of COD reduction and (b) cumulative biogas generation- yield and pattern of HC treated TWE at different seed dosage (Reactor working volume = 2000 mL, Initial conditions- Sample 1 (5% biomass): VS = 4.82 g/L, COD=8320 mg/L, Sample 2 (10% biomass): VS= 4.74 g/L, COD = 8200 mg/L, Sample 3 (20% biomass): VS=4.58 g/L, COD= 7960 mg/L)

5.3.4 Anaerobic Digester performances and Simulation studies for 2000 mL capacity:

The performance of bioreactors having working volume of 2L was again studied for AD of both TWE and HC treated TWE for methane production and evaluated so that the data can be utilized in the development of two separate 'AD' process simulators and for obtaining the optimized values of growth and inhibition parameters as well as the rate parameters of the process model. Table 5.9 and Fig. 5.6 presents the experimental results observed over a period of 35 days of AD for % COD reduced, VFA content, pH, biogas, methane and carbon dioxide generation in the bioreactors for both raw TWE and HC treated TWE after an acclimatization period of 36 and 21 days respectively. The slight differences in the %COD reduction and cumulative biogas yield in this AD process with respect to the AD performance given in section 5.3.3 was due to the difference in the initial COD and VS concentrations of the HC treated TWE sample Fig. 5.6(a) presents the quantum of COD reduction and the cumulative biogas (inclusive of CO_2, CH_4, H_2S, H_2 and NH_3) yield per g of initial VS present in the substrate which indicated that the HC treated TWE provided better results in comparison to the raw TWE as found similar for small scale setup. After 35 days of AD as given in Table 5.9, 350 mL (i.e. 33.33 mL/g VS) of biogas was produced from AD of TWE sample along with 20.71% reduction in COD. Whereas in case of HC treated TWE sample, 670 mL (i.e.68.38 mL/g VS) of biogas was produced along with 42.79 % reduction in COD. The quantum of biogas generation depends on the volatile solid content. Therefore, as observed in Fig. 5.6 (a), the similarity in the COD reduction and biogas yield indicate that the COD reduction was with respect to the degradation of the volatile solid contents present.

Table 5.7 % COD reduction, VFA, pH and cumulative biogas volume in AD of raw and HC treated TWE (Reactor working volume = 2000 mL, seed concentration =10%)

Days	**Raw TWE**						**HC treated TWE**					
	% COD reduction	**VFA (mg/L)**	**pH**	**Biogas Volume (mL)**	**CH$_4$ (mL)**	**CO$_2$ (mL)**	**% reduction**	**VFA (mg/L)**	**pH**	**Biogas Volume (mL)**	**CH$_4$ (mL)**	**CO$_2$ (mL)**
0	0	636.82	7.7	0	0	0	0	476.23	7.83	0	0	0
5	2.93	804.15	6.5	40	0.92	8.4	6.11	722.58	6.32	80	3.44	19.2
10	8.16	845.64	5.81	120	6.48	42	12.72	750.37	5.47	180	17.172	66.6
15	11.51	828.32	5.52	210	19.95	79.8	20.05	711.64	5.28	270	40.23	102.6
20	14.64	820.81	5.18	280	35.28	112	28.85	686.27	5.09	480	89.76	192
25	17.36	806.63	4.96	320	39.36	131.2	34.23	654.79	4.88	580	116.58	226.2
30	19.46	790.54	4.75	340	39.61	132.6	40.10	647.15	4.71	640	124.928	262.4
35	20.71	789.12	4.78	350	39.55	140	42.79	640.46	4.69	670	130.047	268

(**Initial conditions- Raw TWE:** VS = 5.25 g/L, COD = 9560 mg/L, acclimatization time 36 days **HC treated TWE:** VS = 4.9 g/L, COD = 8180 mg/L, acclimatization time 21 days)

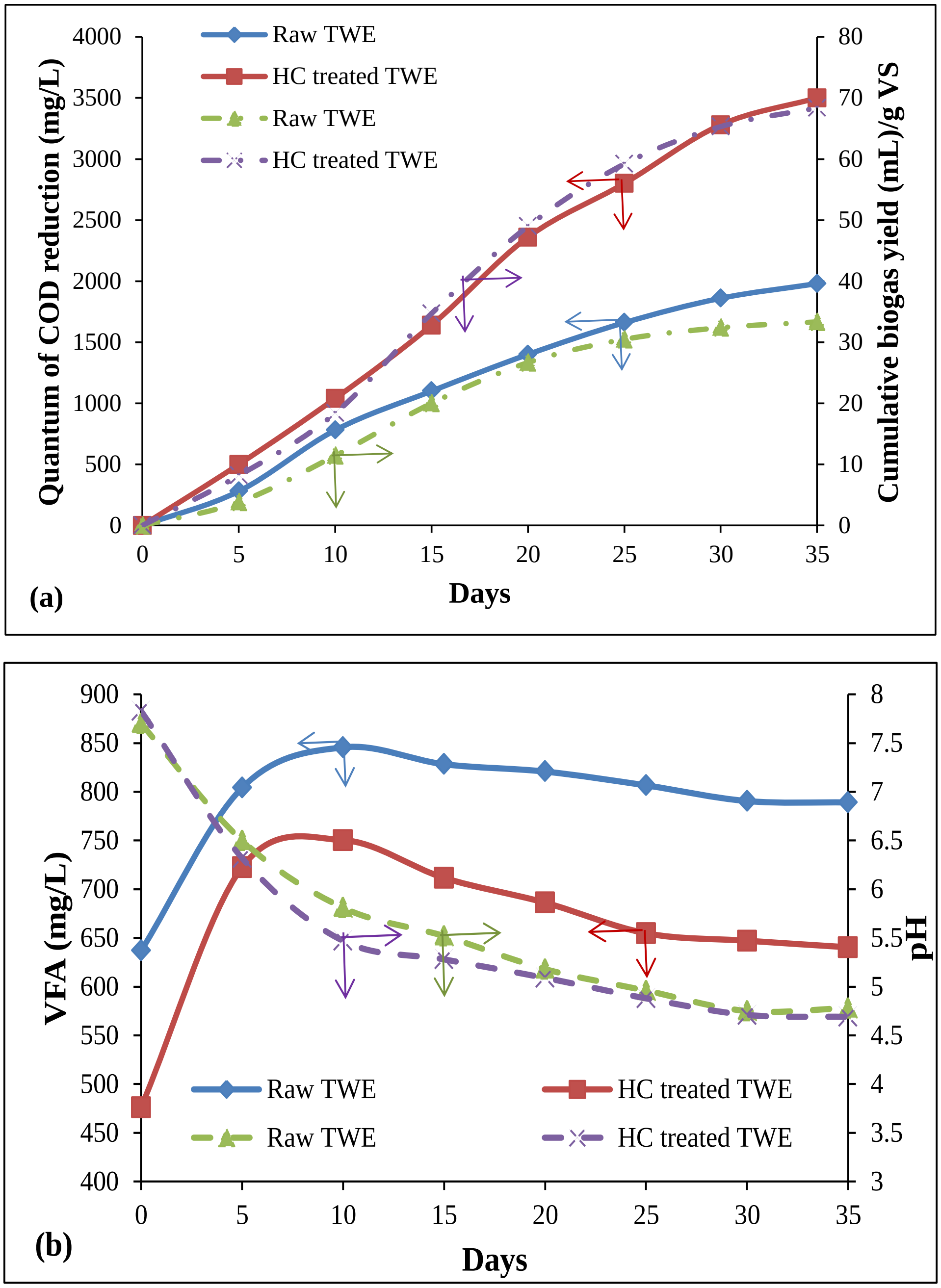


Fig. 5.6 (a) Quantum of COD reduction and cumulative biogas yield (b) VFA and pH in batch AD of raw TWE and HC treated TWE (Reactor working volume = 2000 mL, Initial experimental conditions- Raw TWE: VS = 5.25 g/L, COD = 9560 mg/L, HC treated TWE: VS = 4.9 g/L, COD = 8180 mg/L)

The VFA content and pH variation in the AD process over the period of 35 days were also analyzed in this experimental study which is shown in Fig. 5.6 (b) and data presented in Table 5.9. It was observed from Table 5.9 that during the 35 days of AD, the VFA content of raw TWE changed from 636.82 mg/L to a maximum of 845 mg/L on the 10th day and further slightly decreased and remained constant around 789.12 mg/L in 35 days. In case of HC treated TWE, the VFA content varied from 476.23 mg/L to a maximum of 750.37 mg/L on the 10th day and further decreased to 640.46 mg/L. The initial increase in VFA content observed up to 10 days in both samples is due to the hydrolysis of the volatile solids and acidogenesis reactions, and the further decrease in VFA is due to the subsequent acetogenesis and methanogenesis reactions that occur causing the formation of the biogas. It can be observed from Fig. 5.6(b), that VFA formation in initial 10 days occurred at higher rate in HC treated sample in comparison to raw TWE which can be attributed to the increase in the rate of acidogenesis reactions caused due to the HC treatment of the TWE sample. Moreover, the pH of both the TWE and HC treated TWE samples continuously decreased from its initial value of pH 7.7 to pH 4.7 and pH 7.8 to pH 4.7 respectively. It was observed that the solution pH was above pH 5 up to 15 days for both the HC treated sample and raw TWE sample in the anaerobic digester. Fig. 5.7 presents the pattern of biogas production and the cumulative biogas yield for both the raw and HC treated TWE samples. As the pH decreased below 5 after 15 days, the biogas generation ceased which may be due to the inactivation of the methanogenic bacteria as it cannot thrive in acidic conditions. The drop in pH was faster in initial 10 days for HC pretreated TWE sample. Moreover, the VFA consumption was faster in case of the HC pretreated sample indicating the advantage of HC treatment of the TWE samples in increasing the rate of acetogenesis and methanogenesis reactions. The biogas generation continued up to a period of 15 days and thereafter decreased due to the pH drop and the inhibitory conditions developed for the methanogenic bacteria in the bioreactor. As similar performances were obtained in the bigger (lab reactor of 2.5 L) and smaller (flask of 250 mL) reactor setups, it indicated that scale up of the bioreactor may be carried out for large scale performance with same treatment strategy.

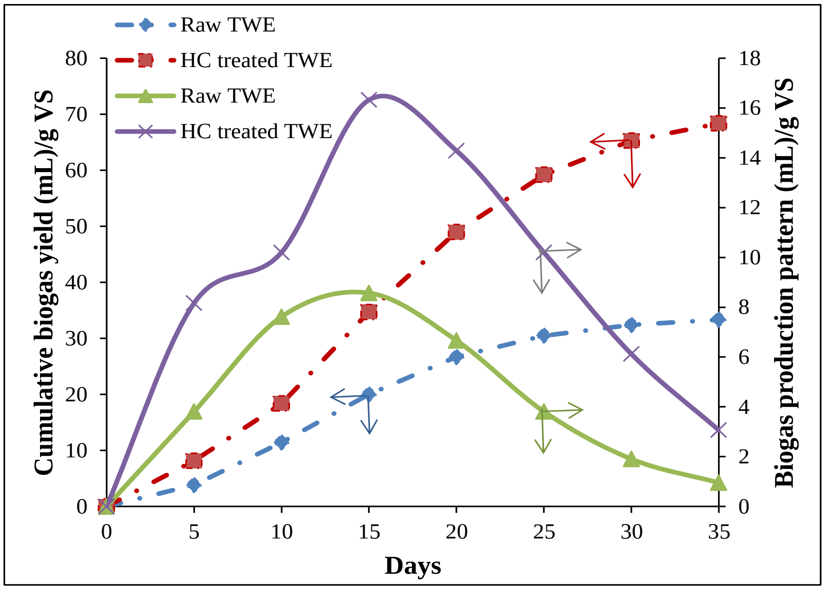


Fig. 5.7 Comparison of cumulative biogas yield, biogas production pattern in batch AD of raw TWE and HC treated TWE (Initial experimental conditions- Raw TWE: VS = 5.25 g/L, COD = 9560 mg/L, HC treated TWE: VS = 4.9 g/L, COD = 8180 mg/L, Reactor working volume = 2000 mL)

The above experimental data obtained with respect to the yield of methane and carbon dioxide, as well as the concentration of VFA from the degradation reactions were used in the development and verification of the simulation predictions of ‘AD’ simulator. The optimum model parameters such as μ_{mi}, K_{Si}, Y_i, $b_{i,}$ and k used in the simulator were obtained by minimizing the error between the experimental and predicted values for the methane gas generation from the anaerobic process. Fig. 5.8 (a) shows the model fit for the experimental data for methane gas production for both the ‘AD’ simulators developed separately for raw TWE and HC treated TWE. The developed simulator with its optimized parameters were used to predict for the concentration of carbon dioxide (S_6), organic polymers (S_0), organic monomers (S_1) and VFA (S_2+S_3+S_4) during the batch AD. The trend in the CO_2 production was a continuous increase observed for both TWE samples which was also according to the trend observed in the experimental data as shown in Fig. 5.8(b). Fig. 5.9(a) presents the simulator predictions for the change in the concentrations of the organic polymers (volatile solids) and the organic monomers during the digestion process. It can be observed that the rate of decrease in the concentration of volatile solids for the HC treated TWE was higher than that of raw TWE. This was also confirmed by the higher hydrolysis rate constant (k) obtained by simulation in case of HC treated TWE at a value of 0.0007 h^{-1} than the value obtained for raw TWE at 0.0001 h^{-1}as shown in Table 5.7. In the case of raw TWE, the concentration of organic monomers continuously increased with time which indicates that the further digestion of generated monomers to form the lower degradation products was slow and thereby caused a continuous increase in the monomer concentration. The predictions of low and constant concentration of organic monomers for the HC treated TWE, indicate the effective consumption of the organic monomers in the subsequent acetogenesis reactions in the digestion process to form lower degradation products.

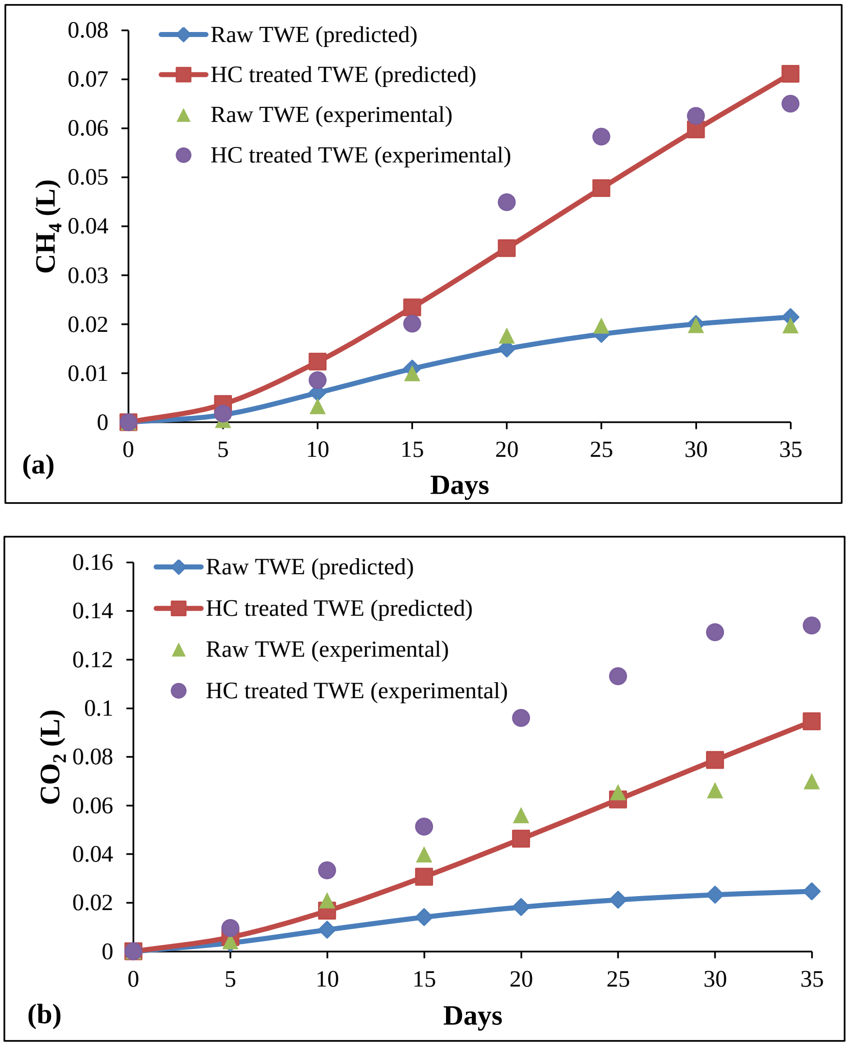


Fig. 5.8 Experimental versus model predicted values of (a) CH_4 production and (b) CO_2 production during AD (Initial experimental conditions- Raw TWE: VS = 5.25 g/L, COD = 9560 mg/L, HC treated TWE: VS = 4.9 g/L, COD = 8180 mg/L, Reactor working volume = 2000 mL, Temperature = 37°C)

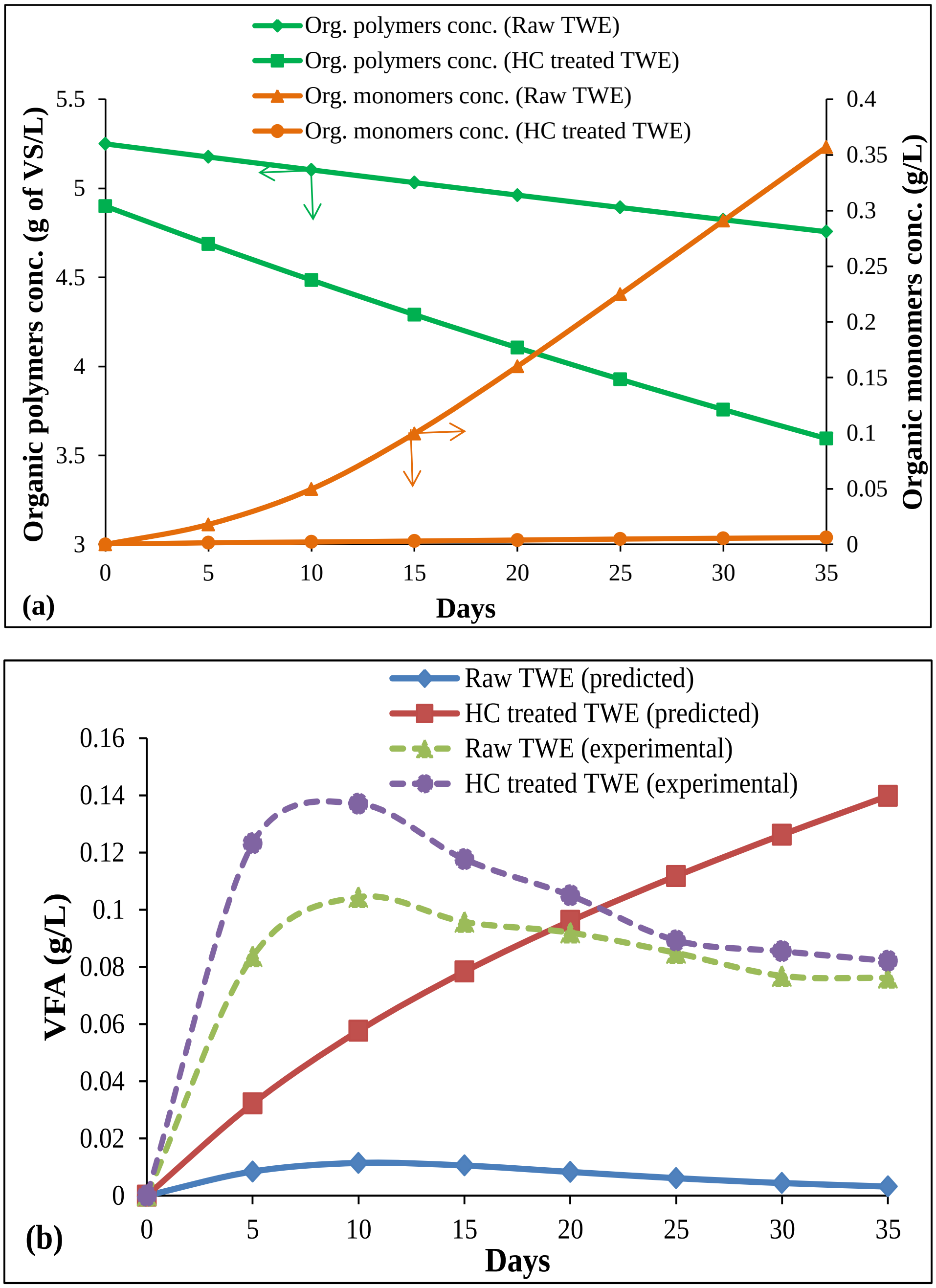


Fig. 5.9 (a) Model predictions of organic polymers (VS) consumption and organic monomers concentration and (b) Experimental versus model predicted values of VFA during AD (Initial experimental conditions- Raw TWE: VS = 5.25 g/L, COD = 9560 mg/L, HC treated TWE: VS = 4.9 g/L, COD = 8180 mg/L, Reactor working volume = 2000 mL, Temperature = 37°C)

The predictions for the VFA content compared with the experimental values are presented in Fig. 5.9 (b). The model predictions considered an initial VFA of zero for both the samples as it corresponds only to the organic monomers formed from the degradation of organic polymers (volatile solids) during the digestion process. It was observed that the model predictions for VFA concentration in case of raw TWE was very low, whereas the predictions were closer to that of experimental values for HC treated sample. Higher rate of VFA formation was predicted in the case of HC treated TWE than the raw TWE which was also confirmed through parameter optimization as given in Table 5.7, where it was observed that the optimum value obtained for the specific growth rate in case of the acidogenesis bacteria (μ_1) for the HC treated TWE was at the value of 0.8591mM which is higher than that obtained for raw TWE at 0.0714mM. This was also confirmed in the trend of the increase in VFA concentration observed in the experimental data in the initial days of AD process.

As the 'AD' simulator was able to represent the AD of HC treated TWE samples more effectively and the main objective of AD was to produce biogas, simulation predictions were further carried out for digestion of HC treated TWE over a period of 120 days predicting the rate of organic polymers (VS) consumption, concentrations of VFA and organic monomers and the yield of biogas (CH_4 and CO_2) for varying volatile solids concentration (5 to 50g/L) in the HC treated TWE feed. Fig. 5.10(a) presents the rate of VS consumption and corresponding VFA formation, Fig. 5.10(b) presents the rate of formation of organic monomers and Fig. 5.11 presents the yield of biogas consisting of both methane and CO_2. For VS loading of 5, 10, 20 and 50 mg/L the volume of CO_2 was 384 mL, 775 mL, 1546 mL, 3938 mL and volume of CH_4 was 274mL, 523 mL, 997 mL 2454 mL and total volume of biogas was 658 mL, 1298 mL, 2543 mL, 6392 mL respectively in 120 days. It was observed that with increase in the organic loading of VS, the rate of formation of organic monomers as well as the rate of formation of biogas increased in the digester performance over the total period of 120 days. Therefore, model simulations indicated that HC treated TWE was more effective when compared to raw TWE for biogas production with higher VS content in the AD process.

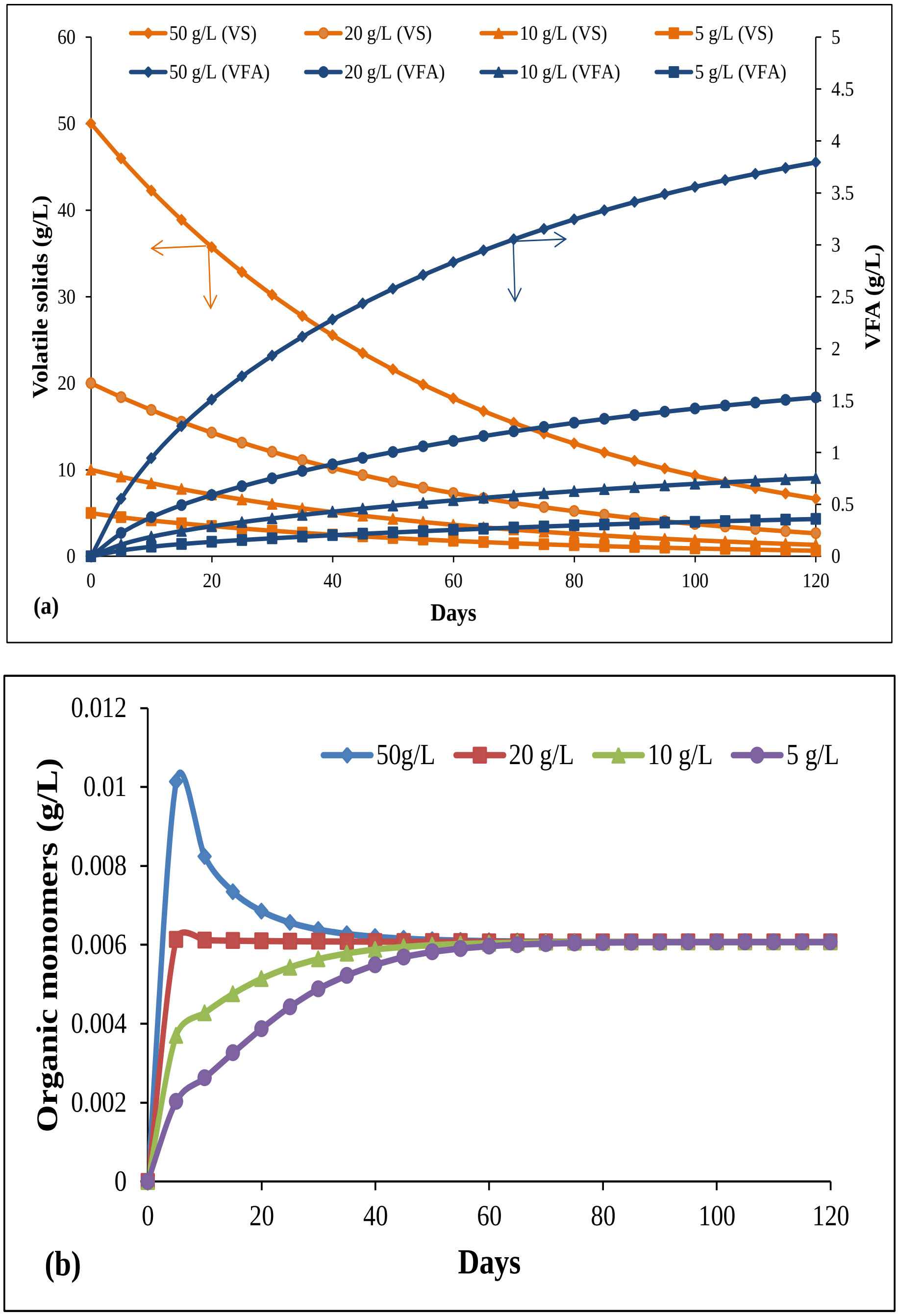


Fig. 5.10 Model Predictions of (a) VS consumption and VFA concentration and (b) organic monomer concentration during AD of HC treated TWE (Reactor working volume = 2000 mL, Temperature = 37°C, Time duration = 120 days)

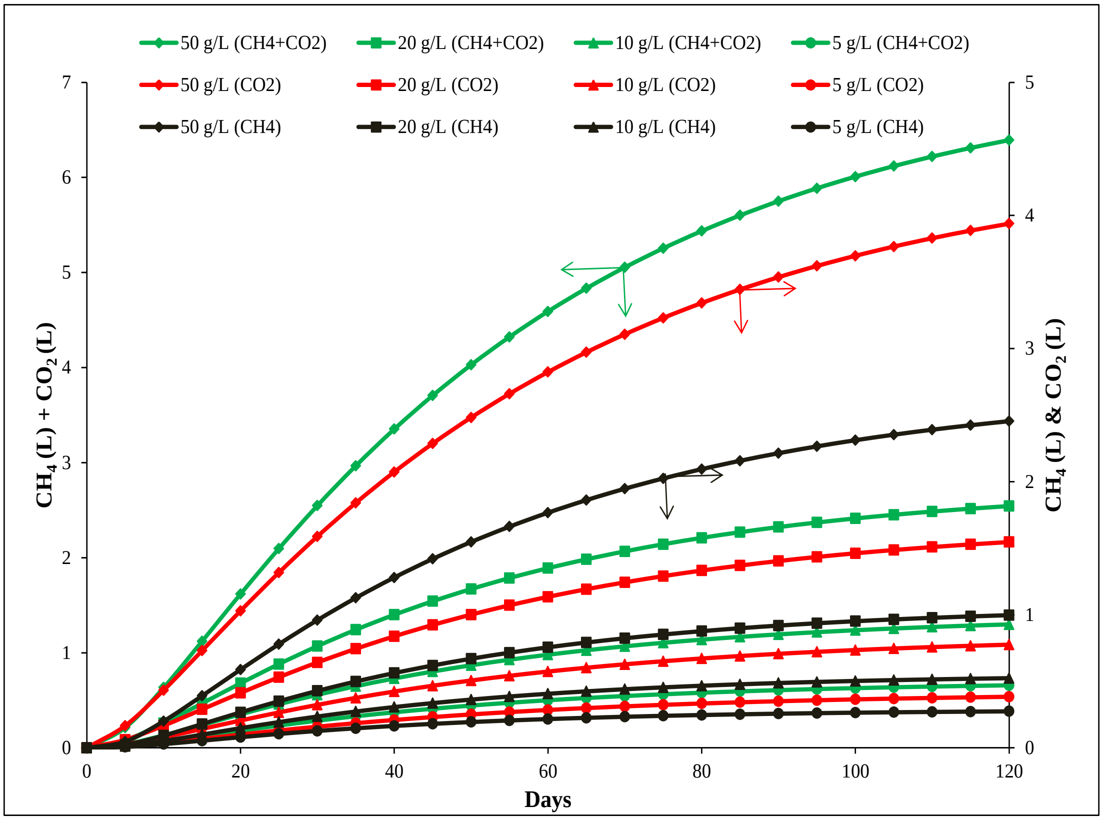


Fig. 5.11 Model Predictions for methane (CH_4) and carbon dioxide (CO_2) production during AD of HC treated TWE (Reactor working volume = 2000 mL, Temperature = 37°C, Time duration = 120 days)

5.3.5 Effect of higher organic loading by adding food waste to HC pretreated TWE to increase the biogas yield:

From the CHNS/O analysis of TWE it was evident that the available carbon was low (10%) and in view of the simulator predictions, it was decided to introduce an external carbon source into HC treated TWE that will have higher VS content so as to make the AD more effective which will also sustain the microbial flora in the digestion system. Therefore, food waste from Institute canteen was taken, ground to fine powder, freeze dried and specific dosage was added into raw TWE and HC treated TWE and AD performed in different bioreactors with different loading time intervals. Bioreactor 1 and Bioreactor 2 was used for AD of HC treated TWE and once the biogas formation started, both were repetitively loaded with feed every 24 h and 48 h respectively. Bioreactor 3 was used for digestion of raw TWE and repetitively loaded with feed every 48 h when biogas formation started. The performance of Bioreactor 1 & 2 was compared with the performance of the control Bioreactor 3. The acclimatization time for Bioreactor 1, Bioreactor 2 and Bioreactor 3 was 19 days, 21 days and 34 days respectively. Once the biogas production started, 50 mL of feed sample with 10% (5 g in 50 ml) food waste which is equivalent to 0.625 g/L of VS content was loaded in respective bioreactors at an interval of 48 h/ 24 h for a total period of 35 days while maintaining a constant substrate volume. The VS content of the HC treated sample at the beginning of loading was 4.9 g/L. The variation in the SCOD, VFA, and pH values was analyzed at pre-determined time intervals and the biogas generation and methane and CO_2 concentrations were analyzed in an interval of 5 days. Fig. 5.12(a) and (b) presents the cumulative biogas and methane production and VFA concentration with corresponding pH whereas Fig. 5.13 presents the concentrations of SCOD for a digestion period of 35 days.

It can be observed from Fig. 5.12(a) that in case of HC treated TWE, there was a significant increase in biogas and methane gas produced (measured every 5 days) up to 30 days. The Bioreactor 2 was providing more biogas production in comparison to Bioreactor 1, which could be due to the undisturbed longer acclimatization time for microbes during OLR of 48 h in comparison to OLR of 24 h. The VFA concentration was also less in Bioreactor 2 than in comparison to Bioreactor 1 as shown in Fig. 5.12(b). The presence of high VFA may be due to high acidogenesis reaction rate in comparison to acetogenesis rate in Bioreactor 1 which lowered the overall pH of the system subsequently causing the inhibition of microbial activity and hence less production of biogas. Similar trends were observed in the AD performances of the bioreactors with both raw and HC treated TWE loaded with food waste, however biogas produced was significantly lower for raw TWE in comparison to HC treated TWE samples. The pH values had decreased from 8.22 to 5.48 in Bioreactor 2, 8.22 to 5.07 in Bioreactor 1 and 8.14 to 5.3 in Bioreactor 3 in 15 to 20 days of operation. In all the three cases the decrease in biogas production can be correlated to the decrease in pH below 5 after 20 days. It was observed that SCOD concentration samples increases continuously in all bioreactor setups as shown in Fig. 5.13, which was favorable for generation of more biogas. It was observed that with the introduction of equivalent quantities of food waste in HC treated TWE samples, biogas generation increased up to 5.4 folds (Bioreactor 1) and 11.8 folds (Bioreactor 2) for an OLR of 24 h and 48 h respectively.

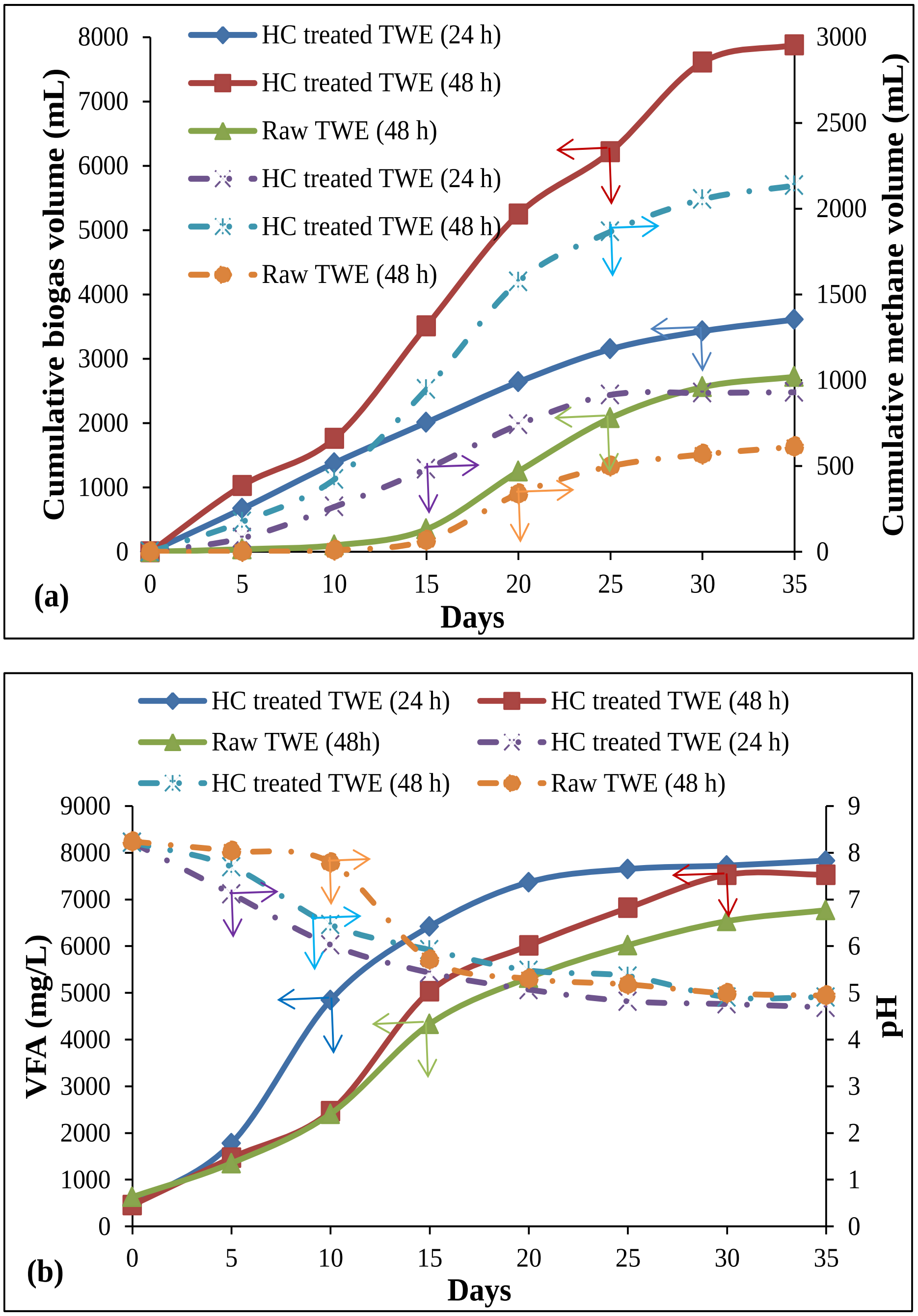


Fig. 5.12 (a) Cumulative biogas production and cumulative methane production and (b) VFA and pH variation during AD of TWE/ HC treated TWE + food waste (Initial experimental conditions- Raw TWE (48 h): VFA = 629.25 mg/L, SCOD = 1780 mg/L, pH = 8.14, HC treated TWE (24 h and 48 h): VFA = 454.68 mg/L, COD = 1920 mg/L, pH = 8.22, Reactor working volume = 2000 mL)

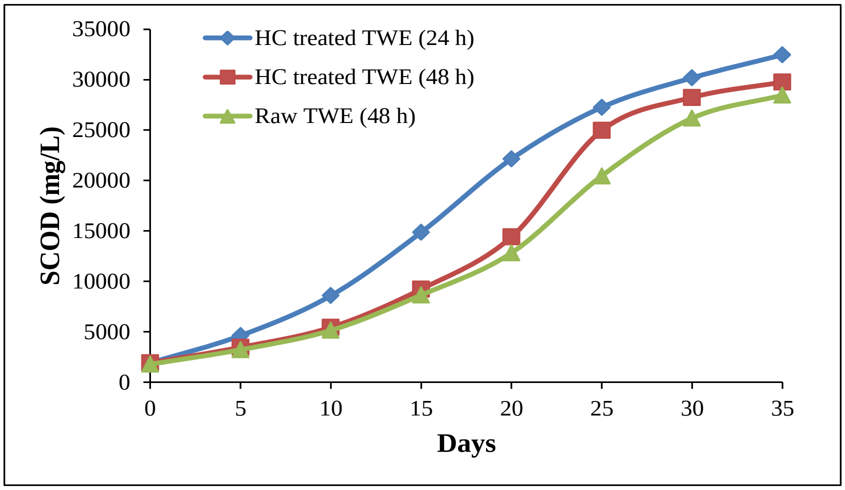


Fig.5.13 Effect on SCOD during AD of TWE/ HC treated TWE + food waste (Initial experimental conditions- Raw TWE (48 h): VFA = 629.25 mg/L, SCOD = 1780 mg/L, pH = 8.14, HC treated TWE (24 h and 48 h): VFA = 454.68 mg/L, COD = 1920 mg/L, pH = 8.22, Reactor working volume = 2000 mL)

5.3.6 Recovery of HC treatment cost from the excess biogas produced by HC treated TWE and organic load using food waste:

In order to analyze for self-sustainability of the entire treatment process, cost analysis was carried out to recover the cost of HC treatment of TWE sample from the excess methane produced during AD with the HC treated TWE sample. The recovery of HC treatment cost from the excess biogas produced by HC treated TWE and organic load using food waste are presented in Table 5.10 and calculations are provided in Appendix D (page no. 202). The energy delivered to the HC reactor system was 2.2 kWh in 2 h and the cost of HC treatment of 2L of TWE is estimated at Rs 5.66. Therefore, the comparison was drawn in terms of volume of biogas, CH_4 and CO_2 produced for raw as well as HC treated TWE with and without organic loading and is presented on Fig. 5.14. The volume of methane produced from the 2 L bioreactors for raw TWE, HC treated TWE, raw TWE loaded with food waste and HC treated TWE loaded with food waste was 40 mL, 130 mL, 612 mL and 2135 mL respectively and the volume of CO_2 produced for raw TWE, HC treated TWE, raw TWE loaded with food waste and HC treated TWE loaded with food waste was 140 mL, 268 mL, 1034 mL and 3152 mL respectively for 35 days of AD. Similarly the volume of biogas produced for raw TWE, HC treated TWE, raw TWE loaded with food waste and HC treated TWE loaded with food waste was 350 mL, 670 mL, 2720 mL and 7880 mL respectively. It was observed that with the introduction of equivalent quantities of food waste in raw and HC treated TWE samples, biogas generation increased up to 7.8 folds (Bioreactor 3) and 11.8 folds (Bioreactor 2) respectively for an OLR of 48 h.

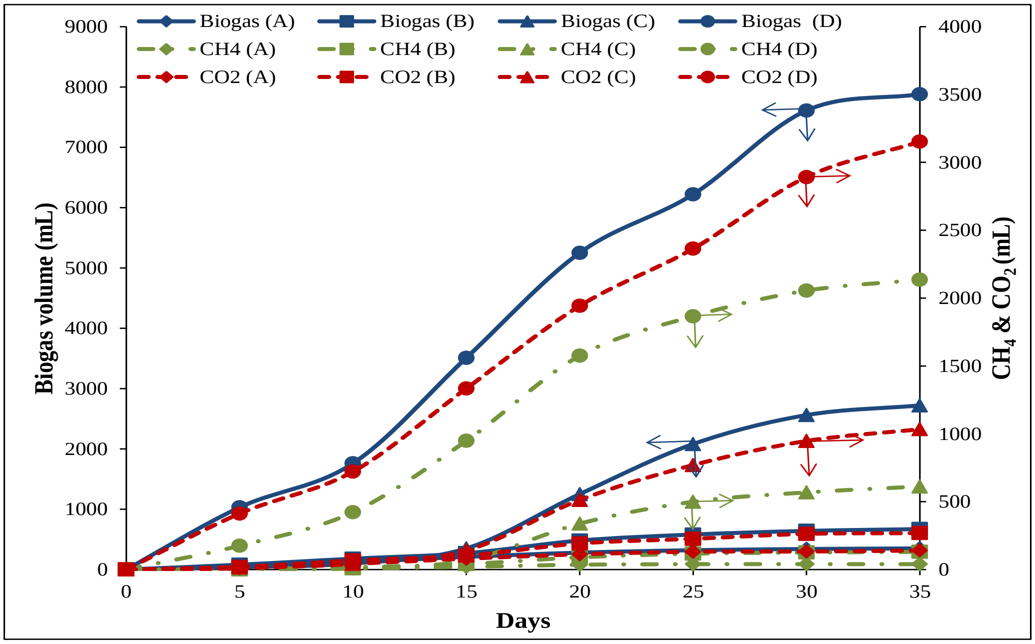


Fig. 5.14 Volume of biogas, methane and carbon dioxide produced during AD of Raw TWE (A), HC treated TWE (B), Raw TWE with organic loading (48 h) (C) and HC treated TWE with organic loading (48 h) (D) (Experimental conditions: Reactor working volume = 2000 mL)

The % composition of methane in biogas obtained from AD of raw TWE, HC treated TWE, raw TWE loaded with food waste and HC treated TWE loaded with food waste was 11.42%, 19.4%, 22.5% and 27% respectively. Considering the market value of biogas having 60% CH_4 at Rs. 1.5 per liter, the cost that can be recovered from biogas using raw TWE, HC treated TWE, raw TWE loaded with food waste and HC treated TWE loaded with food waste will be Rs. 0.10, Rs. 0.33, Rs. 1.52 and Rs. 5.36 respectively. This clearly indicates that approximately 95% of the extra cost of the HC treatment can be recovered from the excess methane produced by introduction of the HC treatment in combination with food waste loading to TWE in AD when compared to the AD of raw TWE alone. Moreover, this also helps in eliminating the highly polluting recalcitrant tannery waste through reduction in COD in the AD process through a cost-effective method. Therefore, the AD of HC treated TWE supplemented with food waste may be considered to achieve close to self-sustainability of the total process.

Table 5.8 Recovery of HC treatment cost from the excess biogas produced by HC treated TWE and organic load using food waste

Substrate	**Biogas volume (mL)**	**Methane concentration**	**Cost of biogas with respective methane concentration (Rs.)**
Raw TWE	350	11.42%	0.1
HC treated TWE	670	19.4%	0.33
Raw TWE + organic loading (48 h)	2720	22.5%	1.52
HC treated TWE + organic loading (48 h)	7880	27%	5.36

5.3.7 Comparison of HC with other pretreatment techniques based on biogas production

Numerous studies as discussed in introduction section showed the efficacy to disintegrate the bio-refractory pollutants present in waste effluent and enhanced the biodegradability which resulted in increase in biogas production. In a study conducted by Ferrer et al., (2009) where low temperature thermal treatment used for the pretreatment of mixed sludge, with an exposure time within range of 9 to 48 hour at 70° C which resulted in an increase of 20% biogas production. Liao et al., (2016) also observed that pretreatment of sewage sludge using low temperature thermal treatment enhanced the biogas yield by 11% as compared to control. In a case of steam explosion as a pretreatment tool, Kepp et al., (2000) reported that use of steam explosion at 165-180 ° C with 30 to 60 min exposure time resulted in 20% increase in biogas production and in a similar study conducted by Zabranska et al., (2006), in which steam explosion at 140°C for 1 min at 0.6 MPa was used for the pretreatment of mixed sludge which resulted in increase in biogas production by 18%. Whereas different studies conducted by Xie et al., (2007), Hogan et al., (2004), and Neis et al., (2008) where US used as disintegration technique for the organic pollutant present in mixed sludge and it resulted in 45%, 50% and 30% increase in biogas production respectively. In a study carried out by Yu et al., (2014), electrochemical treatment was applied as a pretreatment tool for the enhancement of biodegradability which resulted in 60% increase in biogas volume. Wu et al., (2015) studied the efficacy of potassium ferrate oxidation as a pretreatment technique for enhancing the AD rate of activated sludge and they found that cumulative biogas increased by 44% as compared to untreated waste sample. In a study conducted by Cesaro and Belgiorno, (2013), ozonation and US used as a pretreatment techniques for solid waste and results showed that cumulative biogas increased by 37% and 11% as compared to control in ozonation and US respectively. In present study HC was used as pretreatment technique to increase the biodegradability and enhance the digestion rate and it was conducted at 5 bar pressure using slit venturi as a cavitating device for 2 hrs. It was observed that when HC treated sample was subjected to AD, biogas yield was increased by 2 folds in comparison to raw TWE sample. Whereas cumulative biogas production increased by 3 folds when food waste was added at an interval of 48 hrs. during AD of HC treated sample as compared to AD of TWE with a same dosing of food waste. Table 5.11 presented the comparison between pretreatment techniques on the basis of increase in biogas production.

Table 5.9 Comparison of HC with other pretreatment techniques based on biogas production

Type of waste	Pretreatment strategy	Increase in Biogas	Reference
Mixed sludge (66% WAS) (1.5% VSS)	US	45%	(Xie et al., 2007)
Mixed sludge	Thermal ; low temperature 70°C, 9-48 h	20%	(Ferrer et al., 2009)
Mixed sludge	Steam explosion: 140 °C 1 min 0.6 MPa	18%	(Zabranska et al., 2006)
Mixed sludge	Steam explosion: 165–180 °C 30–60 min	20%	(Kepp et al., 2000)
Mixed sludge (62% WAS)	Sonication: 25% of WAS	30%	(Neis et al., 2008)
Mixed sludge (50% WAS)	Sonication: 5 ultrasonic horns	50%	(Hogan et al., 2004)
Wastewater	Electrochemical	60%	(Yu et al., 2014)
Municipal solid waste	Ozonation and US	Ozonation: 37% US: 16%	(Cesaro and Belgiorno, 2013)
Activated sludge	Potassium ferrate oxidation	44%	(Wu et al., 2015)
Sewage sludge (TS=15%)	Low temperature thermal treatment	11%	(Liao et al., 2016)

Tannery wastewater	Hydrodynamic cavitation	Without food waste: 91% With food waste: 189%	Present study

5.4 Summary of the Chapter

The efficacy of HC pretreated TWE was studied for production of biogas along with COD reduction by subjecting to batch AD. The key findings drawn from present study can be summarized as follows;

- The experimental yield of biogas production is very less in comparison to theoretical biogas yield, which is because of the recalcitrant nature of TWE. However the experimental biogas yield for HC treated TWE was twice the yield of raw TWE.
- The AD of HC treated TWE provided better performances in comparison to raw TWE in terms of lower acclimatization time, higher COD reduction and more biogas generation. The cavitational effects have been effective in lowering the acclimatization time for treating 200 mL of HC pretreated TWE sample by 12 days and producing 66.7% higher yield of biogas as compared to raw TWE.
- It was established that the concentration of biomass mixed with TWE had a prominent effect on acclimatization and biogas generation. With higher seed concentration, biogas generation rate per day increased at higher rate in comparison to lower seed concentrations. The maximum 74.24 mL/g VS biogas production yield along with 45.73% reduction in COD was observed for 20% seed concentration over a period of 30 days with acclimatization period of 13 days.
- Though the initial increases in VFA content was observed up to 10 days in both sample. However VFA formation occurred at higher rate in HC treated sample as compared to raw TWE which can be attributed to the increase in the rate of acidogenesis reactions caused due to the HC treatment of the TWE sample.
- The simulation studies indicated that hydrolysis and acidogenesis reaction rates were higher in case of HC treated sample as compared to raw TWE. The hydrolysis rate constant (k) obtained by simulation study in case of HC treated TWE at a value of 0.0007 h^{-1} seven times higher than the value obtained for raw TWE at 0.0001 h^{-1}.

- The addition of food waste to the Raw and HC treated TWE during the AD process, increased the biogas generation. Biogas production increased by adding food waste to TWE feed up to 7.8 and 11.8 folds for raw and HC treated TWE samples respectively with organic loading rate of 48 h respectively.
- Cost analysis was carried out to recover the cost of HC treatment of TWE sample from the excess methane produced during AD with the HC treated TWE sample. Approximately 95% of the extra cost of the HC treatment can be recovered from the methane produced by introduction of the HC treatment in combination with food waste loading to TWE in AD. Therefore, the AD of HC treated TWE supplemented with food waste may be considered to achieve close to self-sustainability of the total process.

The cost of biogas produced by AD of HC treated TWE mixed with food waste recovers the extra cost of HC pretreatment when compared to raw TWE alone, establishing that HC as a pre-treatment tool has potential for COD reduction of the recalcitrant TWE as well as for enhancing the biogas yield when subjected to AD.

CHAPTER 6

Conclusion and recommendation for future work

6.1 Conclusion

This research study establishes that cavitation (HC and US) can be used either as a pretreatment or treatment technique for the enhanced degradation of organic pollutants present in TWE. Also cavitation based hybrid treatment techniques are efficient to treat highly complex industrial waste effluent, i. e. TWE. Intensification of treatment techniques has been achieved by combining cavitation with conventional physico–chemical treatment processes (coagulation) as well as advanced oxidation processes. However, process parameters such as coagulation dosage, inlet operating pressure, cavitation number, ultrasonic amplitude, initial characteristics of pollutants, and dosages of different oxidizing agents etc. which are specific for maximum degradation of organic molecules needs to be optimized for particular hybrid treatment strategy. Based on the present experimental work following important conclusions can be drawn

1. The reduction in organic load and suspended solids from raw waste effluents was primarily dependent on coagulant dosage, residual pH and raw wastewater effluent characteristics. It has been found that pH adjustment using HCl prior to coagulation requires less dosage of alum and also enhances the efficiency of HC pretreatment. In case of HC, lower operating inlet pressure yielded higher COD and TOC reduction for the pretreatment of CTWE as compared to higher operating inlet pressure. Dilution of the CTWE prior to HC treatment was found to be very effective in reduction of the COD, TOC and the TSS of the tannery effluent. The biodegradability index enhanced with pretreatment using combination of coagulation followed by HC and US respectively and it indicates that the pretreated tannery effluent can be treated in a subsequent AD units. Moreover, the energy efficiency evaluation exhibited that coagulation followed by HC for the pretreatment of TWE was found to be more energy efficient as compared to coagulation followed by US.
2. The efficacy of US as individual or with other oxidizing agents was discovered for the treatment of TWE on the basis of COD reduction. The study proved that in case of raw or un-coagulated TWE US as alone is more effective as compared to

US based hybrid treatment methods. It was observed that when US applied in combination with H_2O_2 and Fenton, decrease in COD reduction was observed whereas marginal increase in COD reduction was observed when US combined with sodium hypochlorite and ozone to treat raw TWE. This study shows that hybrid treatment strategies using US in combination with other oxidizing agents do not provide the intensified degradation of organic pollutants present in raw TWE. After reducing the organic load using coagulation, US with other oxidizing agents was successfully utilized for the enhanced degradation of organic pollutants present in TWE. Among all the US based hybrid treatment approaches, coagulation followed by US in combination with Fenton's reagent gave higher percentage reduction in COD. It can be concluded that US based hybrid oxidation processes are not suitable for treatment of raw TWE whereas they are efficient for treatment of TWE after reducing the organic load via coagulation.

3. The potential of HC based hybrid oxidation treatment process was investigated for the treatment of raw TWE and it was found that efficacy of treatment process get influenced by operating inlet pressure and oxidizing agent dosage. This study proved that the hybrid treatment techniques of using HC in combination with three oxidation agents i.e. O_3, H_2O_2 and Fenton's reagent provided intensified treatments with higher degradation efficiencies and an increase in the BI value, making the treated tannery wastewater more suitable for biological treatment. The biodegradability of raw TWE with significant reduction in COD and TOC was enhanced by applying only HC at optimum pressure. Dilution of the raw samples prior to HC did not enhance the HC degradation efficiency and therefore was not feasible as it only increases the operational treatment costs due to the requirement of treatment of larger volumes. The hybrid treatment techniques of using HC in combination with three oxidation agents i.e. O_3, H_2O_2 and Fenton's reagent provided intensified treatments with higher degradation efficiencies and an increase in the BI, making the treated water more suitable for biological treatment. Hybrid HC + Fenton shows the highest synergetic energy efficiency and cost effectiveness than HC and other hybrid process.

4. The efficacy of pretreated TWE using HC for production of biogas along with COD reduction was tested by subjecting the samples to batch AD. The AD of HC treated TWE provided better performances in comparison to raw TWE in terms of lower acclimatization time, higher COD reduction and more biogas generation. The cavitational effects have been effective in lowering the acclimatization time and producing the higher biogas volume. The pH of the slurry is significant, as acidic conditions i.e. pH below 5, caused inactivation of the methanogenic bacteria and biogas generation ceased. It was further established that the concentration of seed biomass mixed with TWE had a prominent effect on acclimatization and biogas generation. The experimental results were successfully validated through 'AD" simulator developed from the mathematical model representing the various degradation reactions along with the bacterial growth rate, decay rate and inhibitory mechanisms which was optimized based on the methane production in the AD process. The simulation studies indicated that hydrolysis, acidogenesis and acetogenesis reaction rates were higher in case of HC treated sample as compared to raw TWE, which resulted in higher COD reduction and biogas generation in AD of HC treated TWE sample. Food waste as an external carbon source was added to raw and HC treated TWE, which enhanced the response of biogas generation.

6.2 Recommendation for future work

Cavitation mainly HC was found to be an effective treatment tool for reducing the recalcitrant organic pollutants present in TWE, and the recommendation for future work for its industrial application are as follows

- In present study, only slit venturi was used as the cavitating device in HC reactor for the treatment of TWE. Different cavitating device based on its geometry may be studied for the treatment of industrial waste effluent and more studies need to be carried out in order to maximize the cavitational effect.
- HC has the potential to enhance the biodegradability of industrial effluent and be an effective pre-treatment tool prior to AD. Different combination of HC and HC based hybrid oxidation processes with biological treatment as a pre-treatment as

well as post treatment may be studied for the treatment of industrial waste effluent.

- New reactor configurations for various hybrid methods such as HC + electro oxidation and HC + photo catalyst may be developed for the treatment of TWE, which can be effectively applied on an industrial scale.
- More studies on modelling and simulation may be conducted to represent the cavitational effect and in order to understand the effect of various process parameters on the degradation rate of organic pollutants.

Appendix A

a) Sample calculation of cavitation number for slit venturi at 5 bar inlet pressure:

Downstream pressure (P_2) = 101325 Pa

Vapor pressure of water at 30°C (P_v) = 4242.14 Pa

Volumetric flow rate (v) = 592 LPH = 1.64×10^{-4} m^3/s

Dimension of the throat of the venturi: W = 1 mm, H = 1 mm, L = 3.14 mm

Flow area: $A_o = 3.14 \times 10^{-6}$ m^2

Velocity at the throat of venturi:

$V_o = V/A_o = 1.64 \times 10^{-4} / 3.14 \times 10^{-6} = 52.23$ m/s

Cavitation number is calculated as:

$$C_v = (P_2 - P_v)/(\frac{1}{2})\rho v^2$$

$$C_v = (101325-4242.14)/[(1/2)\times 1000\times (52.23)^2]$$

$$= 0.07$$

b) Energy efficiency evaluation for HC:

Energy delivered to the system in 120 minutes = 2200 W × 120 × 60 = 1.58×10^7 J

Volume treated in 120 minutes = 8 L

Energy required for per unit volume = $1.58 \times 10^7 / 8 = 1.98\times 10^6$ J/L

Energy efficiency for COD reduction in 120 minutes;

= $2960/ 1.98\times 10^6 = 1.494\times 10^{-3}$ mg/J [for CTWE 1]

= $1110/ 1.98\times 10^6 = 0.56\times 10^{-3}$ mg/J [for CTWE 2]

c) Energy efficiency evaluation for US:

Energy delivered to the system in 120 minutes

= 750 W × 120 × 60 = 5.4×10^6 J

Volume treated in 120 minutes = 300 ml = 0.3 L

Energy required for per unit volume = $5.4 \times 10^6 / 0.3 = 18\times 10^6$ J/L

Energy efficiency for COD reduction in 120 minutes;

= $4400/ 18\times 10^6 = 0.244\times 10^{-3}$ mg/J [for CTWE 1]

= $3520/ 18\times 10^6 = 0.195\times 10^{-3}$ mg/J [for CTWE 2]

d) Energy and cost estimation for coagulation + US system:

Energy efficiency evaluation of treatment processes on the basis of energy delivered:

Energy delivered to the US system in 2 h + orbital shaker system in 15 minutes
= 750W×2h + 1kW×0.25h
= 1.75 kWh

Volume treated in 2 h = 300 mL = 0.3 L
Energy required for treating the one liter of TWE = 1.75 kWh/ 0.3 L = **5.83 kWh/L**

Quantum of COD reduced = 7520 mg
Energy required for the reduction of one mg of COD = 1.75 kWh/7520 mg COD
= **0.00023 kWh/mg COD**

Cost estimation of the treatment:

Cost of the electricity consumed at the rate of 9 Rs per kWh = 1.75 kWh × 9 Rs/kWh
= 15.75 Rs
= 0.222 USD

Cost of the electricity for treating the one liter of TWE = 15.75 Rs/0.3 L = **52.5 Rs/L**
= 0.74 USD/L

Approximate Cost of the commercial grade Alum = 12.5 Rs/kg = 0.176 USD/kg
Optimized dose of Alum = 5g/L Alum
Total g of alum used in 0.3 liters of TWE = (5g/L×0.3L) = 1.5 g
Cost of the 1.5 g Alum = 1.5g×12.5Rs/kg = 0.019 Rs. = 0.00026 USD

Total cost of treatment = Cost of the electricity + Cost of the 4.5g Alum
= 15.75 Rs + 0.019 Rs = 15.77 Rs.
= 0.222 USD

Cost of the treatment for treating the one liter of TWE = 15.77 Rs/0.3 L
= **52.66 Rs/L**
= 0.74 USD/L

Cost of the treatment for the reduction of one mg of COD = 15.77 Rs/7520 mg COD
= **0.002 Rs/mg COD**
= 0.00003USD/mg COD

e) Energy and cost estimation for coagulation + HC system:

Energy efficiency evaluation of treatment processes on the basis of energy delivered:

Energy delivered to the HC system in 2 h = 2.2 kW×2h = 4.4 kWh
Volume treated in 2 h = 8 L
Energy required for treating the one liter of TWE = 4.4 kWh/ 8L = **0.55 kWh/L**
Quantum of COD reduced = 15640 mg
Energy required for the reduction of one mg of COD = 4.4 kWh/15640 mg COD
= **0.00028 kWh/mg COD**

Cost estimation of the treatment:

Cost of the electricity consumed at the rate of 9 Rs per kWh = 4.4 kWh × 9 Rs/kWh
= 39.6 Rs
= 0.559 USD

Approximate Cost of the commercial grade Alum = 12.5 Rs/kg = 0.176 USD/kg
Optimized dose of Alum = 5g/L Alum
Total g of alum used in 8 liters of TWE = (5g/L×8L) = 40 g
Cost of the 40 g Alum = 40g×12.5Rs/kg = 0.5 Rs. = 0.007 USD

Total cost of treatment = Cost of the electricity + Cost of the 40 g Alum
= 39.6 Rs + 0.5 Rs = 40.1 Rs.
= 0.566 USD
Cost of the treatment for treating the one liter of TWE = 40.1 Rs/8 L
= **5 Rs/L**
= 0.07 USD/L

Cost of the treatment for the reduction of one mg of COD = 40.1 Rs/15640 mg COD
= **0.0026 Rs/mg COD**
= 0.000036 USD/mg COD

Appendix B

Energy and cost estimation calculations:

a) US system:

Energy efficiency evaluation of treatment processes on the basis of energy delivered:

Energy delivered to the US system in 2 h = 750W×2h = 1.5 kWh

Volume treated in 2 h = 300 mL = 0.3 L

Energy required for treating the one liter of TWE = 1.5 kWh/ 0.3 L = **5 kWh/L**

Quantum of COD reduced = 1080 mg

Energy required for the reduction of one mg of COD = 1.5 kWh/1080 mg COD

= **0.0014kWh/mg COD**

$$\text{Cavitational yield} = \frac{[\text{COD}]}{\text{P}_\text{E} \times \text{t}} \times \text{V}$$

= 1080 mg × 0.3 L/1.5 kWh = 216 mg L/kWh

Cost estimation of the treatment:

1 USD = 70.90 INR (Rs) as dated on 27/11/2018

Cost of the electricity consumed at the rate of 9 Rs per kWh = 1.5 kWh × 9 Rs/kWh

= 13.5 Rs

= 0.19 USD

Cost of the treatment for treating the one liter of TWE = 13.5 Rs/0.3 L = **45 Rs/L**

= 0.64 USD/L

Cost of the treatment for the reduction of one mg of COD = 13.5 Rs/1080 mg COD

= **0.0125 Rs/mg COD**

= 0.000176 USD/mg COD

b) US + Ozone system:

Energy efficiency evaluation:

Energy delivered to the US + Ozone system in 2 h =

(Energy input to the US + Energy input to the ozonator) kW × time (h)

= (0.75 + 0.3) W × 2h = 2.1 kWh

Volume treated in 2 h = 0.3 L

Energy required for treating the one liter of TWE = 2.1 kWh/0.3 L = **7 kWh/L**

Quantum of COD reduced = 2040 mg

Energy required for the reduction of one mg of COD = 2.1 kWh/2040 mg COD

= **0.001 kWh/mg COD**

$$\text{Cavitational yield} = \frac{[\mathrm{COD}]}{\mathrm{P_E} \times \mathrm{t}} \times \mathrm{V}$$

= 2040 mg × 0.3 L/2.1 kWh = 291.43 mg L/kWh

Cost estimation of the treatment:

Cost of the electricity consumed at the rate of 9 Rs per kWh = 2.1 kWh × 9 Rs/kWh

= 18.9 Rs

= 0.267 USD

Cost of the treatment for treating the one liter of TWE = 18.9 Rs/0.3 L = **63 Rs/L**

= 0.888 USD/L

Cost of the treatment for the reduction of one mg of COD = 18.9 Rs/2040 mg COD

= **0.0093 Rs/mg COD**

= 0.00013 USD/mg COD

c) US + NaOCl system:

Energy efficiency evaluation:

Energy required for treating the one liter of TWE = 1.5 kWh/ 0.3 L = **5 kWh/L**

Quantum of COD reduced = 2220 mg

Energy required for the reduction of one mg of COD = 1.5 kWh/2220 mg

= **0.00068kWh/mg**

$$\text{Cavitational yield} = \frac{[\mathrm{COD}]}{\mathrm{P_E} \times \mathrm{t}} \times \mathrm{V}$$

= 2220 mg × 0.3 L/1.5 kWh = 444 mg L/kWh

Cost estimation of the treatment:

Cost of the electricity consumed at the rate of 9 Rs per kWh = 1.5 kWh × 9 Rs/kWh

= 13.5 Rs

= 0.19 USD

Cost of the electricity consumed for treating the one liter of TWE = 13.5 Rs/0.3L

= 45 Rs /L

= 0.64 USD/L

Approximate Cost of the commercial grade NaOCl (4-6%) = 150 Rs/L = 2.11 USD/L

Optimized dose of NaOCl = 2 g/L of NaOCl (100%) = 40 g/L of NaOCl (4-6%≈ 5%)

Density of 4-6% NaOCl = 1.1 g/mL

Total volume of NaOCl (5%) used in 0.3 liters of TWE = (40 g/L×0.3 L)/1.1g/mL

= 10.9 mL

Cost of the 10.9 mL of NaOCl (5%) = 10.9 mL×150Rs/L = 1.64 Rs. = 0.023 USD

Total cost of treatment = Cost of the electricity + 10.9 mL of NaOCl

= 13.5 Rs + 1.64 Rs = 15.14 Rs.

= 0.21 USD

Cost of the treatment for treating the one liter of TWE = 15.14 Rs/0.3 L

= **50.46 Rs/L**

= 0.71 USD/L

Cost of the treatment for the reduction of one mg of COD = 15.14 Rs/2220 mg COD

= **0.0068 Rs/mg COD**

= 0.00009 USD/mg COD

d) Coagulation:

Energy efficiency evaluation:

Energy delivered to the orbital shaker 15 minutes = 1 kW×0.25h = 0.25 kWh

Volume treated in 15 minutes = 300 mL = 0.3 L

Energy required for treating the one liter of TWE = 0.25 kWh/ 0.3 L = **0.833 kWh/L**

Quantum of COD reduced = 4380 mg

Energy required for the reduction of one mg of COD = 0.25 kWh/4380 mg

= **0.00006 kWh/mg**

Cost estimation of the treatment:

Cost of the electricity consumed at the rate of 9 Rs per kWh = 0.25 kWh × 9 Rs/kWh

= 2.25 Rs

= 0.0317 USD

Approximate Cost of the commercial grade Alum = 12.5 Rs/kg = 0.176 USD/kg

Optimized dose of Alum= 15g/L Alum

Total g of alum used in 0.3 liters of TWE = (15g/L×0.3L) = 4.5 g

Cost of the 4.5 g Alum = 4.5g×12.5Rs/kg = 0.056 Rs. = 0.00079 USD

Total cost of treatment = Cost of the electricity + Cost of the 4.5g Alum

= 2.25 + 0.056 = 2.306 Rs = 0.0325 USD

Cost of the treatment for treating the one liter of TWE = 2.306 Rs/0.3 L

= **7.69 Rs/L**

= 0.108 USD/L

Cost of the treatment for the reduction of one mg of COD = 2.306 Rs/4380 mg COD

= **0.0005 Rs/mg COD**

= 0.000007 USD/mg COD

e) Coagulation + US system:

Energy efficiency evaluation of treatment processes on the basis of energy delivered:

Energy delivered to the US system in 2 h + orbital shaker system in 15 minutes

= 750W×2h + 1kW×0.25h

= 1.75 kWh

Volume treated in 2 h = 300 mL = 0.3 L

Energy required for treating the one liter of TWE = 1.75 kWh/ 0.3 L = **5.83 kWh/L**

Quantum of COD reduced = 5260 mg

Energy required for the reduction of one mg of COD = 1.75 kWh/5260 mg COD

= **0.00033 kWh/mg COD**

Cost estimation of the treatment:

Cost of the electricity consumed at the rate of 9 Rs per kWh = 1.75 kWh × 9 Rs/kWh

= 15.75 Rs

= 0.222 USD

Cost of the electricity for treating the one liter of TWE = 15.75 Rs/0.3 L = **52.5 Rs/L**

= 0.74 USD/L

Approximate Cost of the commercial grade Alum = 12.5 Rs/kg = 0.176 USD/kg

Optimized dose of Alum= 15g/L Alum

Total g of alum used in 0.3 liters of TWE = (15g/L×0.3L) = 4.5 g

Cost of the 4.5 g Alum = 4.5g×12.5Rs/kg = 0.056 Rs. = 0.00079 USD

Total cost of treatment = Cost of the electricity + Cost of the 4.5g Alum

= 15.75 Rs + 0.056 Rs = 15.8 Rs.

= 0.222 USD

Cost of the treatment for treating the one liter of TWE = 15.8 Rs/0.3 L

= **52.66 Rs/L**

= 0.74 USD/L

Cost of the treatment for the reduction of one mg of COD = 15.8 Rs/5260 mg COD

= **0.003 Rs/mg COD**

= 0.00004 USD/mg COD

f) Coagulation + US + H_2O_2 system:

Energy efficiency evaluation:

Energy delivered to the US system in 2 h + orbital shaker 15 minutes

= 750W×2h + 1kW×0.25h

= 1.75 kWh

Volume treated in 2 h = 300 mL = 0.3 L

Energy required for treating the one liter of TWE = 1.75 kWh/ 0.3 L = **5.83 kWh/L**

Quantum of COD reduced = 5900 mg

Energy required for the reduction of one mg of COD = 1.75 kWh/5900 mg COD

= **0.0003 kWh/mg COD**

Cost estimation of the treatment:

Cost of the electricity consumed at the rate of 9 Rs per kWh = 1.75 kWh × 9 Rs/kWh

= 15.75 Rs

= 0.222 USD

Cost of the electricity for treating the one liter of TWE = 15.75 Rs/0.3 L = **52.5 Rs/L**

= 0.74 USD/L

Approximate Cost of the commercial grade Alum = 12.5 Rs/kg = 0.176 USD/kg

Optimized dose of Alum= 15g/L Alum

Total g of alum used in 0.3 liters of TWE = (15g/L×0.3L) = 4.5 g

Cost of the 4.5 g Alum = 4.5g×12.5Rs/kg = 0.056 Rs. = 0.00079 USD

Approximate Cost of the commercial grade H_2O_2 (30% w/w) = 40 Rs/L = 0.6 USD/L

Optimized dose of H_2O_2 = 18 g/L (100%) = 60 g/L of H_2O_2 of 30% (w/w)

Density of 30% (w/w) H_2O_2= 1.11 g/mL

Total volume of H_2O_2 (30% w/w) used in 7 liters of TWE = (60 g/L×0.3L)/1.11g/mL

= 16.2 mL

Cost of the 16.2 mL of H_2O_2 (30% w/w) = 16.2 mL×40Rs/L = 0.648 Rs. = 0.0091 USD

Total cost of treatment =

Cost of the electricity + Cost of the 16.2 mL of H_2O_2 (30% w/w) + Cost of the 4.5g Alum

= 15.75 Rs + 0.648 Rs + 0.056 Rs = 16.45 Rs.

= 0.232 USD

Cost of the treatment for treating the one liter of TWE = 16.45 Rs/0.3 L

= **54.833 Rs/L**

= 0.77 USD/L

Cost of the treatment for the reduction of one mg of COD = 16.45 Rs/5900 mg COD

= **0.0028 Rs/mg COD**

= 0.00004 USD/mg COD

g) Coagulation + US + Fenton's reagent system:

Energy efficiency evaluation:

Energy delivered to the US system in 2 h + orbital shaker 15 minutes

= 750W×2h + 1kW×0.25h

= 1.75 kWh

Volume treated in 2 h = 300 mL = 0.3 L

Energy required for treating the one liter of TWE = 1.75 kWh/ 0.3 L = **5.83 kWh/L**

Quantum of COD reduced = 7060 mg

Energy required for the reduction of one mg of COD = 1.75 kWh/7060 mg COD

= **0.0008 kWh/mg COD**

Cost estimation of the treatment:

Cost of the electricity consumed at the rate of 9 Rs per kWh = 1.75 kWh × 9 Rs/kWh

= 15.75 Rs

= 0.222 USD

Cost of the electricity for treating the one liter of TWE = 15.75 Rs/0.3 L = **52.5 Rs/L**

= 0.74 USD/L

Approximate Cost of the commercial grade Alum = 12.5 Rs/kg = 0.176 USD/kg

Optimized dose of Alum = 15g/L Alum

Total g of alum used in 0.3 liters of TWE = (15g/L×0.3L) = 4.5 g

Cost of the 4.5 g Alum = 4.5g×12.5Rs/kg = 0.056 Rs. = 0.00079 USD

Approximate Cost of the commercial grade H_2O_2 (30% w/w) = 40 Rs/L = 0.6 USD/L

Optimized dose of H_2O_2 = 18 g/L (100%) = 60 g/L of H_2O_2 of 30% (w/w)

Density of 30% (w/w) H_2O_2= 1.11 g/mL

Total volume of H_2O_2 (30% w/w) used in 7 liters of TWE = (60 g/L×0.3L)/1.11g/mL

= 16.2 mL

Cost of the 16.2 mL of H_2O_2 (30% w/w) = 16.2 mL×40Rs/L = 0.648 Rs. = 0.0091 USD

Optimized dose of ferrous sulfate = 4 g/L

Total weight of ferrous sulfate used in 0.3 liters of TWE = 4g/L×0.3L = 1.2 g

Approximate cost of the commercial grade ferrous sulfate = 90 Rs/kg

Cost of the 1.2 g of ferrous sulfate = 1.2 g × 90 Rs/kg = 0.108 Rs.

= 0.0015 USD

Total cost of treatment =

Cost of the electricity + Cost of the 16.2 mL of H_2O_2 (30% w/w) + Cost of the 4.5g Alum + Cost of the 1.2 g of ferrous sulfate

= 15.75 Rs + 0.648 Rs + 0.056 Rs + 0.108

= 14.31 Rs.

= 0.234 USD

Cost of the treatment for treating the one liter of TWE = 16.56 Rs/0.3 L

= **55.2Rs/L**

= 0.78 USD/L

Cost of the treatment for the reduction of one mg of COD = 16.56 Rs/7060 mg COD

= **0.0023 Rs/mg COD**

= 0.000033 USD/mg COD

h) Coagulation + US + NaOCl system:

Energy efficiency evaluation:

Energy delivered to the US system in 2 h + orbital shaker 15 minutes

= 750W×2h + 1kW×0.25h

= 1.75 kWh

Volume treated in 2 h = 300 mL = 0.3 L

Energy required for treating the one liter of TWE = 1.75 kWh/ 0.3 L = **5.83 kWh/L**

Quantum of COD reduced = 5880 mg

Energy required for the reduction of one mg of COD = 1.75 kWh/5880 mg COD

= **0.0003 kWh/mg COD**

Cost estimation of the treatment:

Cost of the electricity consumed at the rate of 9 Rs per kWh = 1.75 kWh × 9 Rs/kWh

= 15.75 Rs

= 0.222 USD

Cost of the electricity for treating the one liter of TWE = 15.75 Rs/0.3 L = **52.5 Rs/L**

= 0.74 USD/L

Approximate Cost of the commercial grade Alum = 12.5 Rs/kg = 0.176 USD/kg

Optimized dose of Alum = 15g/L Alum

Total g of alum used in 0.3 liters of TWE = (15g/L×0.3L) = 4.5 g

Cost of the 4.5 g Alum = 4.5g×12.5Rs/kg = 0.056 Rs. = 0.00079 USD

Approximate Cost of the commercial grade NaOCl (5%) = 150 Rs/L = 2.11 USD/L

Optimized dose of NaOCl = 1.5 g/L (100%) = 30 g/L of NaOCl (5%)

Density of 5% NaOCl = 1.1 g/mL

Total volume of NaOCl (5%) used in 0.3 liters of TWE = (30 g/L×0.3 L)/1.1g/mL

= 8.2 mL

Cost of the 8.2 mL of NaOCl (5%) = 8.2 mL×150 Rs/L = 1.23 Rs. = 0.017 USD

Total cost of treatment

= Cost of the electricity + 8.2 mL of NaOCl + Cost of the 4.5g Alum

= 15.75 Rs + 1.23 Rs + 0.056 Rs = 17.04 Rs. = 0.24 USD

Cost of the treatment for treating the one liter of TWE = 17.04 Rs/0.3 L

= **56.8 Rs/L**

= 0.8 USD/L

Cost of the treatment for the reduction of one mg of COD = 17.04 Rs/5880 mg COD

= **0.0029 Rs/mg COD**

= 0.00004 USD/mg COD

i) Coagulation + US + Ozone system:

Energy efficiency evaluation:

Energy delivered to the US + Ozone system in 2 h + orbital shaker system in 15 minutes

= (0.75 + 0.3) W × 2h + 1kW×0.25h

= 2.35 kWh

Volume treated = 0.3 L

Energy required for treating the one liter of TWE = 2.35 kWh/0.3 L = **7.8 kWh/L**

Quantum of COD reduced = 5840 mg

Energy required for the reduction of one mg of COD = 2.35 kWh/5840 mg COD

= **0.0004 kWh/mg COD**

Cost estimation of the treatment:

Cost of the electricity consumed at the rate of 9 Rs per kWh = 2.35 kWh × 9 Rs/kWh

= 21.15 Rs

= 0.3 USD

Approximate Cost of the commercial grade Alum = 12.5 Rs/kg = 0.176 USD/kg

Optimized dose of Alum = 15g/L Alum

Total g of alum used in 0.3 liters of TWE = (15g/L×0.3L) = 4.5 g

Cost of the 4.5 g Alum = 4.5g×12.5Rs/kg = 0.056 Rs. = 0.00079 USD

Total cost of treatment = Cost of the electricity + Cost of the 4.5g Alum

= 21.15 Rs + 0.056 Rs = 21.21 Rs. = 0.3 USD

Cost of the treatment for treating the one liter of TWE = 21.21 Rs/0.3 L = **70.7 Rs**

= 1 USD/L

Cost of the treatment for the reduction of one mg of COD = 21.21 Rs/5840 mg COD

= **0.0036 Rs/mg COD**

= 0.00005 USD/mg COD

Appendix C

Energy and cost estimation calculations:

1. **HC system:**

Energy efficiency evaluation of treatment processes on the basis of energy delivered:

Energy delivered to the HC system in 2 h = 1.1 kW×2h = 2.2 kWh

Volume treated in 2 h = 7 L

Energy required for treating the one liter of TWE = 2.2 kWh/ 7L = **0.314 kWh/L**

Quantum of COD reduced = 1400 mg

Energy required for the reduction of one mg of COD = 2.2 kWh/1400 mg COD

= **0.0016 kWh/mg COD**

$$\text{Cavitational yield} = \frac{[\text{COD}]}{\text{P}_\text{E} \times \text{t}} \times \text{V}$$

= 1400 mg × 7 L/2.2 kWh = 4454.54 mg L/kWh

Cost estimation for treatment:

1 USD = 68.04 INR (Rs) as dated on 22/05/2018

Cost of the electricity consumed at the rate of 9 Rs per kWh = 2.2 kWh × 9 Rs/kWh

= 19.8 Rs = 0.297 USD

Cost of the treatment for treating the one liter of TWE = 19.8 Rs/7L = **2.8 Rs/L**

= 0.042 USD/L

Cost of the treatment for the reduction of one mg of COD = 19.8 Rs/1400 mg COD

= **0.0141 Rs/mg COD**

= 0.00021 USD/mg COD

2. **HC + Ozone system:**

Energy efficiency evaluation:

Energy delivered to the HC + Ozone system in 2 h =

(Energy input to the HC + Energy input to the ozonator) kW × time (h)

= (1.1 + 0.3) W × 2h

= 2.8 kWh

Volume of TWE treated in 2 h = 7 L

Energy required for treating the one liter of TWE = 2.8kWh/7L = **0.4 kWh/L**

Quantum of COD reduced = 2660 mg

Energy required for the reduction of one mg of COD = 2.8 kWh/2660 mg COD

= **0.0011 kWh/mg COD**

$$\text{Cavitational yield} = \frac{[\text{COD}]}{P_E \times t} \times V$$

= 2660 mg × 7 L/2.8 kWh = 6650.0 mg L/kWh

Cost estimation for treatment:

Cost of the electricity consumed at the rate of 9 Rs per kWh = 2.8 kWh × 9 Rs/kWh

= 25.2 Rs = 0.378 USD

Cost of the treatment for treating the one liter of TWE = 25.2 Rs/7 L = **3.6 Rs/L**

= 0.054 USD/L

Cost of the treatment for the reduction of one mg of COD = 25.2 Rs/2660 mg COD

= **0.0095 Rs/mg COD**

= 0.00014 USD/mg COD

3. HC + H_2O_2 system:

Energy efficiency evaluation:

Energy required for treating the one liter of TWE = 2.2 kWh/ 7L = **0.314 kWh/L**

Quantum of COD reduced = 3140 mg

Energy required for the reduction of one mg of COD = 2.2 kWh/3140mg

= **0.0007kWh/mg**

$$\text{Cavitational yield} = \frac{[\text{COD}]}{P_E \times t} \times V$$

= 3140 mg × 7 L/2.2 kWh = 9990.9 mg L/kWh

Cost estimation for treatment:

Cost of the electricity consumed at the rate of 9 Rs per kWh = 2.2 kWh × 9 Rs/kWh

= 19.8 Rs = 0.297 USD

Cost of the electricity consumed for treating the one liter of TWE = 19.8 Rs/7L

= 2.8 Rs/L

= 0.042 USD/L

Approximate Cost of the commercial grade H_2O_2 (30% w/w) = 40 Rs/L = 0.6 USD/L

Optimized dose of H_2O_2= 9.51g/L = 31.71 g/L of H_2O_2 of 30% (w/w)

Density of 30% (w/w) H_2O_2= 1.11 g/mL

Total volume of H_2O_2 (30% w/w) used in 7 liters of TWE = (31.71g/L×7L)/1.11g/mL

= 200 mL

Cost of the 200 mL of H_2O_2 (30% w/w) = 200 mL×40Rs/L = 8 Rs. = 0.12 USD

Total cost of treatment = Cost of the electricity + Cost of the 200 mL of H_2O_2 (30% w/w)

= 19.8 Rs + 8 Rs = 27.8 Rs

= 0.417 USD

Cost of the treatment for treating the one liter of TWE = 27.8 Rs/7 L

= **3.97 Rs/L**

= 0.059 USD/L

Cost of the treatment for the reduction of one mg of COD = 27.8 Rs/3140 mg COD

= **0.0089 Rs/mg COD**

= 0.00013 USD/mg COD

4. **HC + Fenton's reagent system:**

Energy efficiency evaluation:

Energy required for treating the one liter of TWE = 2.2 kWh/ 7 L = **0.314 kWh/L**

Quantum of COD reduced = 4900 mg

Energy required for the reduction of one mg of COD = 2.2 kWh/4900mg

= **0.0004kWh/mg COD**

$$\text{Cavitational yield} = \frac{[\text{COD}]}{\text{P}_\text{E} \times \text{t}} \times \text{V}$$

= 4900 mg × 7 L/2.2 kWh = 15590.9 mg L/kWh

Cost estimation for treatment:

Cost of the electricity consumed at the rate of 9 Rs per kWh = 2.2 kWh × 9 Rs/kWh

= 19.8 Rs

= 0.297 USD

Cost of the electricity consumed for treating the one liter of TWE

= 19.8 Rs/7 L = 2.8 Rs/L

= 0.042 USD/L

Cost of the 200 mL of H_2O_2 (30% w/w) = 200 mL×40Rs/L = 8 Rs.

= 0.12 USD

Optimized dose of ferrous sulfate = 3 g/L

Total weight of ferrous sulfate used in 7 liters of TWE = 3g/L×7L = 21 g

Approximate cost of the commercial grade ferrous sulfate = 90Rs/kg

= 1.35 USD/kg

Cost of the 21 g of ferrous sulfate = 21 g × 90Rs/kg = 1.89 Rs.

= 0.028 USD

Total cost of treatment =

Cost of the electricity + Cost of the 200 mL of H_2O_2 + Cost of the 21 g of ferrous sulfate

= 19.8 Rs + 8 Rs + 1.89 Rs = 29.69 Rs

= 0.445 USD

Cost of the treatment for treating the one liter of TWE = 29.69 Rs/7 L= **4.24 Rs/L**

= 0.064 USD/L

Cost of the treatment for the reduction of one mg of COD = 29.69 Rs/4900 mg

= **0.0061 Rs/mg COD**

= 0.00009 USD/mg COD

Appendix D

Cost estimation calculations:

HC treatment cost:

Energy delivered to the HC system in 2 h = 1.1 kW×2h = 2.2 kWh

Cost of the electricity consumed at the rate of 9 Rs per kWh = 2.2 kWh × 9 Rs/kWh
= 19.8 Rs

Volume treated in 2 h = 7 L

Cost of the electricity consumed for treating 2 L TWE = 19.8×2/7 = 5.66 Rs/L

Cost of Biogas generated by AD of different samples (data from Fig.14):

Cost of 1 L biogas consisting of 60% methane = 1.5 Rs.

(A)Raw TWE in 2 L bioreactor:

Biogas generated during AD = 350 mL= 0.35 L

Methane present in biogas = 39.55 mL = 0.040 L

Methane percentage in biogas = (0.04×100)/0.35 = 11.42%

Biogas generated consisting of 11.42% methane = 350 mL= 0.35 L

Cost of 1 L biogas consisting of 11.42% methane = (1.5×0.1142)/0.6 = 0.29 Rs.

Cost of 0.35 L biogas consisting of 11.42% methane = 0.29×0.35 = 0.10 Rs.

(B)HC treated TWE in 2 L bioreactor:

Biogas generated during AD = 670 mL= 0.67 L

Methane present in biogas = 130.047 mL = 0.13 L

Methane percentage in biogas = (0.13×100)/0.67 = 19.4%

Biogas generated consisting of 19.4% methane = 670 mL= 0.67 L

Cost of 1 L biogas consisting of 19.4% methane = (1.5×0.194)/0.6 = 0.49 Rs.

Cost of 0.67 L biogas consisting of 19.4% methane = 0.49×0.67 = 0.33 Rs.

(C)Raw TWE in 2 L bioreactor with organic loading every 48 h:

Biogas generated During AD = 2720 mL= 2.72 L

Methane present in biogas = 612 mL = 0.612 L

Methane percentage in biogas = (0.612×100)/2.72 = 22.5%

Biogas generated consisting of 22.5% methane = 2720 mL= 2.72 L

Cost of 1 L biogas consisting of 22.5% methane = (1.5×0.225)/0.6 = 0.56 Rs.

Cost of 2.72 L biogas consisting of 22.5% methane = 0.56×2.72 = 1.52 Rs.

(D)HC treated TWE in 2 L bioreactor with organic loading every 48 h:

Biogas generated during AD = 7880 mL= 7.88 L

Methane present in biogas = 2135 mL = 2.135 L

Methane percentage in biogas = (2.135×100)/7.88 = 27%

Biogas generated consisting of 27% methane = 7880 mL= 7.88 L

Cost of 1 L biogas consisting of 27% methane = (1.5×0.27)/0.6 = 0.68 Rs.

Cost of 7.88 L biogas consisting of 27% methane = 0.68×7.88 = 5.36 Rs.

MATLAB programming for 'AD' simulator:

```
function[error,X] = Bad(Um)
% S0 = 5.25; (Raw TWE)
S0 = 4.9; (HC treated TWE)
S = [0 0 0 0 0 0 0 0 0 0 0 0 0];
PP = [0.0550 0.0125 0.0800 0.0440 0.0240]; %% bacterial Composition
y = [PP S0 S];
t = [0:24*5:24*35];
[t X] = ode15s(@(t,y)ODEModel(t,y,Um),t,y,Um)
y_exp = [0; 0.00172; 0.008586; 0.020115; 0.04488; 0.05829; 0.0625; 0.065]; %% CH4/2 (HC treated)
% y_exp = [0; 0.00046; 0.00324; 0.009975; 0.01764; 0.01968; 0.019805; 0.019775]; %% CH4/2 (raw)
y_model = X(:,13);
 sum1 = 0;
 for i = 1:8
     sum1= sum1 + (y_model(i) - y_exp(i))^2;
 end
 error = sum1;
end
```

```
function[f,X,S0,S] = ODEModel(t,y,Um)
Kla = 4.17;
%% growth rate
Ks = [Um(7) Um(8) Um(9) Um(10) Um(11) Um(12)]; %% Rate Constant
K1 = [0.0321 0.3205 0.0036 10 35 21 29 16]; %% Rate Constant
Y = [Um(13) Um(14) Um(15) Um(16) Um(17)];
b = [Um(18) Um(19) Um(20) Um(21) Um(22)];
f = [10.1 13.5 11.4 16.7 500];     %% conversion factor
S5e = 1/74000;   %equilibrium composition
S6e = 1/21000;  %equilibrium composition
S7e = 1/48500;  %equilibrium composition
Q = 4.93;
FpH = 1;
Vl = 2.0;
Vg = 0.5;
X = y(1:5);
S0 = y(6);
S = y(7:19);
k = Um(6);
% specific growth rate equations
% specific growth rate of acidogens, X1
U(1) = Um(1)*S(1)*FpH/(Ks(1)+S(1))*(1+ S(5)/K1(1));
 % specific growth rate of propionate degrading acetogens, X2
U(2) = Um(2)*S(2)*FpH/(Ks(2)+S(2))*(1+(S(5)/K1(2)));
 % specific growth rate of butyrate degrading acetogens, X3
U(3) = Um(3)*S(3)*FpH/((Ks(3)+(1+S(4)/K1(3))+S(3))*(1+S(5)/K1(4)));
 % specific growth rate of acitoclastic methanogens, X4
U(4) = Um(4)*S(4)*FpH/((Ks(4)+S(4))*(1+S(3)/K1(6))*(1+S(2)/K1(5)));
 % specific growth rate of hydrogenotrophic methanogens, X5
```

```
U(5) =
Um(5)*S(5)*S(6)*FpH/((Ks(5)+S(5))*(Ks(6)+S(6))*(1+S(3)/K1(8))*(1+S(2)/K1(7)));
 % material balance for bacterial group
% Acidogens (X1)
dXdt(1) = U(1)*X(1)-b(1)*X(1);
% propionate degrading acetogens (X2)
dXdt(2) = U(2)*X(2)-b(2)*X(2);
% butyrate degrading acetogens (X3)
dXdt(3) = U(3)*X(3)-b(3)*X(3);
% Acetoclastic metanogens (X4)
dXdt(4) = U(4)*X(4)-b(4)*X(4);
% Hydrogentrophic methanogens (X5)
dXdt(5) = U(5)*X(5)-b(5)*X(5);

% material balance for substrate
% food waste, S0
dS0dt = -k*S0;
% organic monomers, S1
dSdt(1) = -(U(1)/Y(1))*X(1)+k*S0;
% propionate, S2
dsdt(2) = 0.064*(1-f(1)*Y(1))*(U(1)/Y(1))*X(1)-(U(2)/Y(2))*X(2);
% butayrate, S3
dSdt(3) = 0.069*(1-f(1)*Y(1))*(U(1)/Y(1))*X(1)-(U(3)/Y(3))*X(3);
%dSdt(3) = 0.071*(1-f(1)*Y(1))*(U(1)/Y(1))*X(1)-(U(3)/Y(3))*X(3); %% raw
% Acetate, S4
dSdt(4) = 0.114*(1-f(1)*Y(1))*(U(1)/Y(1))*X(1)+(1-
f(2)*Y(2))*(U(2)/Y(2))*X(2)+2*(1-f(3)*Y(3))*(U(3)/Y(3))*X(3)-(U(4)/Y(4))*X(4);
% Hydrogen, S5
dSdt(5) = 0.218*(1-f(1)*Y(1))*(U(1)/Y(1))*X(1)+3*(1-
f(2)*Y(2))*(U(2)/Y(2))*X(2)+2*(1-f(3)*Y(3))*(U(3)/Y(3))*X(3)-(U(5)/Y(5))*X(5);
```

```
%dSdt(5) = 0.131*(1-f(1)*Y(1))*(U(1)/Y(1))*X(1)+3*(1-
f(2)*Y(2))*(U(2)/Y(2))*X(2)+2*(1-f(3)*Y(3))*(U(3)/Y(3))*X(3)-(U(5)/Y(5))*X(5);
%% raw
% Carbondioxide, S6
dSdt(6) = 0.152*(1-f(1)*Y(1))*(U(1)/Y(1))*X(1)+(1-f(2)*Y(2))*(U(2)/Y(2))*X(2)+(1-
f(4)*Y(4))*(U(4)/Y(4))*X(4)-0.25*(1-f(5)*Y(5))*(U(5)/Y(5))*X(5)-
0.5*f(5)*U(5)*X(5);
% methane, X7
dSdt(7) = (1-f(4)*Y(4))*(U(4)/Y(4))*X(4)+0.25*(1-f(5)*Y(5))*(U(5)/Y(5))*X(5);
% gas concentarion and transport, H2
dSdt(8) = 0.218*(1-f(1)*Y(1))*(U(1)/Y(1))*X(1)+3*(1-
f(2)*Y(2))*(U(2)/Y(2))*X(2)+2*(1-f(3)*Y(3))*(U(3)/Y(3))*X(3)-(U(5)/Y(5))*X(5) +
Kla*(S5e-S(8));
%dSdt(8) = 0.131*(1-f(1)*Y(1))*(U(1)/Y(1))*X(1)+3*(1-
f(2)*Y(2))*(U(2)/Y(2))*X(2)+2*(1-f(3)*Y(3))*(U(3)/Y(3))*X(3)-(U(5)/Y(5))*X(5) +
Kla*(S5e-S(8));  %% raw
dSdt(9) = (-Vl*Kla*(S5e-S(8))-Q*S(9))/Vg;
% gas concentarion and transport, CO2
dSdt(10) = 0.152*(1-f(1)*Y(1))*(U(1)/Y(1))*X(1)+(1-f(2)*Y(2))*(U(2)/Y(2))*X(2)+(1-
f(4)*Y(4))*(U(4)/Y(4))*X(4)-0.25*(1-f(5)*Y(5))*(U(5)/Y(5))*X(5)-
0.5*f(5)*U(5)*X(5)+ Kla*(S6e-S(10));
dSdt(11) = (-Vl*Kla*(S6e-S(10))-Q*S(11))/Vg;
% gas concentarion and transport, CH4
dSdt(12)  = (1-f(4)*Y(4))*(U(4)/Y(4))*X(4)-0.25*(1-f(5)*Y(5))*(U(5)/Y(5))*X(5)+
Kla*(S7e-S(12));
dSdt(13) = (-Vl*Kla*(S7e-S(12))- Q*S(13))/Vg;
f = [dXdt(1) dXdt(2) dXdt(3) dXdt(4) dXdt(5) dS0dt dSdt(1) dSdt(2) dSdt(3) dSdt(4)
dSdt(5) dSdt(6) dSdt(7) dSdt(8) dSdt(9) dSdt(10) dSdt(11) dSdt(12) dSdt(13)];
f = f';
end
```

```
Um_guess = [0.8591    0.0540    0.0407    0.0024    0.0891    0.0007    1.4881    1.5340
1.6434    7.7353    0.0046    0.0049   0.0139    0.0123    0.0152    0.0027    0.0025
0.0042    0.0021    0.0039    0.0013    0.0026];  %%(HC treated TWE)
% Um_guess = [0.0714    0.0450    0.0416    0.0021    0.0766    0.0001    2.1343    1.5665
2.0507    5.1476    0.0059    0.0074   0.0062    0.0118    0.0128    0.0027    0.0024
0.0129    0.0021    0.0009    0.0005    0.0023];  %%(raw TWE)

lb = [0.05 0.009 0.009 0.0009 0.05 0.00009 0.042 0.008 0.008 0.1 .001 0.001 0.0053
0.0045 0.0045 0.0019 0.0004 0.0004 0.0001 0.0001 0.0004 0.0004];
ub = [1.79 0.081 0.081 0.025 0.173 0.05 2.778 3.125 3.125 7.81 .008 .01 0.0288 0.02
0.02 0.0033 0.0025 0.017 0.004 0.004 0.0013 0.0042];

[Um,error] = fmincon(@Bad,Um_guess,[],[],[],[],lb,ub);
Um
[error,X] = Bad(Um);
y_exp = [0; 0.00172; 0.008586; 0.020115; 0.04488; 0.05829; 0.0625; 0.065]; %% CH4/2
(HC treated)
%y_exp = [0; 0.00046; 0.00324; 0.009975; 0.01764; 0.01968; 0.019805; 0.019775]; %%
CH4/2 (raw TWE)
y_model = X(:,13);
x = 0:5:35;
figure(1)
plot(x,y_exp,'*',x,y_model)
xlabel('Time (days)');
ylabel('CH4 (L)');
legend('Exp','Model')
```

References

Al-amoudi, A., Lovitt, R.W., 2007. Fouling strategies and the cleaning system of NF membranes and factors affecting cleaning efficiency 303, 4–28. https://doi.org/10.1016/j.memsci.2007.06.002

Apaydin, O., Kurt, U., Gonullu, M.T., 2009. An Investigation on the treatment of tannery wastewater by electrocoagulation. Glob. NEST J. 11, 546–555.

APHA, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington DC, 1998., 1998.

Ates, E., Orhon, D., Tunay, O., 1997. Characterization of tannery wastewaters for pretreatment-selected case studies. Water Sci. Technol. 36, 217–223. https://doi.org/10.1016/S0273-1223(97)00390-9

Ayoub, G.M., Hamzeh, A., Semerjian, L., 2011. Post treatment of tannery wastewater using lime / bittern coagulation and activated carbon adsorption. Desalination 273, 359–365. https://doi.org/10.1016/j.desal.2011.01.045

Bagal, M. V., Gogate, P.R., 2013. Degradation of 2,4-dinitrophenol using a combination of hydrodynamic cavitation, chemical and advanced oxidation processes. Ultrason. Sonochem. 20, 1226–1235. https://doi.org/10.1016/j.ultsonch.2013.02.004

Bagal, M. V., Gogate, P.R., 2012. Sonochemical degradation of alachlor in the presence of process intensifying additives. Sep. Purif. Technol. 90, 92–100. https://doi.org/10.1016/j.seppur.2012.02.019

Bagal, M. V, Gogate, P.R., 2014. Wastewater treatment using hybrid treatment schemes based on cavitation and Fenton chemistry : A review. Ultrason. Sonochem. 21, 1–14. https://doi.org/10.1016/j.ultsonch.2013.07.009

Bahena, C.L., Martınez, S.S., Guzma, D.M., Hernandez, M. del R.T., 2008. Sonophotocatalytic degradation of alazine and gesaprim commercial herbicides in TiO 2 slurry. Chemosphere 71, 982–989. https://doi.org/10.1016/j.chemosphere.2007.11.007

Banu, J.R., Kaliappan, S., Yeom, I.T., 2007. Treatment of domestic wastewater using upflow anaerobic sludge blanket reactor. Int. J. Environ. Sci. Technol. 4, 363–370. https://doi.org/10.1007/BF03326295

Barik, A.J., Gogate, P.R., 2018. Hybrid treatment strategies for 2,4,6-trichlorophenol degradation based on combination of hydrodynamic cavitation and AOPs. Ultrason. Sonochem. 40, 383–394. https://doi.org/10.1016/j.ultsonch.2017.07.029

Barik, A.J., Gogate, P.R., 2016. Degradation of 4-chloro 2-aminophenol using a novel combined process based on hydrodynamic cavitation, UV photolysis and ozone. Ultrason. Sonochem. 30, 70–78. https://doi.org/10.1016/j.ultsonch.2015.11.007

Bautista, P., Mohedano, A.F., Casas, J.A., Zazo, J.A., Rodriguez, J.J., 2001. An overview of the application of Fenton oxidation to industrial wastewaters treatment. J. Chem. Technol.

Biotechnol. 83, 1323–1338. https://doi.org/10.1002/jctb

Bharagava, R.N., Saxena, G., Mulla, S.I., Patel, D.K., 2018. Characterization and identification of recalcitrant organic pollutants (ROPs) in tannery wastewater and its phytotoxicity evaluation for environmental safety. Arch. Environ. Contam. Toxicol. 75, 259–272. https://doi.org/10.1007/s00244-017-0490-x

Buchauer, K., 1998. A comparison of two simple titration procedures to determine volatile fatty acids in influents to waste-water and sludge treatment processes. Water SA 24, 49–56.

Buswell, A.M., Mueller, H.F., 1952. Mechanism of methane fermentation. Ind. Eng. Chem. Res. 44, 550–552.

Cai, M., Su, J., Zhu, Y., Wei, X., Jin, M., Zhang, H., Dong, C., Wei, Z., 2016. Decolorization of azo dyes Orange G using hydrodynamic cavitation coupled with heterogeneous Fenton process. Ultrason. Sonochem. 28, 302–310. https://doi.org/10.1016/j.ultsonch.2015.08.001

Castillo, M., Barcelo, D., 1999. Determination of organic pollutants in industrial wastewater effluents, in: In Techniques and Instrumentation in Analytical Chemistry. Elsevier Science, pp. 537–583.

Cesaro, A., Belgiorno, V., 2013. Sonolysis and ozonation as pretreatment for anaerobic digestion of solid organic waste. Ultrason. Sonochem. 20, 931–936. https://doi.org/10.1016/j.ultsonch.2012.10.017

Chakinala, A.G., Gogate, P.R., Burgess, A.E., Bremner, D.H., 2008. Treatment of industrial wastewater effluents using hydrodynamic cavitation and the advanced Fenton process. Ultrason. Sonochem. 15, 49–54. https://doi.org/10.1016/j.ultsonch.2007.01.003

Choi, D.W., Lee, W.G., Lim, S.J., Kim, B.J., Chang, H.N., 2003. Simulation on Long-term Operation of an Anaerobic Bioreactor for Korean Food Wastes. Biotechnol. Bioprocess Eng. 8, 23–31.

Costa, C.R., Botta, C.M.R., Espindola, E.L.G., Olivi, P., 2008. Electrochemical treatment of tannery wastewater using DSA® electrodes. J. Hazard. Mater. 15, 616–627. https://doi.org/10.1016/j.jhazmat.2007.09.005

Dantas, T.L.P., Jose, H.J., Moreira, R. de F.P.M., 2003. Fenton and Photo-Fenton oxidation of tannery wastewater. Acta Sci. Technol. 25, 91–95. https://doi.org/10.4025/actascitechnol.v25i1.2254

Daryapurkar, R.A., Nandy, T., Kaul, S.N., Deshpande, C. V, Szpyrkowicz, L., Environmental, N., 2001. International Journal of Evaluation of kinetic constants for anaerobic fixed film fixed bed reactors treating tannery wastewater 37–41. https://doi.org/10.1080/00207230108711371

Dasgupta, J., Mondal, D., Chakraborty, S., Sikder, J., Curcio, S., Arafat, H.A., 2015. Nanofiltration based water reclamation from tannery effluent following coagulation pretreatment. Ecotoxicol. Environ. Saf. 121, 22–30. https://doi.org/10.1016/j.ecoenv.2015.07.006

David, B., 2009. Sonochemical degradation of PAH in aqueous solution . Part I : Monocomponent PAH solution. Ultrason. Sonochem. 16, 260–265. https://doi.org/10.1016/j.ultsonch.2008.07.013

Deghles, A., Kurt, U., 2016. Treatment of tannery wastewater by a hybrid electrocoagulation / electrodialysis process. Chem. Eng. Process. Process Intensif. 104, 43–50. https://doi.org/10.1016/j.cep.2016.02.009

Deghles, A., Kurt, U., 2015. Treatment of raw tannery wastewater by electrocoagulation technique : optimization of effective parameters using Taguchi method optimization of effective parameters using Taguchi method. Desalin. Water Treat. 1–12. https://doi.org/10.1080/19443994.2015.1074622

Denac, M., Miguel, A., Dunn, J., 1988. Modeling Dynamic Experiments on the Anaerobic Degradation of Molasses Wastewater. Biotechnol. Bioeng. 31, 1–10.

Di Iaconi, C., Del Moro, G., Sanctis, M. De, Rossetti, S., 2010. A chemically enhanced biological process for lowering operative costs and solid residues of industrial recalcitrant wastewater treatment. Water Res. 44, 3635–3644. https://doi.org/10.1016/j.watres.2010.04.017

Dixit, S., Yadav, A., Dwivedi, P.D., Das, M., 2015. Toxic hazards of leather industry and technologies to combat threat : a review. J. Clean. Prod. 87, 39–49. https://doi.org/10.1016/j.jclepro.2014.10.017

Dogruel, S., Genceli, E.A., Babuna, F.G., Orhon, D., 2004. Ozonation of nonbiodegradable organics in tannery wastewater. J. Environ. Sci. Heal. - Part A Toxic/Hazardous Subst. Environ. Eng. 39, 1705–1715. https://doi.org/10.1081/ESE-120037871

Durai, G., Rajasimman, M., 2011. Biological treatment of tannery wastewater - A review. J. Environ. Sci. Technol. 4, 1–17.

El-sheikh, M.A., Saleh, H.I., Flora, J.R., Abdel-ghany, M.R., 2011. Biological tannery wastewater treatment using two stage UASB reactors. DES 276, 253–259. https://doi.org/10.1016/j.desal.2011.03.060

Elmagd, A.M.A., Mahmoud, M.S., 2014. Tannery Wastewater Treatment Using Activated Sludge Process System (Lab Scale Modeling). Int. J. Eng. Tech. Res. 2, 21–28.

Ferrer, I., Serrano, E., Ponsa, S., Vazquez, F., Font, X., 2009. Enhancement of thermophilic anaerobic sludge digestion by 70 ^{o}C pre-treatment: Energy considerations. J. Residuals Sci. Technol. 6, 8.

Francony, A., Pctrier, C., 1996. Sonochemical degradation of carbon tetrachloride in aqueous solution at two frequencies : 20 kHz and 500 kHz. Ultrason. Sonochem. 3, S77–S82.

Gallego-Molina, A., Mendoza-Roca, J.A., Aguado, D., Galiana-Aleixandre, M. V., 2013. Reducing pollution from the deliming-bating operation in a tannery. Wastewater reuse by microfiltration membranes. Chem. Eng. Res. Des. 91, 369–376. https://doi.org/10.1016/j.cherd.2012.08.003

Ganesh, R., Balaji, G., Ramanujam, R.A., 2006. Biodegradation of tannery wastewater using sequencing batch reactor — Respirometric assessment. Bioresour. Technol. 97, 1815–1821. https://doi.org/10.1016/j.biortech.2005.09.003

Genschow, E., Hegemann, W., Maschke, C., 1996. Biological sulfate removal from tannery wastewater in a two-stage anaerobic treatment. Water Res. 30, 2072–2078. https://doi.org/10.1016/0043-1354(96)00332-6

George, S., Pandit, P., Gupta, A.B., Agarwal, M., 2009. Modeling and simulation studies for aluminium-fluoride interactions in nalgonda defluoridation process. Chem. Prod. Process Model. 4. https://doi.org/10.2202/1934-2659.1367

Gogate, P.R., Pandit, A.B., 2004a. A review of imperative technologies for wastewater treatment II : hybrid methods 8, 553–597. https://doi.org/10.1016/S1093-0191(03)00031-5

Gogate, P.R., Pandit, A.B., 2004b. A review of imperative technologies for wastewater treatment I : oxidation technologies at ambient conditions. Adv. Environ. Res. 8, 501–551. https://doi.org/10.1016/S1093-0191(03)00032-7

Gogate, P.R., Pandit, A.B., 2001. Hydrodynamic cavitation reactors : A state of the art review. Rev. Chem. Eng. 17.

Gogate, P.R., Patil, P.N., 2015. Combined treatment technology based on synergism between hydrodynamic cavitation and advanced oxidation processes. Ultrason. Sonochem. 25, 60–69. https://doi.org/10.1016/j.ultsonch.2014.08.016

Gomes, L., Troiani, E.P., Malpass, G.R.P., Nozaki, J., 2015. Opuntia ficus indica as a polyelectrolyte source for the treatment of tannery wastewater. Desalin. Water Treat. 3994, 1–7. https://doi.org/10.1080/19443994.2015.1035677

Guo, Z., Feng, R., 2009. Ultrasonic irradiation-induced degradation of low-concentration bisphenol A in aqueous solution. J. Hazard. Mater. 163, 855–860. https://doi.org/10.1016/j.jhazmat.2008.07.038

Guo, Z., Zheng, Z., Zheng, S., Hu, W., Feng, R., 2005. Effect of various sono-oxidation parameters on the removal of aqueous 2,4-dinitrophenol. Ultrason. Sonochem. 12, 461–465. https://doi.org/10.1016/j.ultsonch.2004.07.006

Han, J., Liu, Y., Singhal, N., Wang, L., Gao, W., 2012. Comparative photocatalytic degradation of estrone in water by ZnO and TiO 2 under artificial UVA and solar irradiation. Chem. Eng. J. 213, 150–162. https://doi.org/10.1016/j.cej.2012.09.066

Haydar, S., Aziz, J.A., 2009a. Coagulation – flocculation studies of tannery wastewater using combination of alum with cationic and anionic polymers. J. Hazard. Mater. 168, 1035–1040. https://doi.org/10.1016/j.jhazmat.2009.02.140

Haydar, S., Aziz, J.A., 2009b. Coagulation – flocculation studies of tannery wastewater using cationic polymers as a replacement of metal salts Sajjad Haydar and Javed Anwar Aziz. Water Sci. Technol. 381–391. https://doi.org/10.2166/wst.2009.864

Hogan, F., Mormede, S., Clark, P., Crane, M., 2004. Ultrasonic sludge treatment for enhanced anaerobic digestion. Water Sci. Technol. 50, 25–32.

Houshyar, Z., Baradar, A., Fatehifar, E., 2012. Influence of ozonation process on characteristics of pre-alkalized tannery effluents. Chem. Eng. J. 191, 59–65. https://doi.org/10.1016/j.cej.2012.02.053

Jawale, R.H., Gogate, P.R., Pandit, A.B., 2014. Treatment of cyanide containing wastewater using cavitation based approach. Ultrason. Sonochem. 21, 1392–1399. https://doi.org/10.1016/j.ultsonch.2014.01.025

Joshi, R.K., Gogate, P.R., 2012. Degradation of dichlorvos using hydrodynamic cavitation based treatment strategies. Ultrason. Sonochem. 19, 532–539. https://doi.org/10.1016/j.ultsonch.2011.11.005

Kabdasli, I., Tiinay, O., Orhon, D., 1999. Wastewater control and management in a leather tanning district. Water Sci. Technol. 40, 261–267. https://doi.org/10.1016/S0273-1223(99)00393-5

Kalyuzhnyi, S.V., 1997. Batch anaerobic digestion of glucose and its mathematical modeling. II. descrition, verification and application of model. Bioresour. Technol. 59, 249–258.

Kepp, U., Machenbach, I., Weisz, N., Solhelm, O.E., 2000. Enhanced stabilisation of sewage sludge through thermal hydrolysis - Three years of experience with full scale plant BT - Disposal and Utilisation of Sewage Sludge: Treatment Methods and Application Modalities, October 13, 1999 - October 15, 1999. Water Sci. Technol. 42, 89–96.

Kim, I.S., Ekpeghere, K.I., Ha, S.Y., Kim, B.S., Song, B., Kim, J.T., Kim, H.G., Koh, S.C., 2014. Full-scale biological treatment of tannery wastewater using the novel microbial consortium BM-S-1. J. Environ. Sci. Heal. - Part A Toxic/Hazardous Subst. Environ. Eng. 49, 355–364. https://doi.org/10.1080/10934529.2014.846707

Kongjao, S., Damronglerd, S., 2008. Simultaneous removal of organic and inorganic pollutants in tannery wastewater using electrocoagulation technique. Korean J. Chem. Eng. 25, 703–709.

Konstantinou, I.K., Albanis, T.A., 2004. TiO 2 -assisted photocatalytic degradation of azo dyes in aqueous solution : kinetic and mechanistic investigations A review. Appl. Catal. B Environ. 49, 1–14. https://doi.org/10.1016/j.apcatb.2003.11.010

Koteswari, Y.N., Ramanibai, R., 2003. The effect of tannery effluent on the colonization rate of plankters : A microcosm study. Turkish J. Biol. 27, 163–170.

Ku, Y., Tu, Y., Ma, C., 2005. Effect of hydrogen peroxide on the decomposition of monochlorophenols by sonolysis in aqueous solution. Water Res. 39, 1093–1098. https://doi.org/10.1016/j.watres.2004.11.036

Kurt, U., Apaydin, O., Gonullu, M.T., 2007. Reduction of COD in wastewater from an organized tannery industrial region by Electro-Fenton process. J. Hazard. Mater. 143, 33–40. https://doi.org/10.1016/j.jhazmat.2006.08.065

Labanda, J., Khaidar, M.S., Llorens, J., 2009. Feasibility study on the recovery of chromium (III) by polymer enhanced ultra fi ltration. Desalination 249, 577–581. https://doi.org/10.1016/j.desal.2008.06.031

Ladwani, K.D., Ladwani, K.D., Ramteke, D.S., Deo, S., 2016. Detection and identification of organic compounds in wastewater of final effluent treatment plant by FTIR and GC-MS. J. Adv. Chem. Sci. 2, 465–468.

Lefebvre, O., Vasudevan, N., Torrijos, M., Thanasekaran, K., Moletta, R., 2006. Anaerobic digestion of tannery soak liquor with an aerobic. Water Res. 40, 1492–1500. https://doi.org/10.1016/j.watres.2006.02.004

Lefebvre, O., Vasudevan, N., Torrijos, M., Thanasekaran, K., Moletta, R., 2005. Halophilic biological treatment of tannery soak liquor in a sequencing batch reactor. Water Res. 39, 1471–1480. https://doi.org/10.1016/j.watres.2004.12.038

Leonard, K.S., Mccubbin, D., Lovett, M.B., 1995. Physico-chemical characterisation of radionuclides discharged from a nuclear establishment 175, 9–24.

Leta, S., Assefa, L., Gumaelius, L., Dalhammar, G., 2004. Biological nitrogen and organic matter removal from tannery wastewater in pilot plant operations in Ethiopia 333–339. https://doi.org/10.1007/s00253-004-1715-2

Liao, X., Li, H., Zhang, Y., Liu, C., Chen, Q., 2016. Accelerated high-solids anaerobic digestion of sewage sludge using low-temperature thermal pretreatment. Int. Biodeterior. Biodegradation 106, 141–149. https://doi.org/10.1016/j.ibiod.2015.10.023

Lim, M., Son, Y., Yang, J., Khim, J., 2008. Addition of chlorinated compounds in the sonochemical degradation of 2-chlorophenol. Jpn. J. Appl. Phys. 47, 4123–4126. https://doi.org/10.1143/JJAP.47.4123

Liu, H., Liang, M.Y., Liu, C.S., Gao, Y.X., Zhou, J.M., 2009. Catalytic degradation of phenol in sonolysis by coal ash and H 2 O 2 / O 3. Chem. Eng. J. 153, 131–137. https://doi.org/10.1016/j.cej.2009.06.030

Lofrano, G., Belgiorno, V., Gallo, M., Raimo, A., 2006. Toxicity reduction in leather tanningwastewater by improved coagulation flocculation process. Glob. NEST J. 8, 151–158.

Lofrano, G., Meriç, S., Belgiorno, V., Napoli, R.M.A., 2007. Fenton’s oxidation of various-based tanning materials. Desalination 211, 10–21. https://doi.org/10.1016/j.desal.2006.03.589

Lofrano, G., Meric, S., Emel, G., Orhon, D., 2013. Chemical and biological treatment technologies for leather tannery chemicals and wastewaters : A review. Sci. Total Environ. 461–462, 265–281. https://doi.org/10.1016/j.scitotenv.2013.05.004

Mahamuni, N.N., Pandit, A.B., 2006. Effect of additives on ultrasonic degradation of phenol. Ultrason. Sonochem. 13, 165–174. https://doi.org/10.1016/j.ultsonch.2005.01.004

Mandal, T., Dasgupta, D., Mandal, S., Datta, S., 2010. Treatment of leather industry wastewater by aerobic biological and Fenton oxidation process. J. Hazard. Mater. 180, 204–211. https://doi.org/10.1016/j.jhazmat.2010.04.014

Mannucci, A., Munz, G., Mori, G., Lubello, C., 2010. Anaerobic treatment of vegetable tannery wastewaters : A review. Desalination 264, 1–8. https://doi.org/10.1016/j.desal.2010.07.021

Marousek, J., Haskova, S., Marouskova, A., Myskova, K., Vanickova, R., Vachal, J., Vochozka, M., Zeman, R., Zak, J., 2015. Financial and biotechnological assessment of new oil extraction technology. Energy Sources, Part A Recover. Util. Environ. Eff. 37, 1723–1728. https://doi.org/10.1080/15567036.2015.1048391

Marousek, J., Itoh, S., Higa, O., Kondo, Y., Ueno, M., Suwa, R., Komiya, Y., Tominaga, J., Kawamitsu, Y., 2013. Pressure shockwaves to enhance oil extraction from Jatropha curcas L. Biotechnol. Biotechnol. Equip. 27, 3654–3658. https://doi.org/10.5504/BBEQ.2012.0143

Marousek, J., Kolář, L., Vochozka, M., Stehel, V., Maroušková, A., 2017. Novel method for cultivating beetroot reduces nitrate content. J. Clean. Prod. 168, 60–62. https://doi.org/10.1016/j.jclepro.2017.08.233

Marousek, J., Kwan, J.T.H., 2013. Use of pressure manifestations following the water plasma expansion for phytomass disintegration. Water Sci. Technol. 67, 1695–1700. https://doi.org/10.2166/wst.2013.041

Mason, T.J., 2000. Large scale sonochemical processing: Aspiration and actuality. Ultrason. Sonochem. 7, 145–149. https://doi.org/10.1016/S1350-4177(99)00041-3

Metcalf & Eddy, I., 2003. Wastewater engineering, Treatment and Reuse, Fourth Edition. https://doi.org/Doi 10.1016/J.Ijpharm.2006.12.047

Mishra, K.P., Gogate, P.R., 2010. Intensification of degradation of Rhodamine B using hydrodynamic cavitation in the presence of additives. Sep. Purif. Technol. 75, 385–391. https://doi.org/10.1016/j.seppur.2010.09.008

Modenes, A.N., Espinoza-Quinones, F.R., Borba, F.H., Manenti, D.R., 2012. Performance evaluation of an integrated photo-Fenton - Electrocoagulation process applied to pollutant removal from tannery effluent in batch system. Chem. Eng. J. 197, 1–9. https://doi.org/10.1016/j.cej.2012.05.015

Munz, G., Angelis, D. De, Gori, R., Mori, G., Casarci, M., Lubello, C., 2009. The role of tannins in conventional and membrane treatment of tannery wastewater 164, 733–739. https://doi.org/10.1016/j.jhazmat.2008.08.070

Munz, G., Gori, R., Cammilli, L., Lubello, C., 2008. Bioresource Technology Characterization of tannery wastewater and biomass in a membrane bioreactor using respirometric analysis 99, 8612–8618. https://doi.org/10.1016/j.biortech.2008.04.004

Munz, G., Gori, R., Mori, G., Lubello, C., 2007. Powdered activated carbon and membrane bioreactors (MBR- PAC) for tannery wastewater treatment : long term effect on biological and filtration process performances. Desalination 207, 349–360.

https://doi.org/10.1016/j.desal.2006.08.010

Munz, G., Gualtiero, M., Salvadori, L., Claudia, B., Claudio, L., 2008. Process efficiency and microbial monitoring in MBR (membrane bioreactor) and CASP (conventional activated sludge process) treatment of tannery wastewater. Bioresour. Technol. 99, 8559–8564. https://doi.org/10.1016/j.biortech.2008.04.006

Nanda, S., Sarangi, P.K., Abraham, J., 2010. Cyanobacterial remediation of industrial effluents I . Tannery effluents. New York Sci. J. 3, 32–36.

Nanzai, B., Okitsu, K., Takenaka, N., Bandow, H., 2009. Sonochemical Degradation of Alkylbenzene Sulfonates and Kinetics Analysis with a Langmuir Type Mechanism. J. Phys. Chem. C 113, 3735–3739.

Naumczyk, J., Rusiniak, M., 2005. Physicochemical and Chemical Purification of Tannery Wastewaters. Polish J. Environ. Stud. 14, 789–797.

Neis, U., Nickel, K., Lundén, A., 2008. Improving anaerobic and aerobic degradation by ultrasonic disintegration of biomass. J. Environ. Sci. Heal. - Part A Toxic/Hazardous Subst. Environ. Eng. 43, 1541–1545. https://doi.org/10.1080/10934520802293701

Neppolian, B., Jung, H., Choi, H., Lee, J.H., Kang, J.W., 2002. Sonolytic degradation of methyl tert-butyl ether: The role of coupled fenton process and persulphate ion. Water Res. 36, 4699–4708. https://doi.org/10.1016/S0043-1354(02)00211-7

Noorjahan, C.M., 2014. Physicochemical Characteristics, Identification of Bacteria and Biodegradation of Industrial Effluent. J. Bioremediation Biodegrad. 5, 32–39. https://doi.org/10.4172/2155-6199.100021

Orhon, D., Ates Genceli, E., Sozen, S., 2000. Experimental evaluation of the nitrification kinetics for tannery wastewaters. Water SA 26, 43–50.

Padoley, K. V, Kumar, V., Mudliar, S.N., Pandey, R.A., Pandit, A.B., 2012. Cavitationally induced biodegradability enhancement of a distillery wastewater. J. Hazard. Mater. 219–220, 69–74. https://doi.org/10.1016/j.jhazmat.2012.03.054

Pang, Y.L., Abdullah, A.Z., Bhatia, S., 2011. Review on sonochemical methods in the presence of catalysts and chemical additives for treatment of organic pollutants in wastewater. Desalination 277, 1–14. https://doi.org/10.1016/j.desal.2011.04.049

Parthasarathy, S., Gomes, R.L., Manickam, S., 2016a. Process intensification of anaerobically digested palm oil mill effluent (AAD-POME) treatment using combined chitosan coagulation, hydrogen peroxide (H2O2) and Fenton’s oxidation. Clean Technol. Environ. Policy 18, 219–230. https://doi.org/10.1007/s10098-015-1009-7

Parthasarathy, S., Mohammed, R.R., Fong, C.M., Gomes, R.L., Manickam, S., 2016b. A novel hybrid approach of activated carbon and ultrasound cavitation for the intensification of palm oil mill effluent (POME) polishing. J. Clean. Prod. 112, 1218–1226. https://doi.org/10.1016/j.jclepro.2015.05.125

Patil, P.N., Bote, S.D., Gogate, P.R., 2014. Degradation of imidacloprid using combined advanced oxidation processes based on hydrodynamic cavitation. Ultrason. Sonochem. 21, 1770–1777. https://doi.org/10.1016/j.ultsonch.2014.02.024

Patil, P.N., Gogate, P.R., 2012. Degradation of methyl parathion using hydrodynamic cavitation : Effect of operating parameters and intensification using additives. Sep. Purif. Technol. 95, 172–179. https://doi.org/10.1016/j.seppur.2012.04.019

Pradhan, A.A., Gogate, P.R., 2010a. Removal of p -nitrophenol using hydrodynamic cavitation and Fenton chemistry at pilot scale operation. Chem. Eng. J. 156, 77–82. https://doi.org/10.1016/j.cej.2009.09.042

Pradhan, A.A., Gogate, P.R., 2010b. Degradation of p-nitrophenol using acoustic cavitation and Fenton chemistry. J. Hazard. Mater. 173, 517–522. https://doi.org/10.1016/j.jhazmat.2009.08.115

Preethi, V., Kalyani, K.S.P., Iyappan, K., Srinivasakannan, C., Balasubramaniam, N., Vedaraman, N., 2009. Ozonation of tannery effluent for removal of cod and color 166, 150–154. https://doi.org/10.1016/j.jhazmat.2008.11.035

Priya, M.H., Madras, G., 2006. Kinetics of TiO 2 -catalyzed ultrasonic degradation of rhodamine dyes. Ind. Eng. Chem. Res. 45, 913–921.

Rajoriya, S., Bargole, S., George, S., Saharan, V.K., 2018. Treatment of textile dyeing industry effluent using hydrodynamic cavitation in combination with advanced oxidation reagents. J. Hazard. Mater. 344, 1109–1115. https://doi.org/10.1016/j.jhazmat.2017.12.005

Rajoriya, S., Bargole, S., Saharan, V.K., 2017a. Degradation of a cationic dye (Rhodamine 6G) using hydrodynamic cavitation coupled with other oxidative agents: Reaction mechanism and pathway. Ultrason. Sonochem. 34, 183–194. https://doi.org/10.1016/j.ultsonch.2016.05.028

Rajoriya, S., Bargole, S., Saharan, V.K., 2017b. Degradation of reactive blue 13 using hydrodynamic cavitation: Effect of geometrical parameters and different oxidizing additives. Ultrason. Sonochem. 37, 192–202. https://doi.org/10.1016/j.ultsonch.2017.01.005

Rajoriya, S., Carpenter, J., Saharan, V.K., Pandit, A.B., 2016. Hydrodynamic cavitation: An advanced oxidation process for the degradation of bio-refractory pollutants. Rev. Chem. Eng. 32, 379–411. https://doi.org/10.1515/revce-2015-0075

Ram, B., Bajpai, P.K., Parwana, H.K., 1999. Kinetics of chrome-tannery effluent treatment by the activated-sludge system. Process Biochem. 35, 255–265. https://doi.org/10.1016/S0032-9592(99)00062-X

Ramteke, P.W., Awasthi, S., Srinath, T., Joseph, B., 2010. Efficiency assessment of Common Effluent Treatment Plant (CETP) treating tannery effluents. Environ. Monit. Assess. 169, 125–131. https://doi.org/10.1007/s10661-009-1156-6

Randhavane, S.B., Khambete, A.K., 2017. Hydrodynamic cavitation: An approach to degrade Chlorpyrifos pesticide from real effluent. KSCE J. Civ. Eng. 0, 1–7.

https://doi.org/10.1007/s12205-017-2045-0

Ranganathan, K., Kabadgi, S.D., 2011. Studies on Feasibility of Reverse Osmosis (Membrane) Technology for Treatment of Tannery Wastewater. J. Environ. Prot. (Irvine,. Calif). 2, 37–46. https://doi.org/10.4236/jep.2011.21004

Raut-Jadhav, S., Badve, M.P., Pinjari, D. V., Saini, D.R., Sonawane, S.H., Pandit, A.B., 2016a. Treatment of the pesticide industry effluent using hydrodynamic cavitation and its combination with process intensifying additives (H2O2and ozone). Chem. Eng. J. 295, 326–335. https://doi.org/10.1016/j.cej.2016.03.019

Raut-jadhav, S., Kumar, V., Pinjari, D., Sonawane, S., Saini, D., Pandit, A., 2013. Synergetic effect of combination of AOP ' s (hydrodynamic cavitation and H 2 O 2) on the degradation of neonicotinoid class of insecticide. J. Hazard. Mater. 261, 139–147. https://doi.org/10.1016/j.jhazmat.2013.07.012

Raut-Jadhav, S., Saharan, V.K., Pinjari, D., Sonawane, S., Saini, D., Pandit, A., 2013. Synergetic effect of combination of AOP's (hydrodynamic cavitation and H2O2) on the degradation of neonicotinoid class of insecticide. J. Hazard. Mater. 261, 139–147. https://doi.org/10.1016/j.jhazmat.2013.07.012

Raut-Jadhav, S., Saini, D., Sonawane, S., Pandit, A., 2016b. Effect of process intensifying parameters on the hydrodynamic cavitation based degradation of commercial pesticide (methomyl) in the aqueous solution. Ultrason. Sonochem. 28, 283–293. https://doi.org/10.1016/j.ultsonch.2015.08.004

Reiera-Torres, M., Gutierrez-Bouzan, C., Crespi, M., 2010. Combination of coagulation – fl occulation and nano fi ltration techniques for dye removal and water reuse in textile ef fl uents. Desalination 252, 53–59. https://doi.org/10.1016/j.desal.2009.11.002

Reyes, T.G., Crisosto, J.M., 2016. Characterization of dissolved organic matter in river water by conventional methods and direct sample analysis-time of flight-mass spectrometry. J. Chem. 1–11. https://doi.org/10.1155/2016/1537370

Saharan, V.K., Pinjari, D. V., Gogate, P.R., Pandit, A.B., 2014. Advanced oxidation technologies for wastewater treatment: An overview, Industrial Wastewater Treatment, Recycling and Reuse. Elsevier Ltd. https://doi.org/10.1016/B978-0-08-099968-5.00003-9

Saharan, V.K., Rizwani, M.A., Malani, A.A., Pandit, A.B., 2013. Ultrasonics Sonochemistry Effect of geometry of hydrodynamically cavitating device on degradation of orange-G. Ultrason. Sonochem. 20, 345–353. https://doi.org/10.1016/j.ultsonch.2012.08.011

Sauer, T.P., Casaril, L., Oberziner, B., Jos, H.J., F, R. De, Moreira, M., 2006. Advanced oxidation processes applied to tannery wastewater containing Direct Black 38 — Elimination and degradation kinetics 135, 274–279. https://doi.org/10.1016/j.jhazmat.2005.11.063

Saxena, G., Chandra, R., Bharagava, R.N., 2016. Environmental Pollution , Toxicity Profile and Treatment Approaches for Tannery Wastewater and Its Chemical Pollutants. Rev. Environ.

Contam. Toxicol. 240, 31–69. https://doi.org/10.1007/398

Saxena, S., Rajoriya, S., Saharan, V.K., George, S., 2018a. An advanced pretreatment strategy involving hydrodynamic and acoustic cavitation along with alum coagulation for the mineralization and biodegradability enhancement of tannery waste e ffl uent. Ultrason. Sonochem. 44, 299–309. https://doi.org/10.1016/j.ultsonch.2018.02.035

Saxena, S., Saharan, V.K., George, S., 2018b. Enhanced synergistic degradation efficiency using hybrid hydrodynamic cavitation for treatment of tannery waste effluent. J. Clean. Prod. 198, 1406–1421. https://doi.org/10.1016/j.jclepro.2018.07.135

Schädle, T., Pejcic, B., Mizaikoff, B., 2016. Monitoring dissolved carbon dioxide and methane in brine environments at high pressure using IR-ATR spectroscopy. R. Soc. Chem. 8, 756–762. https://doi.org/10.1039/c5ay02744f

Schrank, S.G., Gebhardt, W., Jose, H.J., Moreira, R.F.P.M., Schroder, H.F., 2017. Ozone treatment of tannery wastewater monitored by conventional and substance specific wastewater analyses. Ozone Sci. Eng. 39, 159–187. https://doi.org/10.1080/01919512.2016.1273090

Schrank, S.G., Jose, H.J., Moreira, R.F.P.M., Schroder, H.F., 2005. Applicability of fenton and H2O2/UV reactions in the treatment of tannery wastewaters. Chemosphere 60, 644–655. https://doi.org/10.1016/j.chemosphere.2005.01.033

Schrank, S.G., Jose, H.J., Moreira, R.F.P.M., Schroder, H.F., 2004. Elucidation of the behavior of tannery wastewater under advanced oxidation conditions. Chemosphere 56, 411–423. https://doi.org/10.1016/j.chemosphere.2004.04.012

Sengil, L.A., Kulac, S., Ozacar, M., 2009. Treatment of tannery liming drum wastewater by electrocoagulation. J. Hazard. Mater. 167, 940–946. https://doi.org/10.1016/j.jhazmat.2009.01.099

Sharma, S., Malaviya, P., 2013. Bioremediation of tannery wastewater by Aspergillus niger SPFSL2-a isolated from tannery sludge. J. Basic Appl. Sci 2, 88–93.

Sher, F., Malik, A., Liu, H., 2013. Industrial polymer effluent treatment by chemical coagulation and flocculation. Biochem. Pharmacol. 1, 684–689. https://doi.org/10.1016/j.jece.2013.07.003

Shriwas, A.K., Gogate, P.R., 2011. Ultrasonic degradation of methyl Parathion in aqueous solutions: Intensification using additives and scale up aspects. Sep. Purif. Technol. 79, 1–7. https://doi.org/10.1016/j.seppur.2011.02.034

Sivakumar, M., Pandit, A.B., 2001. Ultrasound enhanced degradation of Rhodamine B: Optimization with power density. Ultrason. Sonochem. 8, 233–240. https://doi.org/10.1016/S1350-4177(01)00082-7

Sivaprakasam, S., Mahadevan, S., Sekar, S., Rajakumar, S., 2008. Biological treatment of tannery wastewater by using salt-tolerant bacterial strains. Microb. Cell Fact. 7, 1–7. https://doi.org/10.1186/1475-2859-7-15

Smidt, E., Bohm, K., Schwanninger, M., 2011. The Application of FT-IR Spectroscopy in Waste Management. Fourier Transform. - New Anal. Approaches FTIR Strateg. 405–430. https://doi.org/10.5772/15998

Song, S., Xia, M., He, Z., Ying, H., Bosheng, L., Chen, J., 2007. Degradation of p -nitrotoluene in aqueous solution by ozonation combined with sonolysis. J. Hazard. Mater. 144, 532–537. https://doi.org/10.1016/j.jhazmat.2006.10.067

Song, Z., Williams, C.J., Edyvean, R.G.J., 2004. Treatment of tannery wastewater by chemical coagulation. Desalination 164, 249–259.

Song, Z., Williams, C.J., Edyvean, R.G.J., 2003. Tannery Wastewater Treatment Using an Upflow Anaerobic Fixed Biofilm Reactor (UAFBR). Environ. Eng. Sci. 20, 587–599. https://doi.org/10.1089/109287503770736104

Srinivasan, S. V., Mary, G.P.S., Kalyanaraman, C., Sureshkumar, P.S., Balakameswari, K.S., Suthanthararajan, R., Ravindranath, E., 2012. Combined advanced oxidation and biological treatment of tannery effluent. Clean Technol. Environ. Policy 14, 251–256. https://doi.org/10.1007/s10098-011-0393-x

Stoller, M., Sacco, O., Sannino, D., Chianese, A., 2013. Successful Integration of Membrane Technologies in a Conventional Purification Process of Tannery Wastewater Streams. Membranes (Basel). 3, 126–135. https://doi.org/10.3390/membranes3030126

Suganthi, V., Mahalakshmi, M., Balasubramanian, N., 2013. Development of hybrid membrane bioreactor for tannery effluent treatment. Desalination 309, 231–236. https://doi.org/10.1016/j.desal.2012.10.014

Sun, J.H., Sun, S.P., Sun, J.Y., Sun, R.X., Qiao, L.P., Guo, H.Q., Fan, M.H., 2007. Degradation of azo dye Acid black 1 using low concentration iron of Fenton process facilitated by ultrasonic irradiation. Ultrason. Sonochem. 14, 761–766. https://doi.org/10.1016/j.ultsonch.2006.12.010

Sundarapandiyan, S., Chandrasekar, R., Ramanaiah, B., Krishnan, S., Saravanan, P., 2010. Electrochemical oxidation and reuse of tannery saline wastewater. J. Hazard. Mater. 180, 197–203. https://doi.org/10.1016/j.jhazmat.2010.04.013

Sundarapandiyan, S., Chandrasekar, R., Ramanaiah, B., Krishnan, S., Saravanan, P., 2010. Electrochemical oxidation and reuse of tannery saline wastewater. J. Hazard. Mater. 180, 197–203. https://doi.org/10.1016/j.jhazmat.2010.04.013

Szpyrkowicz, L., Kaul, S.N., Neti, R.N., 2005a. Tannery wastewater treatment by electro-oxidation coupled with a biological process. J. Appl. Electrochem. 35, 381–390. https://doi.org/10.1007/s10800-005-0796-7

Szpyrkowicz, L., Kaul, S.N., Neti, R.N., Satyanarayan, S., 2005b. Influence of anode material on electrochemical oxidation for the treatment of tannery wastewater. Water Res. 39, 1601–1613. https://doi.org/10.1016/j.watres.2005.01.016

Szpyrkowicz, L., Kelsall, G.H., Kaul, S.N., De Faveri, M., 2001. Performance of electrochemical reactor for treatment of tannery wastewaters. Chem. Eng. Sci. 56, 1579–1586. https://doi.org/10.1016/S0009-2509(00)00385-7

Thanekar, P., Panda, M., Gogate, P.R., 2018. Degradation of carbamazepine using hydrodynamic cavitation combined with advanced oxidation processes. Ultrason. Sonochem. 40, 567–576. https://doi.org/10.1016/j.ultsonch.2017.08.001

Valeika, V., Beleska, K., Sirvaityte, J., 2012. Alkali-free method of hide preparation for tanning. Brazilian J. Chem. Eng. 29, 315–323. https://doi.org/10.1590/S0104-66322012000200012

Verheijen, L.A.H.M., Wiersema, D., Hulshoff Pol, L.W., 1996. Management of Waste from Animal Product Processing, in: Centre, I.A. (Ed.), Livestock and the Environment: Finding a Balance. Wageningen, The Netherlands, p. 88.

Wang, J., Ma, T., Zhang, Z., Zhang, X., 2006. Investigation on the sonocatalytic degradation of parathion in the presence of nanometer rutile titanium dioxide (TiO 2) catalyst. J. Hazard. Mater. 137, 972–980. https://doi.org/10.1016/j.jhazmat.2006.03.022

Wang, J., Sun, W., Zhang, Z., Zhang, X., 2007. Sonocatalytic degradation of methyl parathion in the presence of micron-sized and nano-sized rutile titanium dioxide catalysts and comparison of their sonocatalytic abilities. J. Mol. Catal. A Chem. 272, 84–90. https://doi.org/10.1016/j.molcata.2007.03.018

Wang, J., Wang, X., Guo, P., Yu, J., 2011. Degradation of reactive brilliant red K-2BP in aqueous solution using swirling jet-induced cavitation combined with H 2 O 2. Ultrason. Sonochem. 18, 494–500. https://doi.org/10.1016/j.ultsonch.2010.08.006

Wu, C., Jin, L., Zhang, P., Zhang, G., 2015. Effects of potassium ferrate oxidation on sludge disintegration , dewaterability and anaerobic biodegradation. Int. Biodeterior. Biodegradation 102, 137–142. https://doi.org/10.1016/j.ibiod.2015.01.002

Xie, R., Xing, Y., Ghani, Y.A., Ooi, K., Ng, S., 2007. Full-scale demonstration of an ultrasonic disintegration technology in enhancing anaerobic digestion of mixed primary and thickened secondary sewage sludge. J. Environ. Eng. Sci. 6, 533–541. https://doi.org/10.1139/S07-013

Ying Shih, M., Chi Fanga, S., Jih Gaw, L., 2010. Degradation of carbofuran in aqueous solution by ultrasound and Fenton processes: Effect of system parameters and kinetic study. J. Hazard. Mater. 178, 320–325. https://doi.org/10.1016/j.jhazmat.2010.01.081

Yoon, R.-H., Luttrell, G.H., 1992. Method for separating fine particles by selective hydrophobic coagulation. 5,161,694. https://doi.org/US005485919A

Yu, B., Xu, J., Yuan, H., Lou, Z., Lin, J., Zhu, N., 2014. Enhancement of anaerobic digestion of waste activated sludge by electrochemical pretreatment. Fuel 130, 279–285. https://doi.org/10.1016/j.fuel.2014.04.031

Zabranska, J., Dohanyos, M., Jenicek, P., Kutil, J., 2006. Disintegration of excess activated sludge - Evaluation and experience of full-scale applications. Water Sci. Technol. 53, 229–236. https://doi.org/10.2166/wst.2006.425

Zhang, H., Jiang, M., Wang, Z., Wu, F., 2007. Decolorisation of CI Reactive Black 8 by zero-valent iron powder with / without ultrasonic irradiation. Color. Technol. 123, 203–208. https://doi.org/10.1111/j.1478-4408.2007.00079.x