A

Dissertation Report

On

"Multi-Objective Optimization of Treatment of Dairy Wastewater by Electro-coagulation Process and Modelling of Adsorption Kinetics, Adsorption Isotherms"

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JAIPUR – 302017, (RAJASTHAN) INDIA

DECLARATION

I, Saurabh Gupta hereby certify that the work presented in this thesis titled "**Multi-Objective Optimization of Treatment of Dairy Wastewater by Electro-coagulation Process and Modelling of Adsorption Kinetics, Adsorption Isotherms**" submitted in partial fulfilment of the award of the degree of Master of Technology in Environment Engineering, in the Department of Civil Engineering, Malaviya National Institute of Technology, Jaipur is an authentic record of my own work unless otherwise referenced or acknowledged. The results presented in this thesis have not been submitted in part or full, to any other University or Institute for award of any degree.

The thesis was completed under the guidance of Dr. Sanjay Mathur, Associate Professor, Department of Civil Engineering, Malaviya National Institute of Technology Jaipur.

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CERTIFICATE

This is to certify that the work reported in this thesis entitled "**Multi-Objective Optimization of Treatment of Dairy Wastewater by Electro-coagulation Process and Modelling of Adsorption Kinetics, Adsorption Isotherms**" has been carried out by **Mr. Saurabh Gupta** and submitted to Department of Civil Engineering, Malaviya National Institute of Technology, Jaipur in partial fulfilment for the award of the degree of Master of Technology in Environmental Engineering. It is a bonafide record of research work carried out by him under my guidance and supervision. This Report has been found satisfactory by me and is approved for submission.

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ABSTRACT

Industrial dairy effluents are characterized by high biological oxygen demand (BOD) and chemical oxygen demand (COD) concentrations and contain fats, nutrients, lactose, as well as detergents and sanitizing agents. Due to the high pollution load of dairy wastewater, the milk-processing industries discharging untreated/partially treated wastewater can cause serious environmental problems.

In the present study, treatment of simulated dairy waste water(SDW) by electrocoagulation process has been investigated using aluminum electrodes. Experiments were conducted in a laboratory scale batch reactor. Full factorial central composite design (CCD) was employed for optimization of 4 responses: chemical oxygen demand(COD), 3-day biological oxygen demand(BOD), anode consumption and specific electrical energy consumption(SEEC). Three factors namely current density (1.92-2.88 mA/cm^2), pH (6-8) & conductivity (1000-2000 μS/cm) with each factor at three levels were used. Regression model equations were developed which were validated by high R^2 values of 96.05%, 94.60%, 97.45% and 99.65% for COD, BOD, anode consumption and SEEC respectively. According to normal probability plot of externally studentized residuals, the quadratic model obtained well satisfied the ANOVA. Optimization was targeted for maximum COD removal and minimum operating cost. The optimized conditions as suggested by the model were: applied current density-2.209 mA/cm^2, pH-6.86, and conductivity- 2000 μS/cm. Optimum COD and BOD removal efficiencies were 79.45% and 81.02% respectively while anode consumption and SEEC was 0.065 mg/mg COD and 0.068 J/mg COD respectively. These results were used for experimental verification, which was in good agreement with the predicted results.

The kinetic analysis carried out for the present process indicates that the adsorption system follows pseudo-second-order kinetic model (R^2 =0.9818), and the rate-limiting step is the surface adsorption that involves chemisorption. Finally, the equilibrium data fit well with the Freundlich adsorption isotherm model(R^2=0.9969) and indicate multilayer adsorption taking place.

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Nomenclature

List of symbols

A and B   Redlich-Peterson constant

C_0 Initial COD concentration

C_e COD adsorbed at equilibrium

C_f Final COD concentration

F   F-value

g   Redlich Peterson exponent

K_f Freundlich constant

K_l Langmuir constant

k_1 Rate constant of first order adsorption

k_2 Rate constant of second order adsorption

p   p-value

q   Amount of COD adsorbed on the adsorbent at time t

q_e COD adsorbed per unit mass of adsorbent

q_{max} Maximum adsorption capacity

R^2 Coefficient of determination

S   Surface area of electrodes

t   Electrolysis time

V   Volume of the reactor

W   Mass of dissolved anode

χ^2 Chi square

α   Initial adsorption rate

β   Extent of surface coverage and the activation energy for chemisorptions

List of abbreviations

AC   Anode consumption

ANOVA   Analysis of variance

Al   Aluminum

BIS   Bureau of Indian standards

BOD   Biochemical oxygen demand

CCD   Central composite design

CI   Cheese Industry

COD   Chemical oxygen demand

DC   Direct current

DF   Degree of freedom

DI   Dairy industry

DOE   Design of experiments

EC   Electrocoagulation

MS   Mean of squares

NaCl   Sodium chloride

RMSE   Root mean square error

RSM   Response surface methodology

SE   Standard error

SEEC   Specific electrical energy consumption

SDW   Synthetic Dairy wastewater

SS   Sum of Squares

S/V   Surface area of electrodes to volume of the reactor

Ti/Pt   Platinized titanium

TS   Total solids

TSS   Total suspended solids

TDS   Total dissolved solids

YB   Yogurt and buttermilk

1.0 Introduction

1.1 Background of the problem

Increasing growth of industries has resulted in the production and release of noxious substances into the environment, which has affected normal operations, flora and fauna and created health hazards. These wastes are released in the form of solids, liquid effluent and slurries containing a wide variety of organic and inorganic chemicals. Thus, pollution is a necessary sin of all developments. To prevent the excessive effect on environment, efficient and environmentally safe waste treatment technologies are needed.

Rapid growth in the demand for milk and milk products has led to advancements in veterinary science, which has subsequently led to steady growth in the production of milk per head of cattle (Kushwaha, et al., 2011). India ranks first in milk production, accounting for 18.5% of world production. India recorded a growth of 6.26% whereas world milk production increases by 3.1% (Press Information Bureau, 2016). This has caused the massive growth of dairy industries in most countries of the world including India. Consequently, the amount of dairy wastewater generated and discharged from dairy industries has also increased.

The dairy industry is one of the most polluting of industries, not only regarding the volume of effluent generated but also regarding its characteristics as well. It generates about 0.2–10 litres of effluent per litre of processed milk (Vourch, et al., 2008) with an average generation of about 2.5 litres of wastewater per litre of the milk processed (Ramasamy, et al., 2004). Since, the dairy industry produces various products, such as milk, yogurt, butter, ice-cream, and various types of desserts and cheese, the effluent characteristics also vary widely both in quantity and quality, depending on the type of system and the methods of operation used (Kushwaha, et al., 2011).

Dairy wastewaters are characterized by high biological oxygen demand (BOD) and chemical oxygen demand (COD) concentrations and contain fats, nutrients, lactose, as well as detergents and sanitizing agents (USDA-SCS, 1992). Due to the high pollution load of dairy wastewater, the milk-processing industries discharging untreated/partially

treated wastewater cause serious environmental problems (Montuelle, et al., 1992) such as the increase in the microbial biomass, depletion of the dissolved oxygen concentration, mushroom and algae proliferation, deposits of mud and eutrophication of receiving surface waters (Aitbara, et al., 2014).

1.2 Minimal standards for discharge of dairy effluents

Table 1 enlists minimal standards for effluent discharge from dairy industries as prescribed by **World Bank Report,1996** and **Central Pollution Control Board(*CPCB*)**.

Table 1: Minimal standards for discharge of effluents from the dairy industry

Parameter	Maximum value (mg/l)	
	World Bank report[*]	CPCB, India
pH	6-9	6.5-8.5
BOD_5	50	100
COD	250	-
Total Suspended Solids	50	150
Oil& Grease	10	10
Total Nitrogen	10	-
Total Phosphorous	2	-
Temperature Increase	$<3^0C^a$	-
Coliform Bacteria	400 Most probable number/100ml	-

Note: [*]Effluent requirements are for direct discharge to surface waters

[a]At the edge of a scientifically established mixing zone which takes into account ambient water quality, receiving water use, potential receptors and assimilative capacity.

Source: (International Finance Corporatiion, 2007)

: http://www.cpcb.nic.in/Industry-specific-standards/Effluent/DairyIndustry.pdf

1.3 Dairy wastewater treatment technologies

Dairy wastewaters are treated by aerobic/anaerobic biological processes such as activated sludge process, aerated lagoons, trickling filters, sequencing batch reactor (SBR), anaerobic sludge blanket (UASB) reactor, anaerobic filters, etc. Coagulation/flocculation, nano-filtration, reverse osmosis, adsorption processes have also been employed.

Table 2: Advantages & disadvantages of aerobic, anaerobic and electrochemical processes

Treatment	Advantages	Disadvantages
Anaerobic	• Smaller reactor size is required. • Energy is produced in the form of methane. • Very high Loading rate of 31 kg COD/m^3 d has been reported.	• Effluent quality in terms of COD is fair but further treatment is required. Nutrient removal is very poor • Fats in wastewater shows the inhibitory action • There is need for alkalinity addition to maintain the pH • Poor performance with regard to shock loading.
Aerobic	• Excellent effluent quality in terms of COD, BOD and nutrient removal • Oil & grease do not cause serious problems • 6-8 times greater biomass is produced compared to anaerobic process. • Excellent performance with regard to shock loading. • No need of alkalinity addition	• requires larger land area • High energy is required • High production of Excess sludge
Electrochemical	• Simple equipment, easy mode of operation, low	• Lack of exact reactor design configuration and modelling

	retention time and high sedimentation velocity. • Small quantity of sludge produced • EC flocs are much larger, contains less bound water, acid-resistant and more stable compared to chemical flocs, and therefore, can be separated faster by filtration. • More efficient and rapid removal of organic pollutants from waste water • dosage of the coagulant can be controlled by adjusting the current which makes automation of the system very easy. • Gas bubbles produced during electrolysis carries the pollutant to the top of the solution where it can be easily concentrated, collected, and removed	procedures as its design depends upon complex electrochemical interactions, colloidal forces and hydrodynamics. • Maintenance of a constant pH is difficult as one cannot control the production of H^+, OH^- and Cl^- ions. • When Al is used as anode material, a passive oxide film develops on the surface of anode leading to an increase in the applied potential and wastage of energy. • Use of electricity may be expensive. • High conductivity of the wastewater suspension is required. • Gelatinous hydroxide may tend to solubilize in some cases • Although EC technique has reached a stage of profitable commercialization, yet the amount of scientific attention it has received is still very primitive.

Source: (Kushwaha, et al., 2011), (Mollah, et al., 2001)

Anaerobic processes treat only the carbonaceous pollutant, and nutrient removal is poor. So, further treatment is necessary for anaerobically treated dairy wastewater. The primary drawback of aerobic treatment methods is the high-energy requirement (Kushwaha, et al., 2011). Also, biological processes require big spaces and long time of treatment and generate a great amount of sludge (Demirel, et al., 2005). Also, high costs are associated with chemical treatments that have made the conventional chemical

coagulation technique less acceptable. Among physicochemical methods, electro-coagulation (EC) is one of the processes which offer high removal efficiencies in compact reactors, with moderate operating cost. With the ever increasing standard of drinking water supply and the stringent environmental regulations regarding the wastewater discharge, electrochemical technologies have regained their importance worldwide during the past two decades (Chen, 2004). The electrochemical process is characterized as being easy to use and operate, having the simple equipment, reduced sludge production and no requirement for chemical handling (Sinha & Mathur, 2015). EC has been successfully applied to treat a vast variety of waste waters including textile waste water, paper-mill waste water, laundry waste water, tannery waste, latex particles, etc. Since dairy wastewater is considered as stable oil in water effluents, EC process could be used for their treatment (Bensadok, et al., 2011).

EC method implies sacrificial anode, where the metal cations of coagulation are released in situ when the electric current is applied. At the same time, the reactions of electrolysis generate hydrogen bubbles to cathode and oxygen bubbles to the anode, which favours flotation of the particles (Aitbara, et al., 2014).

1.4 Objectives of the study

In the present study, Electro-coagulation has been used to treat simulated dairy wastewater. Systematic experimental investigations with aluminum electrodes were carried out to understand the effect of different operating parameters on the efficiency of dairy waste water treatment. The results of the investigation were used to develop the numerical relationships between different variables. Design of Experiments(DOE) was employed to obtain sufficient information to optimize the process with the lesser number of experiments. Central composite design (CCD) and Response Surface Methodology (RSM) has been used for the modelling, analyzing and optimization of following responses:

  i.   % COD removal
 ii.   % BOD removal
iii.   Anode Consumption(AC)
 iv.   Specific Electrical Energy Consumption(SEEC)

for the following process parameter settings:

i. Current Density
ii. pH
iii. Conductivity

The increase in energy input in the process results in more anode sacrifice and more COD/BOD removal. However, availability of pollutant in the solution is a limiting factor. Excess energy input results in disintegration of flocs which causes loss of COD/ BOD removal efficiency, excessive dissolution of aluminium in water which has neuro-toxic effects, and loss of energy through heating of electrodes. Therefore, optimization was targeted for maximum COD removal for minimum energy input. Further, adsorption kinetics and adsorption isotherm studies have been carried out. Adsorption kinetics helps in the prediction of adsorption rate while isotherm studies assist in understanding surface properties, adsorption mechanism, and interaction between the adsorbent and adsorbate.

2.0 Literature Review

2.1 Sources of wastewater in dairy industry

In the dairy industry, effluents are generated in an intermittent way and the flow rates of the effluents changes significantly (Kolarski & Nyhuis, 1995). In the dairy industry, some quantity of wastewater gets created during starting, equilibrating, stopping, and rinsing of the processing units (flushing water, first rinse water, etc.) (Vourch, et al., 2008). However, the dairy effluents are primarily generated from the cleaning and washing operations in the milk processing plants. It is estimated that about 2% of the total milk processed is washed out into drains (Munavalli & Saler, 2009). These can be further classified into three categories:

i. Cooling water- water used in various utilities such as cooling tower, water softener, boiler, back washing and air compressor. As cooling water is usually free from pollutants, it is discharged into the storm water piping system without any treatment.

ii. Sanitary wastewater- includes water used for cleaning of tanks and tankers, milk cans, dairy floor, etc. The sanitary waste water is in general piped directly to the sewage treatment plant with or without first having being mixed with industrial waste water. The effluent generated is high in quantity and contains high organic load.

iii. Industrial wastewater- comes up from the discharge of sour whey, acidic, curdled milk, spillage of milk and products thereof and from cleaning of equipment (CIP) that has been in contact with milk products. The concentration and composition of the waste depend on the production programme, operating methods and the design of the processing plants. The effluent generated is highly unstable in nature and biodegradable (Judal, et al., 2015).

Table 3 shows various sources of wastewater in dairy industry published by Environment Protection Authority, State Government of Victoria in June 1997.

Table 3: Sources of wastewater from Milk based food industry (Robinson, 1997)

Operations	Processes	Sources of waste
Preparation Stages	Milk receiving/Storage	• Poor drainage of tankers • Spills and leaks from hoses and pipes • Spills from storage silos/ tanks • Foaming • Cleaning operations
	Pasteurization/ ultra heat treatment	• Liquid losses/leaks • Recovery of downgraded product • Cleaning operations • Foaming • Deposits on the surfaces of pasteurization and heating equipment
	Homogenization	• Liquid losses/leaks • Cleaning operations
	Separation/ Clarification (Centrifuge, reverse osmosis)	• Foaming • Cleaning operations • Pipe leaks
Product processing stages	Market milk	• Foaming • Product washing • Cleaning operations • Overfilling • Poor drainage • Sludge removal from • Clarifier/Separators • Leaks • Damaged milk packages • Cleaning of filling machinery
	Cheese making	• Overfilling vats • Incomplete separation of whey from curd • Using salt in cheese making • Spills and leaks • Cleaning operations
	Butter making	• Vacreation and salt use • Product washing • Cleaning operations
	Powder manufacture	• Spills of powder handling • Start-up and shut-down losses • Plant malfunction • Stack losses • Cleaning of evaporators • Bagging losses

2.2 Characteristics of dairy wastewater

Dairy wastewater contains milk solids, sanitizers, detergents, milk wastes, and cleaning water. It is characterized by high concentrations of nutrients, and organic and inorganic contents (USDA-SCS, 1992). Dairy wastewater contains organics which add towards their high biochemical oxygen demand (BOD) and chemical oxygen demand (COD). The total COD of dairy wastewater is largely influenced by the milk, cream, or whey (Wildbrett, 1998). Dairy wastes are white in colour and usually slightly alkaline in nature and become acidic quite rapidly due to the fermentation of milk sugar to lactic acid (Kolhe, et al., 2009). In dairy wastewaters, nitrogen originates mainly from milk proteins and is either present in organic nitrogen form such as proteins, urea and nucleic acids, or as ions such as NH_4^+, NO_2^-, and NO_3^-. Phosphorus is found mainly in inorganic forms such as orthophosphate (PO_4^{-3}) and polyphosphate ($P_2O_7^{-4}$) as well as in organic forms also. The detergents and their additives are also present in small quantities in dairy wastewater. They may be alkaline or acidic, and very often contain additives like sequestering agents, phosphates, surfactants, etc. (Kushwaha, et al., 2011). Noteworthy amounts of *Na, Cl, K, Ca, Mg, Fe, Co, Ni, Mn* are also always present in dairy wastewater. The presence of high concentration of *Na* and *Cl* is due to the use of large amount of alkaline cleaners in the dairy plant (Demirel, et al., 2005).

Table 4 shows the characteristics of dairy industry wastewaters

Table 4: Characteristics of dairy industry wastewaters (composition in mg/l, except for pH, Conductivity and Turbidity)

Waste Type	COD	BOD	pH	TSS	TS	Grease	P	C (uS/cm)	T (NTU)	References
DI	2300	1270				500	36.3		1000	(Aitbara, et al., 2014)
DI	7855.25 ±703.05	3486.3 ±235.2	7.65	1724.17 ±149.14				8010 ±1300		(Bazrafshan, et al., 2013)
DI	1900-2700	1200-1800	7.2-8.8	500-740						(Daneshwar, et al., 2004)
DI	1200-1900	6.5-7					710-945	520-560		(Yavuz, et al., 2010)
DI	1596	796	7.5	1871				1960		(Ghahremani, et al., 2012)
DI	18300		6.0-7.5	10200		4570		1200		(Sengil & Ozacar, 2006)
YB	1500	1000	7.20	191						(Koyuncu, et al., 2000)
DI	2080		5.43				21.8		281.75	(Shivayogimath & Meti, 2015)
DI	4100	2100	6.6-9.0	660	3050		15.15			(Sivakumar & Asha, 2012)
DI	790	530	6.5	729	2532					(Patil, et al., 2014)
DI	1500-3000	350-600	5.5-7.5	250-600					15-30	(Sarkar, et al., 2006)
CI	15500		5.2					17000		(Un, et al., 2013)
DI	430-15200	650-6240	4.7-11.0	250-2750						(Passeggi, et al., 2009)
DI	980–7500	680–4500		300						(Kolarski & Nyhuis, 1995)

DI: Dairy Industry; CI: Cheese Industry; YB: Yogurt and buttermilk; P: Phosphorous; C: Conductivity; T: Turbidity

2.3 Electro-coagulation Process

Electro-coagulation is an electrochemical method to treat water/wastewater in which sacrificial anodes corrode to release active coagulant precursors (usually iron or aluminium cations) into the solution. Associated electrolytic reactions evolve gas (usually hydrogen bubbles) at the cathode (Holt, et al., 2005). Electro-coagulation involves various chemical and physical phenomena that use consumable electrodes for the supply of ions into the pollutant system (Khandekar & Saroha, 2013). The schematic diagram of EC reactor is shown in Figure 1.
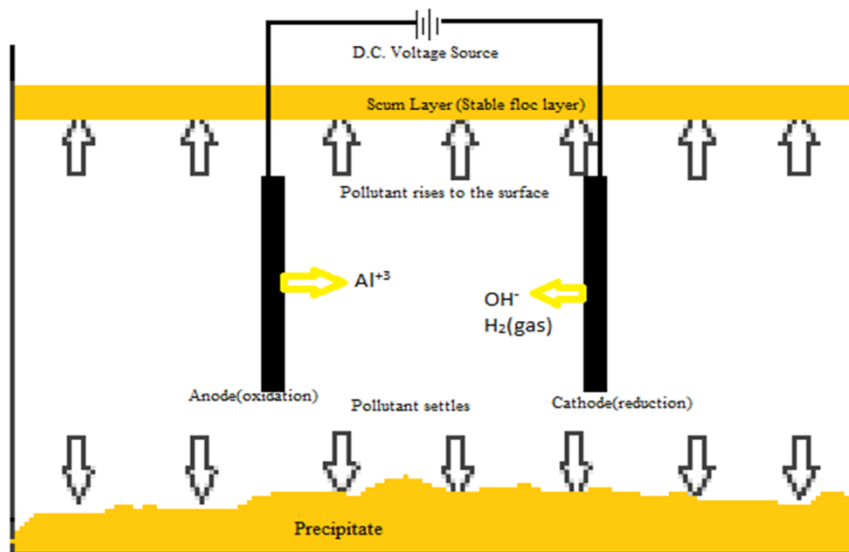
Figure 1: Schematic diagram of the EC process.

In EC the coagulating ions are produced in situ, and it involves the following successive stages (Khandekar & Saroha, 2013):

   i.   Anode dissolution
  ii.   Formation of OH^- ions and H_2 at the cathode
 iii.   Electrolytic reactions at electrode surfaces
  iv.   Adsorption of coagulant on colloidal pollutants
   v.   Removal of colloids by sedimentation or flotation

In EC, the selection of the electrode material and the mode of combination of anode and cathode are the important parameters (Khandekar & Saroha, 2013). Aluminum and iron are commonly used electrodes as they are cheap, readily available and very effective used. For the present study, aluminum electrodes have been used. When the

current is applied to the electrodes, the anode undergoes electrolytic oxidation and forms metal ions(aqueous Al^{3+} species) which act as coagulants. At the cathode, the reactions of electrolysis generate OH^- ions and hydrogen bubbles to the cathode. Production of hydrogen bubbles to cathode and oxygen bubbles to the anode favours flotation of the particles. These bubbles while moving upward, collides with suspended particles in the water, adheres to them and carries the pollutant material to the liquid surface. They form a stable floc layer at the top surface of the reactor. The Al^{3+} ions further react to form $Al(OH)_3$ flocs. The electrochemical reactions (Equation (2.1)& (2.2)) are followed by the chemical one (Equation (2.3)) (Hu, et al., 2005), (Modirshahla, et al., 2007), (Yilmaz, et al., 2005). Since pH increases in the vicinity of the cathode, a corrosion of aluminium takes place according to the Equation(2.4) (Mollah, et al., 2004) (Kobya, et al., 2003) (Tchamango, et al., 2010):

$$Al \rightarrow Al^{3+} + 3e^- \tag{2.1}$$

$$3H_2O + 3e^- \rightarrow 3/2H_2 + 3OH^- \tag{2.2}$$

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \tag{2.3}$$

$$Al + 3H_2O + OH^- \rightarrow Al(OH)^-_4 + 3/2H_2 \tag{2.4}$$

The Al^{3+} and OH^- ions produced at the electrodes can react to form various mono-nuclear ($Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$) and poly-nuclear species ($Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}(OH)_{34}^{5+}$, $Al_{13}O_4(OH)_{24}^{7+}$), which are finally transformed into aluminium hydroxide: $Al(OH)_3$. The large specific area of $Al(OH)_3$ then facilitates compound adsorption and traps the colloids (Mollah, et al., 2004) (Kobya, et al., 2003) (Tchamango, et al., 2010). The EC process is an amalgamation of different processes including oxidation, coagulation, flocculation and flotation (Sinha, et al., 2015).

Electro-coagulation is an efficient technique because adsorption of hydroxide on mineral surfaces are 100 times greater on 'in situ' rather than on pre-precipitated hydroxides when metal hydroxides are used as the coagulant (Mollah, et al., 2004). Flocs formed by EC are fairly large which enclose less bound water and are more stable. Thus, they can be easily removed by filtration. The process requires no chemical addition which reduces the possibility of the creation of secondary pollutants. This minimizes the sludge generation and ultimately eliminates some of the harmful chemicals used as coagulants in the conventional effluent treatment methods. Electro-

coagulation process can efficiently destabilise small colloidal particles and generates a lower quantity of sludge compared to other processes. It is an environment-friendly process as it can be operated by green processes, such as solar, windmills and fuel cells (Khandekar & Saroha, 2013).

2.3.1 Electrode connection

In electro-coagulation, electrode material and electrode arrangement plays an important role in the cost of the process. The electrodes in the EC reactor can be connected in three different types mainly: monopolar-parallel(MP-P), monopolar-serial(MP-S) and bipolar-parallel(BP-P) as shown in figure 2. It has been found that MP-P mode is the most cost effective and is preferred as a low cost treatment (Demirci, et al., 2015).
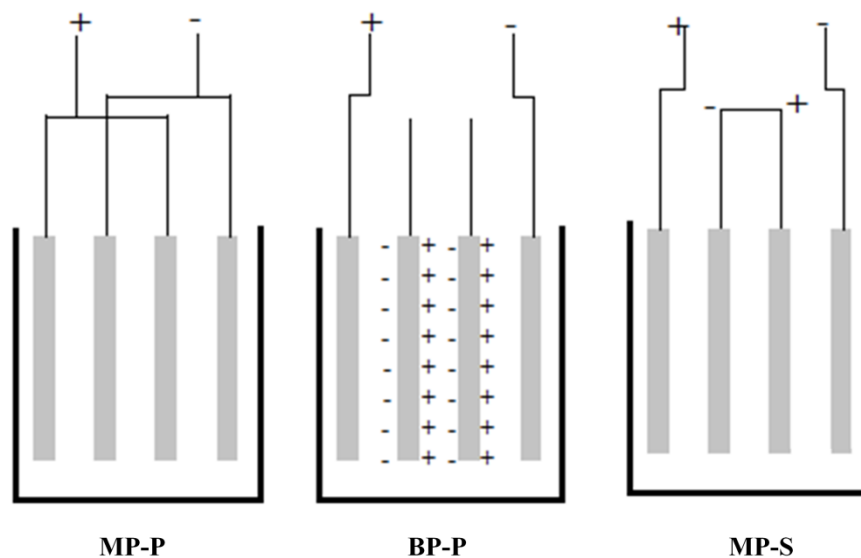
Figure 2: Schematic view of the EC reactors

2.3.2 Batch and continuous mode of operation

Batch and continuous mode of operation have been used in electro-coagulation for the removal of a wide range of pollutants. A batch reactor's dynamic nature helps to study the range of operating conditions and is more favourable for research work. Continuous systems are suitable for industrial processes that generate large effluent volumes whereas the batch reactors are suitable for laboratory and pilot plant scale applications. A continuous system functions under steady state conditions, so it maintains a constant effluent flow rate and fixed pollutant concentration.

A batch reactor does not have inflow or outflow of the effluent during electrolysis. In batch mode, since the coagulant is continuously generated in the reactor with the dissolution of the anode, reactors exhibits time dependent behaviour. The anode material is hydrolysed and is capable of aggregating the pollutants. As a result, the concentration of the coagulant, pollutant, and pH keeps on changing with time (Khandekar & Saroha, 2013).

2.3.3 Effect of various parameters

i. *Solution conductivity*: Operating cost of the system and efficiency of the treatment are dependent on the solution conductivity. It is necessary to have some minimum conductivity for the flow of the electric current. When the conductivity of the wastewater is low, it has to be adjusted by adding sufficient amount of salts such as sodium chloride or sodium sulphate. There is a reduction in the cell voltage at the constant current density or an increase in the current density at constant cell voltage with an increase in the conductivity of the solution. Thus, energy consumption is also reduced with an increase in the conductivity (Bayramoglu, et al., 2004).

ii. *pH of the solution*: The pH of the solution is a vital operational parameter in electro-coagulation. The maximum pollutant removal efficiency is obtained at an optimum solution pH for a particular pollutant (Khandekar & Saroha, 2013). Generally, the pH of the medium changes during the process depending on the initial pH and type of electrode material. In the case of aluminum, the final pH is higher for initial pH<8.The difference between initial and final pH values diminishes for initial pH>8 (Kobya, et al., 2003). In comparison to chemical coagulation, EC treatment increases the pH of the solution when it is in an acidic, neutral or slightly alkaline region and reduces when it is highly alkaline (Mouedhen, et al., 2008). The power consumption is high at neutral pH due to the variation of conductivity. When conductivity is high enough, pH effect becomes significant (Chen, 2004).

iii. ***Current density***: Current density determines the bubble production rate, coagulant dosage rate, size and growth of the flocs, which can affect the effectiveness of the electro-coagulation process. The anode dissolution rate increases with an increase in the current density,. This leads to an increase in the number of metal hydroxide flocs resulting in an increase in the pollutant removal efficiency (Khandekar & Saroha, 2013). A large current means a small electro-coagulation unit. However, when high current is used, there is a high chance of wasting electrical energy in heating up the water. Also, too large current density would result in a considerable decrease in the current efficiency. In order that the electro-coagulation system can operate for a long period of time without maintenance, its current density is suggested as 20–25 A/m^2 unless there are measures taken for a periodical cleaning of the surface of electrodes. The current efficiency for aluminum electrode could be between 120–140% while that for iron is around 100%. Current efficiency above 100% for aluminum can be credited to the pitting corrosion effect particularly when there are chlorine ions present (Chen, 2004). An increase in current density above the optimum current density does not result in an increase in the pollutant removal efficiency as sufficient number of metal hydroxide flocs are available for the sedimentation of the pollutant (Khandekar & Saroha, 2013).

iv. ***Inter-electrode distance***: The inter-electrode distance plays an important role in the electro-coagulation as the electrostatic field depends on the distance between the cathode and the anode. The maximum pollutant removal efficiency is achieved at an optimum distance between the electrodes. When the inter-electrode distance is minimum, the pollutant removal efficiency is low. This is because the generated metal hydroxides which act as the flocs and remove the pollutant by sedimentation get broken down by collision with each other due to high electrostatic attraction (Daneshwar, et al., 2004). The pollutant removal efficiency increases with an increase in the inter-electrode distance from the minimum till the optimum distance between the electrodes. This is due to the fact that by further increasing the distance between the electrodes, there is a decrease in the electrostatic effects resulting in a slower movement of the generated ions. It provides more time for the generated metal hydroxide to

agglomerate to form the flocs resulting in an increase in the removal efficiency of the pollutant in the solution. On further increasing the electrode distance more than the optimum electrode distance, there is a reduction in the pollutant removal efficiency. This is due to the fact that the travel time of the ions increases with an increase in the distance between the electrodes. This leads to a decrease in the electrostatic attraction resulting in the less formation of flocs needed to coagulate the pollutant.

v. ***Effect of agitation speed***: If coagulant matter does not disperse in the reactor well, contents of the reactor cannot be homogenous and regional differences can be observed (Bayar, et al., 2011). The agitation helps to maintain uniform conditions and avoids the formation of concentration gradient in the electrolysis cell. Further, the agitation in the electrolysis cell imparts velocity for the movement of the generated ions. With an increase in agitation speed up to the optimum agitation speed, there is an increase in the pollutant removal efficiency. This is due to the fact that with an increase in the mobility of the generated ions, the flocs are formed much earlier resulting in an increase in the pollutant removal efficiency for a particular electrolysis time. But with a further increase in the agitation speed beyond the optimum value, there is a decrease in the pollutant removal efficiency as the flocs get degraded by collision with each other due to high agitation speed (Modirshahla, et al., 2008). The flocs break down into very small sizes which are difficult to be removed from the reactor.

vi. ***Retention time***: The pollutant removal efficiency is also a function of the electrolysis time. The pollutant removal efficiency increases with an increase in the electrolysis time. But beyond the optimum electrolysis time, the pollutant removal efficiency becomes constant and does not increase with an increase in the electrolysis time. The metal hydroxides are formed by the dissolution of the anode. For a fixed current density, the number of generated metal hydroxide increases with an increase in the electrolysis time. For a longer electrolysis time, there is an increase in the generation of flocs resulting in an increase in the pollutant removal efficiency. For an electrolysis time beyond the optimum

electrolysis time, the pollutant removal efficiency does not increase as sufficient numbers of flocs are available for the removal of the pollutant.

vii.   ***Initial pollutant concentration***: When initial pollutant concentration is increased, removal efficiency increases due to the existence of excess colloids for the adsorption in high pollutant concentrations (Sengil & Ozacar, 2006).

viii. ***Temperature***:   It affects reaction rates, floc formation and conductivity. Depending on the pollutant, increasing temperature can have a positive or a negative effect on removal efficiency.

2.4 Research findings in the recent past

Several studies have been carried out on electro-coagulation of dairy wastewater. EC is an emerging promising technique and a lot of research work is being carried out in this area.

(Tchamango, et al., 2010) compared chemical coagulation and electro-coagulation They used aluminum electrodes on artificial wastewater derived from solutions of milk powder and COD was reduced to 61%. A similar treatment applied to phosphate and lactose solutions revealed that lactose was not eliminated, a fact that could account for the rather poor lowering of the COD. The efficiency of the electro-coagulation technique was almost identical as compared to chemical coagulation treatment with aluminium sulphate. The wastewaters treated by electro-coagulation exhibited a lower conductivity and a neutral pH value (by contrast to the acid nature of the solution treated by the chemical coagulation). This shows that it may be possible to recycle the treated water for some industrial uses. Moreover, the electro-coagulation process uses fewer reagents: the mass of the aluminium anode dissolved during the treatment is lesser compared to the amount of the aluminium salt used in chemical coagulation. These two observations undoubtedly show that the electro-coagulation technique is more performing.

(Sengil & Ozacar, 2006) investigated the removal of COD and oil–grease from dairy wastewater by electro-coagulation with bipolar electrodes in parallel connection and obtained using iron electrode, 98% removal of COD and 99% removal of grease. They found an increase in the removal efficiency of COD and oil–grease up to 100% when the concentration of *NaCl* salt in the solution is 0.3 g/L. They also studied adsorption isotherms and concluded that the adsorption isotherm with hydroxo-cationic complexes can be better described by the Freundlich adsorption isotherm model.

(Ghahremani, et al., 2012) investigated different electrode materials (iron, aluminum and stainless steel) and electrode gaps (2, 4, 6 cm) for the treatment of dairy industry wastewater and observed that the removal efficiency is directly proportional to the electrode material and inversely proportional to electrode gaps. An optimal COD removal was achieved with the iron electrode and at electrode gap of 2 cm.

(Bensadok, et al., 2011) investigated removal of COD, phosphate and turbidity using *Al-Al* and *Al-Ti/Pt* electrodes systems for the treatment of milk liquid fractions. The maximum removal efficiency was obtained with the use of both cathode and anode made of aluminum (*Al–Al* system). Optimal values of current density, *NaCl* concentration, initial pH, and electrolysis time were 50 A/m^2, 1.5 g/L, 6.6 and 2 min respectively. The removal efficiency of COD and turbidity were 80% and 96% respectively. Corresponding energy consumption was very low and equal to 0.03 kWh/kg for COD. They observed the occurrence of indirect electrochemical degradation of the dissolved polluting matter and the occurrence of aluminum cathodic dissolution which contributes to the improvement of the coagulation process. The results indicated that soluble COD and phosphate might be eliminated by indirect oxidation, whereas turbidity is removed only by coagulation process and depends mainly on aluminum concentration.

(Yavuz, et al., 2010) used a combined electrode system consisting of iron and aluminum as sacrificial electrodes. A pole changer device was employed to change the polarization at given time intervals to generate iron and aluminum based coagulants to ensure homogenous consumption of these electrodes. 79.2% COD removal was achieved at the current density of 15 mA/cm^2 and natural pH. They reported that 20 min electrolysis is enough since insignificant variations in COD removal were observed after this time.

(Kushwaha, et al., 2010) used bipolar iron electrodes in parallel connection and conducted RSM modelling and optimization of the EC process. Optimum values of current density, dosage of sodium chloride, electrolysis time and pH were found to be 270A/m^2, 0g/L, 50 min, and 7.0, respectively. Optimum COD removal efficiency was found to be ≈70%.They observed that charge neutralization of anionic colloids present in the SDW by Fe^{2+} along with electro-floatation and electro-oxidation were the main reason for COD removal. Thus, the mechanism of COD removal by EC seems to be a combination of electro-coagulation, electro-floatation and electro-oxidation.

Thus, it is clear that electrochemical treatment with iron electrode consumes more energy and requires more electrolysis time (current density of the order of 18-270 A/m^2, electrolysis time 50-70 min) which in turn, causes high consumption of electrode. Moreover, the treated water is left with colour, rendering it unfit for disposal in water

bodies, while the electrolysis with aluminum electrode requires a substantially low amount of energy and electrolysis time.

(Aitbara, et al., 2014) conducted continuous treatment of industrial dairy effluent by electro-coagulation using aluminum electrodes and examined the effect of operational parameters, such as initial pH, current density, inlet flow rate, and the temperature(10-35ºC) of waste water. A flow rate of around 20 mL/min caused nearly 95% turbidity removal is with a reasonable energy consumption of 3.6 kWh/m^3.The maximum elimination of pollutants was observed at a pH close to neutrality (pH 7.3). For the temperatures beyond 20°C, the reduction ratio of turbidity decreases with the rise in the temperature. The kinetics becomes faster; the mobility of the formed ions increases considerably and their probabilities of collision to form the aluminum hydroxide, is reduced. Also, the increase in the temperature leads to an increase in the solubility of the precipitates of aluminum hydroxide formed. Consequently, the effectiveness of the reduction of turbidity decreases.

2.4.1 Research gap

The above review shows that there is lack of literature on:

  i.   RSM modelling on batch EC process using aluminum electrodes
 ii.   Adsorption kinetics
iii.   Adsorption isotherms

Therefore, the above sections have been studied in this thesis.

3.0 Materials and methods

3.1 EC apparatus

A reactor of 2L effective volume was used to conduct the batch experiments. Electrodes were connected in the mono-polar mode. Two aluminum electrodes of dimensions: 10cm width, 7.8cm height, 0.3cm thickness; with the purity of 98.99% and surface area of 156 cm^2 were used. The electrode gap was 2 cm for all experiments. Electrodes were connected to a DC power supply(*Testronix*, 0-30V,0- 5A) in mono-polar configuration. Magnetic stirrer at 50 rpm was used to stir the solution to get homogeneous wastewater-flocs mixture. The batch EC cell with mono-polar electrode connection is shown in figure 3. No exact reactor design configuration has been suggested in the literature. However, the ratio of surface area of the electrode(S) to the volume of the reactor(V) is available. In the present work, S/V ratio is kept as $7.8m^2/m^3$ which is within the cited range in the literature (Mameri, et al., 1998).
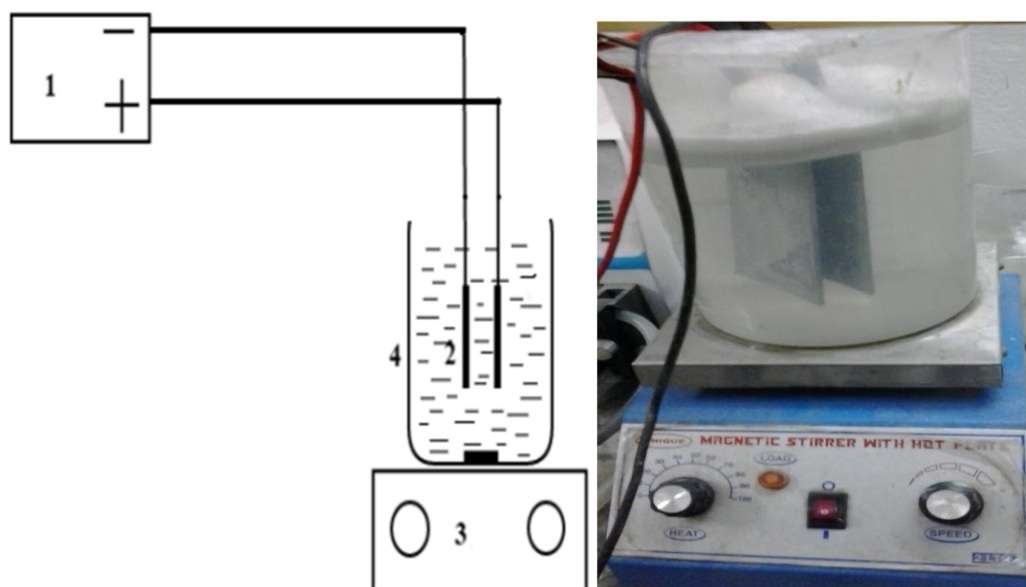
Figure 3: Diagram of the experimental setup. (1): DC power supply, (2): electrodes, (3): magnetic stirrer, and (4): EC reactor

3.2 Instruments used

1. DC power supply unit: The instrument is manufactured by *KUSAM-MECO (Model: KM-PS-305D-II)* with 0-30V/0~5A dual output with inbuilt ammeter and voltmeter.

2. Closed Reflux apparatus: The instrument manufactured by *HACH (DRB 200)* is used for digesting the COD samples.

3. *UV/VIS* Spectrophotometer: This instrument manufactured by *SHIMADZU (UV-1800)* is used for determining the initial COD of dairy wastewater and the final COD of the samples taken during the experimental run. Since the COD of the dairy wastewater is high, samples have to be diluted before digestion and the reading obtained should be multiplied by the dilution factor.

4. Auto digital pH meter: The instrument manufactured by *LABTRONICS(Model: LT-11)* is used for measuring and adjusting the pH of the solution. The instrument is calibrated at pH 7 and pH 4 before taking pH of the sample.

5. Magnetic stirrer: It is manufactured by *REMI(5 Ml capacity)* and is used for maintaining homogeneity in the solution.

6. Conductivity meter: A conductivity meter manufactured by *LUTRON* of model *CD-4302* with range of 2-20 mS is used for measuring conductivity in the solution.

7. Digital Nephelometer: It is manufactured by *Electronics India* of model *341 E* having an accuracy of 2% F.S.±1 digit. The range of the instrument is 0 to 19.9 NTU and 20 to 99.9 NTU.

8. Digital weighing balance of *CAS* series, model number *CAUW 220 D* with range of 1 mg to 220 gm.

9. Glass ware - pipettes, test tubes, COD digestion vials, measuring cylinders, conical flasks, WHATMAN filter paper, dilution water, etc.

3.3 Experimental procedure

In the present work freshly prepared Simulated Dairy Wastewater(SDW) was used to prevent any change in the composition of wastewater throughout the study. **'Nestle Everyday Dairy Creamer'** manufactured by **'Nestle India Ltd'** was used to prepare SDW. Artificial dairy effluents were prepared by dissolution of 1g commercial milk powder in per litre of tap water. The characteristics of waste water used are presented in Table 5.

Table 5: Characteristics of wastewater used

Characteristics	Value
Chemical oxygen demand(COD)(mg/L)	1300±50
Biochemical oxygen demand(BOD) (mg/L)	950±60
Total solids(mg/L)	1791±150
Total dissolved solids(mg/L)	1062±140
Total suspended solids(mg/L)	729±10
Turbidity(NTU)	470±10
pH	7.60±0.20
Conductivity(μS/cm)	750±10

Passivation is undesirable for electro-coagulation and anode dissolution. The accumulation of an inhibiting layer on the electrode's surface is usually due to salt deposits or possible oxidation. Passivation layer provides resistance which increases the energy consumption but does not increase coagulant or bubble production rates. Also, it prevents the effective current transport between the anode and cathode (Khandekar & Saroha, 2013). To remove any passivating material electrodes were dipped in HCl (35%)for 10 minutes followed by a water wash for the removal of impurities from the electrode surface and oven dried. After oven drying, the electrodes were abraded with sand paper before EC experiments.

0.1N H_2SO_4 and 0.1N $NaOH$ solutions were used to adjust the pH to a desirable value before the beginning of the experiment. The conductivity of the wastewater was also adjusted to the desired value between 1000μs/cm-2000μS/cm by adding an appropriate

amount of *NaCl*. BOD was measured using dilution method. Samples were taken at every 5 minutes till the end of the experiment from the reactor. The set-up run time was 30 minutes. All the experiments were accomplished at room temperature. All the samples were filtered with WHATMAN 1.2 μm filter paper. Current was maintained constant during the run.

The % COD and BOD removal are calculated using the following relationships:

$$\% \ COD \ removal = \frac{(C_0 - C_f) * 100}{C_i}$$

where C_o and C_f are the initial and final COD concentrations (mg/l) after T (min).

$$\% \ BOD \ removal = \frac{(I - F) - (I' - F')(X/Y)}{D}$$

where,

I'= D.O.$_{initial}$ of 300 ml of dilution water.

F'= D.O.$_{final}$ of 300 ml of dilution water.

I= D.O.$_{initial}$ of sample in 300 ml B.O.D. bottle.

F= D.O.$_{final}$ of sample in 300 ml B.O.D. bottle.

X= (300 ml-volume of sample)

Y= 300 ml

D= Fractional dilution

Anode consumption was calculated using Faraday's law. In case of aluminum electrodes, the values of the electrode-mass dissolved are considerably higher than those predicted by Faraday's law (Donini, et al., 1994), (Canizares, et al., 2005). Therefore, a correction factor has to be employed (Secula, et al., 2012).

$$Anode \ consumption = \frac{I * T * M}{f * Z * F * V * C_0 * \frac{Y_T}{100}}$$

where,

I is the current in ampere.

T is time in sec.

M is the molecular mass of Al (27 g/mol).

Z is valency number (Z=3 for aluminium).

f is the ratio of electrochemical dissolution.

F is Faraday's constant (96485C=mol).

V is volume of the solution (L).

Y_T is removal efficiency at time T(%).

Specific electrical energy consumption(SEEC) is defined as the amount of electrical energy consumed per unit mass of pollutant removed (Bensadok, et al., 2011).It is calculated using the following relationship:

$$SEEC(J/mg) = \frac{(I. \int_0^T U. dT)}{V. C_0. \frac{Y_T}{100}}$$

where U is the voltage and T is time in minutes.

3.4 Analytical methods used

The physicochemical parameters were analyzed by the methods described in standard methods for the examination of water and waste water, 22nd edition for all the experiments. (Lenore, et al., 2012).

3.5 Statistical methods used

Design of Experiments(DOE) and statistical models is used to study the effect of various factors on the treatment parameters of dairy waste water. In the present work, three-level three-factorial central composite design(CCD) based on response surface methodology(RSM) was used as an experimental design tool to explain the effect of main operating parameters and their interactions. A series of runs were conducted, and data was collected for each run. Literature survey and parametric investigations suggested that current density, pH and conductivity are important operational parameters for dairy wastewater treatment using the EC process. The experimental data was analyzed using Design Expert 10.0.0 trial version for mathematical modelling, analysis and optimization of the process. The adequacy of the developed model was assessed through analysis of variance (ANOVA). Model graphs and actual *vs.* predicted plots were used to show and interpret the effects and interactions.

3.5.1 Design of experiments

Design of experiments (DOE) is a systematic method to establish the relationship between factors that affect a process and the output of that process. In other words, it is used to determine cause-and-effect relationships. It is a process of developing the experiment so that the suitable data that can be analyzed by statistical methods will be collected, resulting in applicable and objective conclusions. There are three basic principles of experimental design:

i. ***Replication***: It means repetition of the basic experiment. Replication has two important properties:

   a. It allows to obtain an estimate of the experimental error.

   b. If the sample mean is used to estimate the effect of a factor in the experiment, replication allows to obtain a more precise estimate of this effect.

ii. ***Randomization***: The characteristic of taking observations in an experiment in a random order is referred to as randomization. It is the process of assigning the various levels of the investigated factors to the experimental units in a random manner. Properly randomizing the experiment also helps in "averaging out" the effects of extraneous factors that could be present.

iii. ***Blocking:*** It is a design technique used to improve the accuracy with which comparisons among factors of interests are made. Thus, it is used to eliminate those factors which can affect the experimental response but in which we are not directly interested (Montgomery, 2005).

The design of an experiment involves the following steps:

   i. Recognition of and statement of the problem

   ii. Choice of factors, levels and ranges

   iii. Selection of the response variable

   iv. Choice of experimental design

   v. Performing the experiment

   vi. Statistical analysis of the data

   vii. Conclusions and recommendations

Steps i-iii are part of the pre-experimental planning. In practice, steps ii and iii are often done simultaneously or in reverse order (Montgomery, 2005).

3.5.2 Response Surface Methodology

Conventionally, the efficiency of the system is determined by changing one factor at a time while keeping the other factors constant which ignores complex interactions among the factors. Response Surface Methodology(RSM) is a collection of mathematical and statistical techniques which are useful for the modelling and analysis of problems in which a response of concern is influenced by several factors, and the objective is to optimize the response (Montgomery, 2005). Thus, the main advantage of RSM is that it is an effective statistical method to understand complex interactions between variables and responses and assess their relative significance of several affecting factors. Moreover, there are less number of experiments needed to be performed to obtain enough information for the optimization of the process. It also provides mathematical models defining relationships between factors and responses (Kushwaha, et al., 2010). The first step in RSM is to find an appropriate approximation for the true functional relationship(low-order polynomial) between responses and a set of independent variables. If the response is modelled well by a linear function of the independent variables, then the function is the **first-order model** (Montgomery, 2005).

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \cdots + \beta_n x_n + C$$

Higher order polynomials such as **second-order model** should be used, if there is curvature in the system (Montgomery, 2005).

$$y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \sum \sum_{i<j} \beta_{ij} x_i x_j + C$$

For maximization problem, experiments are carried out along the path of steepest ascent until no further increase in the response. The set of values of independent variables with no further increase in response is known as the optimal region. In the present study, the RSM has been used to determine the relation between %COD removal/ % BOD removal/anode consumption/ SEEC with operating parameters such as pH, applied current density and conductivity.

3.5.3 Central Composite Design

Central Composite Design(CCD) is a most popular response surface method design for fitting and analyzing response surfaces. CCD has three types of design points as shown in figure 4:
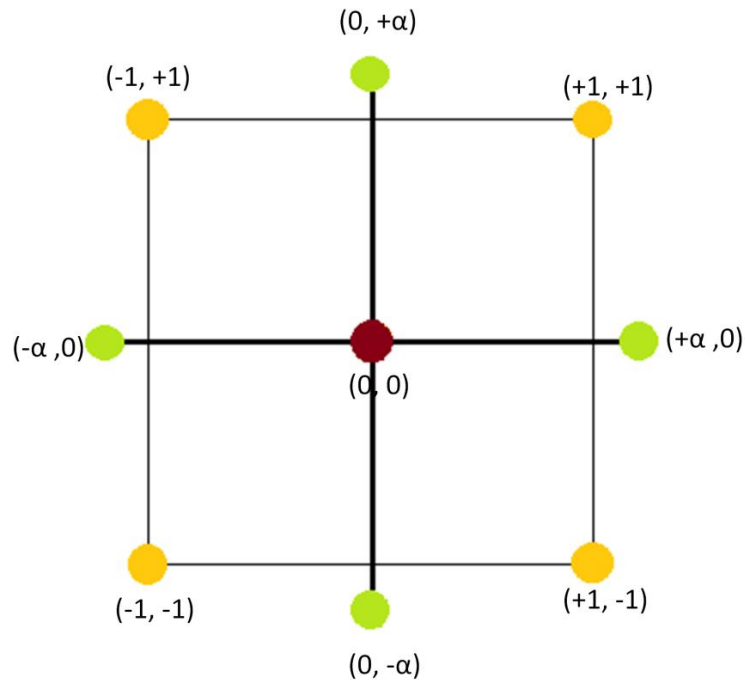
Figure 4: Design points in central composite design(2-factor problem)

i. ***Centre points(0,0)***: They are located at the centre and are used to detect curvature in the response. Thus, they contribute in the estimation of the coefficients of quadratic terms. Centre points are generally repeated 4-6 times for a good estimate of the experimental error (pure error) (Expert, 2016).

ii. ***Axial points{(+α, 0), (0, +α), (-α, 0), (0, -α)}***: They are located at a distance α from the centre point. These points are also used to estimate the coefficients of quadratic terms. The value for alpha(α) is calculated for both rotatability and orthogonality of blocks. When the value of α is equal to 1, the design is referred as **face-centred central composite design** (Expert, 2016).

iii. ***Factorial points{(-1, -1), (+1, -1), (-1, +1), (+1, +1)}***: They are located at the corners and are mainly used to estimate the coefficients of linear terms and two-way interactions (Expert, 2016).

In CCD, factors are varied at a minimum of three levels: minimum, middle and maximum or -1, 0, +1in terms of coded units (Expert, 2016).

3.5.4 Design Expert Software

In the present work, Design Expert software has been used to design the experiments, analyse and optimize the system. There are various designs available in the software such as factorial design, fractional factorial design, response surface design, mixture designs. Three main parts of design expert are as follows:

i. ***Constructing the design***: It involves deciding the important factors and responses and conducting the experiments as per the design table.

ii. ***Design analysis and mathematical modelling***: The analysis can be done once the response data has been entered. It involves diagnostics of design using Normal Probability Plots, Actual *vs.* Predicted Plots, ANOVA, Residual Plots, Box-Cox Plot for Power Transformations, and Plots of Leverage and Influence Statistics. It also provides model-graphs which include Interaction, One-Factor, 3-D Surfaces, Contours and Cubes for representation of results. A polynomial relationship between various factors and the response in terms of coded factors (-1, 0, +1) or actual factors can be developed in this part.

iii. ***Optimization of the process***: The optimization section in Design-Expert explores a combination of factor levels that simultaneously satisfy the conditions placed on each of the factors and responses. To use optimization, each response is first analyzed to set up an appropriate model. Optimization of one response or the simultaneous optimization of multiple responses can be done numerically or graphically.

4.0 Results and discussion

4.1 Experimental design and parameter settings

Parameter settings were done through experimental investigation and literature study. Parametric investigations provide a basis to identify major operational parameters and their respective ranges for the design of experiments. The effects of operational parameters like pH, current density, electrolysis time, SEEC, anode consumption and conductivity were studied.

4.1.1 Initial COD

The initial COD was decided according to previous studies available in the literature on dairy wastewater which used industrial dairy effluent. The initial COD of the industrial dairy wastewater varied from 430-18300 mg/L in various studies as shown in Table 4. However, in most of the studies it was between 1200-3000 mg/L (Aitbara, et al., 2014), (Deshannavar, et al., 2012), (Yavuz, et al., 2010), (Ghahremani, et al., 2012), (Shivayogimath & Meti, 2015), (Sarkar, et al., 2006), (Koyuncu, et al., 2000). As shown in Figure 5, when the initial concentration of COD is increased from 900-1700 mg/L, COD removal increases from 76.43 to 81.12%. The reason for this is the existence of excess colloids for the adsorption in high COD concentrations (Sengil & Ozacar, 2006). In the present study, initial COD was kept at 1300 mg/L.
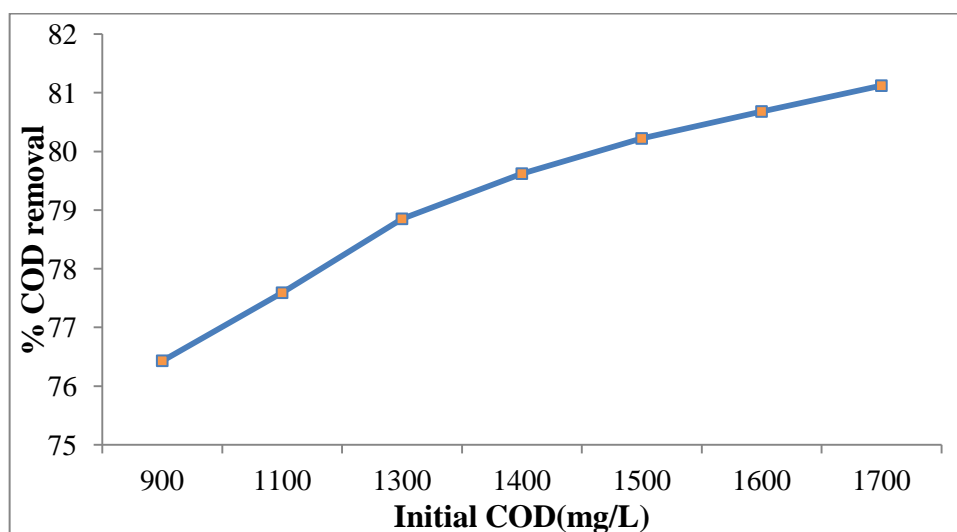
Figure 5: Effect of initial concentration on the removal efficiency of COD (pH=7, current density=2.21 mA/cm^2, conductivity=2000 µS/cm, electrolysis time=30 min)

4.1.2 Current density

Current is the most sensitive parameter as it can influence the effectiveness of EC treatment. It determines not only the amount of coagulant but also the rate and the size of the bubbles produced at the electrodes (Aitbara, et al., 2014). Current density and electrolysis time are inter-dependent. If the current density is less, electrolysis time will be more for COD/BOD removal and vice versa. Experimental study were carried out to determine the range of current density. The electrolysis time was kept constant at 45 minutes and the current was varied from 0.5A to 0.9A. The inter-electrode distance was kept at 2 cm. Conductivity was kept at 1500 μS/cm, and pH was adjusted to 7. Samples were collected after every 5 minutes and COD removal was observed. The results are shown in Figure 6, and detailed results are presented in Appendix A. From Figure 6, it can be seen that %COD removal is low at 1.60 mA/cm^2. Maximum COD removal of 77.81% was obtained at 2.40 mA/cm^2 in 30 minutes electrolysis time. %COD removal decreases at and above 2.56 mA/cm^2. Thus, the investigational results showed that at higher current densities, more coagulant (aluminium) is available per unit time, which is unnecessary, as it reduces COD removal, is uneconomical in terms of energy consumption and excess residual aluminium has the neuro-toxic effect. Therefore, the current density was selected in the range 1.92-2.88 mA/cm^2 to account for interaction effects.
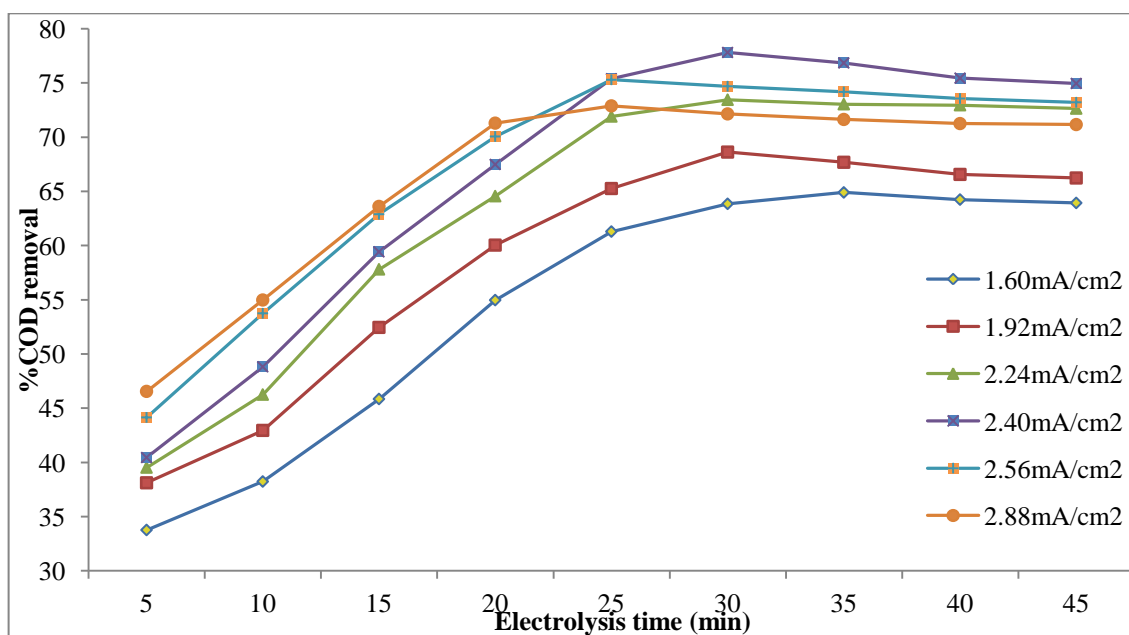
Figure 6: Variation of % COD removal with electrolysis time at different current densities(pH=7,conductivity=1500 μS/cm)

4.1.3 Electrolysis time

Electrolysis time is an important parameter in EC process. From Figure 6, it can be observed that for a fixed current density COD removal efficiency increases with increase in electrolysis time. Up to 55-65% COD removal occurs in initial 15 minutes. As the time progresses, the increase in COD removal keeps decreasing. This is because the availability of the pollutant in the solution becomes a limiting factor. From Figure 6, it can be observed that at lower current density i.e. 1.60 mA/cm^2, optimum COD removal of 64.90% is obtained at electrolysis time of 35 minutes, while at higher current densities of more than 2.56 mA/cm^2, optimum COD removal is achieved in electrolysis time of 25 minutes. The current density is selected in the range of 1.92-2.88 mA/cm^2 and the electrolysis time in this range is 25-30 minutes. Also, the reduction in COD removal after achieving the optimum is low. Therefore, electrolysis time can be kept constant at 30 minutes for all experiments. Beyond 30 minutes %COD removal decreases and also causes higher energy consumption.

4.1.4 pH

When the pH lies between 4 and 9, Al^{3+} and OH^- ions generated by the electrodes react to form various monomeric species which are transformed finally into amorphous insoluble compounds $Al(OH)_3$ by polymerization kinetic complexes/ precipitation. The formed precipitate increases solubility when the solution becomes very basic (Aitbara, et al., 2014). The solid $Al(OH)_3$ is most prevalent between pH 6 and 8, and above pH 9, the soluble species $Al(OH)^-_4$ is the predominant species (Sinha, et al., 2012).This can also be observed from solubility diagram shown in Figure 7 (Holt, et al., 2002). Thus, the three levels of pH were kept between 6 and 8. The effluent pH after EC lied between 8.29-8.64 depending on the initial pH. When the initial pH was between 6-8, effluent pH was above 8 within 10 minutes of electrolysis time. This is also evident from the fact that 55-65% COD removal occurs in initial 15 minutes as discussed in 4.1.3.
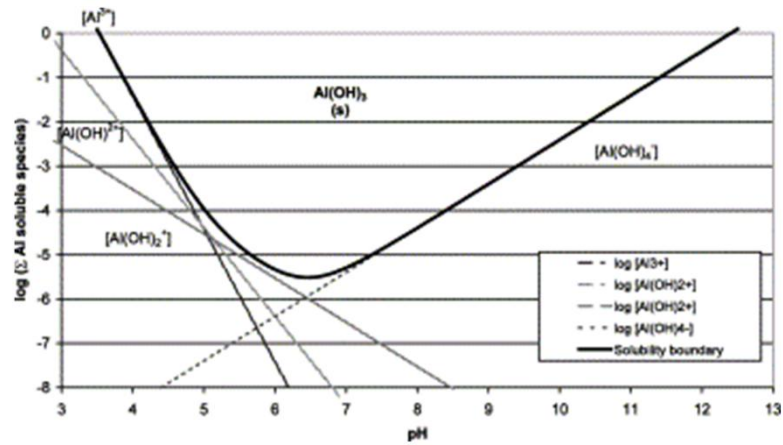
Figure 7: Solubility diagram of aluminum hydroxide *Al(OH)₃* considering only mononuclear species of *Al*

4.1.5 Conductivity

The conductivity of the simulated dairy wastewater was 740-750 µS/cm, which was low. Due to low conductivity, energy consumption was high, and COD removal was low. Thus, the conductivity was increased by adding *NaCl*. There is a negligible effect on the initial pH of wastewater due to the addition of *NaCl*. *NaCl* was used because chloride ions can considerably reduce the adverse effect of other anions such as HCO_3^-, SO_4^{2-}. The existence of the carbonate or sulphate ions would cause the precipitation of Ca^{2+} or Mg^{2+} ions that forms an insulating layer on the surface of the electrodes. This insulating layer would sharply increase the potential between electrodes and causes a major decrease in the current efficiency. Therefore among the anions present, there should be 20% Cl^- to ensure a normal operation of electro-coagulation in water treatment. The addition of *NaCl* would also result in the decrease in power consumption because of the increase in conductivity. Moreover, the electrochemically generated chlorine was found to be effective in water disinfections (Chen, 2004). From Figure 8, it can be observed that there is only a small increase in COD removal efficiency beyond 1500µS/cm. Therefore, the three levels of conductivity were kept between 1000-2000µS/cm.
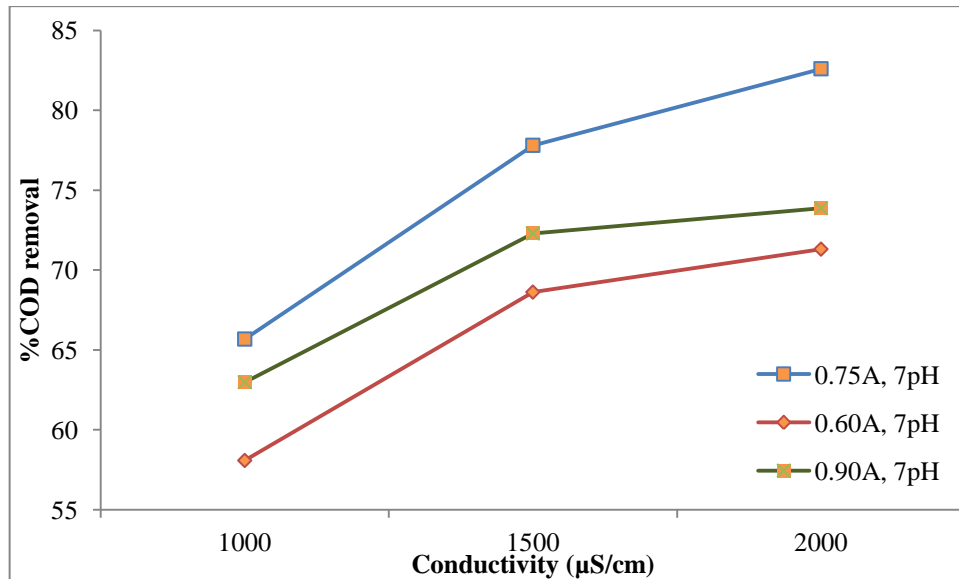
Figure 8: Variation of % COD removal with conductivity at different currents

4.1.6 Anode consumption

Current density, conductivity and the electrolysis time determine the amount of aluminum dissolved in the solution. Increasing the current density and the electrolysis time increases the anode dissolution which increases the COD removal, while increasing conductivity in the solution decreases the anode consumption as shown in Figure 9. As the conductivity is increased, COD removal also increases, thus increasing the cost-effectiveness of the process. From Figure 10, it is established that coagulant matter (aluminum hydroxide) was used more inefficiently with increasing current density. This is because the rate of hydrogen gas released form cathode increases in spite of the increase in the amount of aluminum given to the medium and flocking feeding rate. As the number of hydrogen bubbles increases, they attach to the crystals of coagulant more and cause these crystals to float on the surface of reactor more rapidly (floatation effect) (Bayar, et al., 2011).When the current density is in the range of 2.24-2.4 mA/cm^2, COD removal increases more than the increase in anode consumption, and their ratio almost becomes constant. Thus, coagulant matter was used more efficiently here compared to other range of current densities. Beyond the current density of 2.4 mA/cm^2, COD removal starts decreasing as shown in Figure 6 while the anode consumption keeps increasing. Thus, their ratio decreases. Anode consumption was reported in the range of 0.052-0.150 mg/mg COD removed for the current density of 1.92-2.88 mA/cm^2.
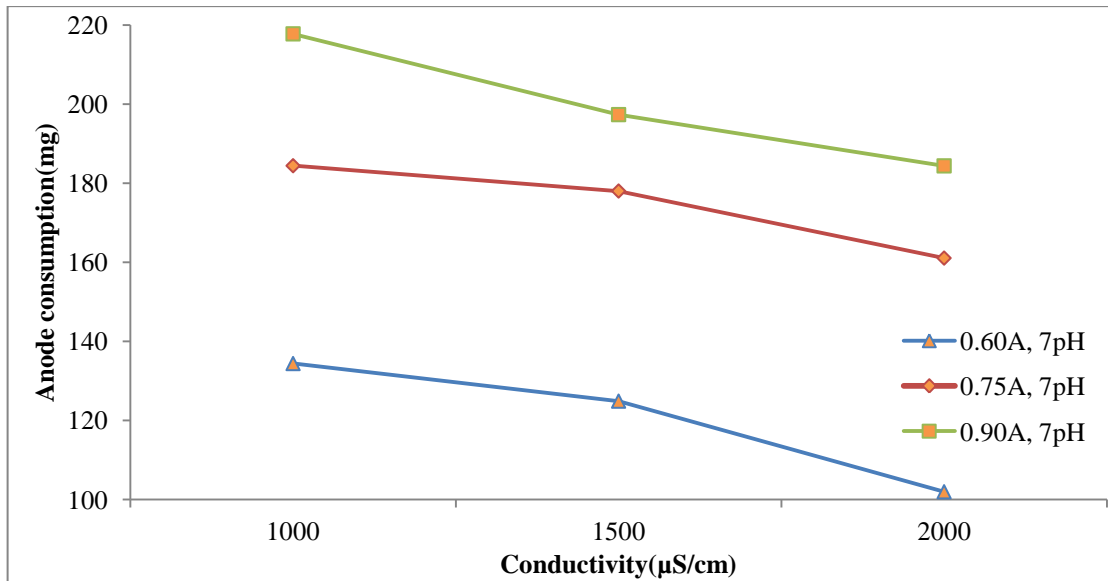
Figure 9: Variation of anode consumption with conductivity and current
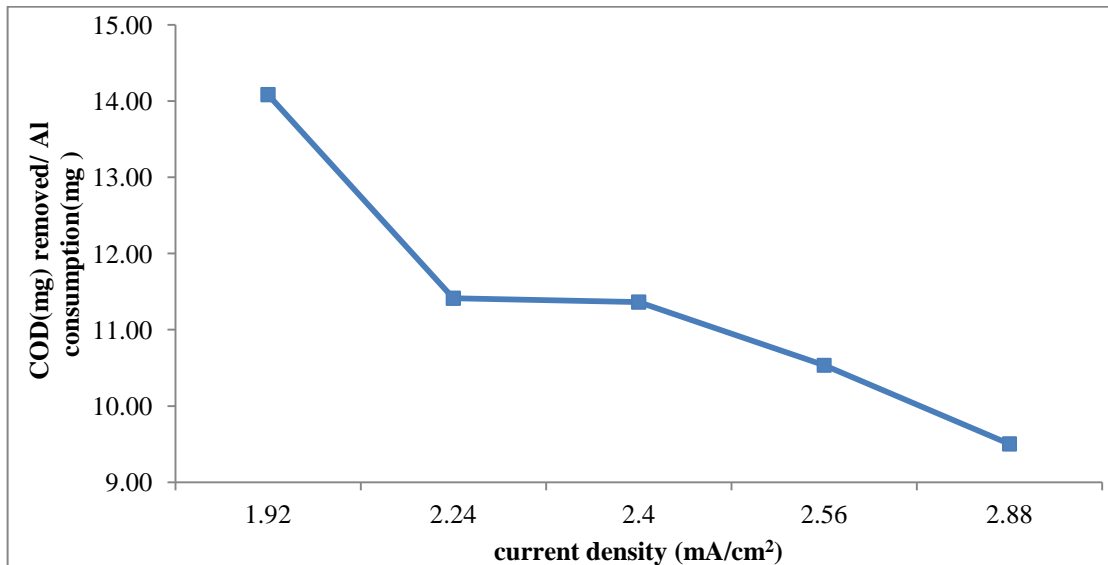
Figure 10: The change of COD removed per aluminum amount as a function current
density (pH=7,conductivity=1500μS/cm)

4.1.7 Specific electrical energy consumption(SEEC)

SEEC is affected by the applied voltage, current, electrolysis time and conductivity. Increasing the conductivity will result in a decrease in SEEC. This is due to reduction in the cell voltage at constant current density with an increase in the conductivity of the solution. SEEC was reported in the range 0.075-0.270 J/mg COD removed for current density in the range of 1.92-2.88 mA/cm^2. From Figure 11, it can be seen that there is wastage of electrical energy beyond current density of 2.4 mA/cm^2 as the residual COD starts increasing.

When the current density is 1.60 mA/cm^2, COD removal of 54.97% is achieved in 20 minutes electrolysis time with energy consumption of 0.042 J/mg COD removed, while the similar COD removal of 54.98% is achieved in only 10 minutes when the current density is 2.88 mA/cm^2 with energy consumption of 0.076 J/mg COD removed. Thus, the priority of process parameters should be determined since, under low current density, the volume of the reactor to be used needs to be increased. However, aluminum can be used more effectively as shown in Figure 10 and energy consumption of the system also decreases. On the other hand, when higher current densities are applied, time of the reaction shortens, and the energy consumption increases (Bayar, et al., 2011).
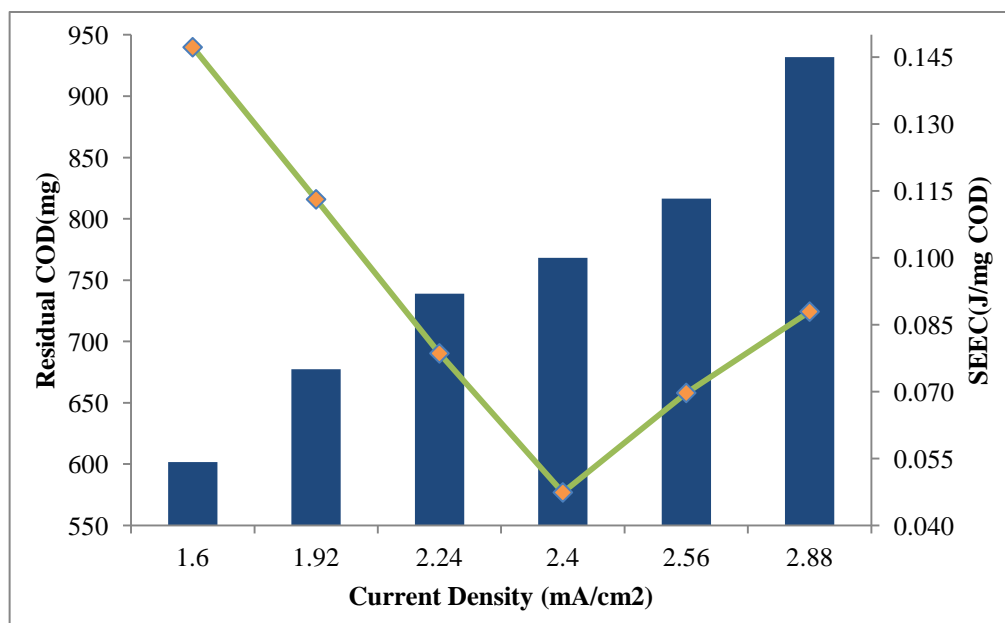
Figure 11: Effect of current density on SEEC and residual COD (pH=7, conductivity= 1500 μS/cm)

Thus, from the above observations, it is clear that electrolysis time of 30 minutes is sufficient for initial COD of 1300 mg/L. Current density, pH and conductivity are the three major operating parameters which govern the EC process. These three parameters were used to develop statistical models. Table 6 gives variables and their levels.

Table 6: Factors and their levels used for EC treatment of SDW

Variables	Factor	levels		
		-1	0	1
A	Current density (mA/cm^2)	1.92	2.40	2.88
B	pH	6.00	7.00	8.00
C	Conductivity (µS/cm)	1000	1500	2000

Once the desired value ranges of the factors had been defined by CCD, they were coded to lie at ±1 for the factorial points, 0 for the centre points (Montgomery, 2005).

4.2 Development of regression model equation

The design wizard of the Design Expert software gave central composite design (CCD) as the most appropriate design for optimization, RSM and numeric factors criteria. Table 7 gives the experimental design matrix. The effects and interactions of the three factors were studied on four responses: %COD removal, %BOD removal, anode consumption(AC) and SEEC. Total 19 experiments were designed based on three factor and three-level central composite design based on RSM to optimize the output parameters. The experimental design matrix comprised of 14 factorial runs and five centre point runs.

Table 7: Experimental design matrix

Run	A: Current density (mA/cm^2)	B: pH	C: Conductivity (µS/cm)
1	1.92	8	1000
2	2.40	7	1500
3	2.40	6	1500
4	2.88	7	1500
5	2.88	8	1000
6	2.40	7	1500
7	1.92	6	1000
8	2.40	7	1500
9	2.40	8	1500
10	2.40	7	1500
11	2.40	7	1500
12	1.92	8	2000
13	2.40	7	2000
14	2.88	6	2000
15	2.88	8	2000
16	2.88	6	1000
17	1.92	7	1500
18	1.92	6	2000
19	2.40	7	1000

Table 8 gives the responses for the input parameters which are obtained from EC experiments as well as their corresponding predicted values. The experiments were performed triplicates, and the average value of each response has been presented.

Table 8: Dairy wastewater treatment results

Run	%COD removal		% BOD removal		AC(mg/mg COD)		SEEC(J/mg COD)	
	Exp.	Pred.	Exp.	Pred.	Exp.	Pred.	Exp.	Pred.
1	55.95	53.77	60.19	60.40	0.104	0.104	0.150	0.150
2	77.81	76.99	80.57	79.87	0.084	0.086	0.098	0.098
3	67.33	70.14	69.33	72.52	0.093	0.089	0.113	0.111
4	72.29	72.64	75.33	76.42	0.105	0.113	0.145	0.152
5	60.59	61.30	64.95	64.20	0.150	0.147	0.259	0.256
6	74.95	76.99	77.95	79.87	0.086	0.086	0.095	0.098
7	54.84	53.35	59.24	57.44	0.092	0.094	0.153	0.156
8	76.35	76.99	79.42	79.87	0.087	0.086	0.096	0.098
9	72.47	71.04	75.81	74.20	0.098	0.107	0.105	0.107
10	78.92	76.99	81.63	79.87	0.089	0.086	0.100	0.098
11	79.64	76.99	82.95	79.87	0.091	0.086	0.101	0.098
12	66.04	66.87	69.33	70.06	0.079	0.078	0.070	0.072
13	82.60	80.81	84.76	82.90	0.075	0.076	0.081	0.078
14	69.85	69.77	73.14	72.50	0.105	0.105	0.131	0.131
15	68.05	69.21	71.52	72.90	0.131	0.129	0.134	0.131
16	58.16	57.01	64.19	63.04	0.134	0.135	0.269	0.266
17	68.62	69.64	71.71	72.20	0.071	0.067	0.075	0.068
18	68.44	68.39	67.52	67.86	0.052	0.055	0.068	0.070
19	65.68	68.85	69.90	73.34	0.101	0.104	0.180	0.184

Exp.=Experimental values, Pred.= Predicted values

The software suggested quadratic models to obtain regression equations for all the four responses. The regression model equation for % COD removal, % BOD removal, anode consumption(AC)(mg/mg COD removed) and SEEC(J/mg COD removed) in terms of coded factors are given by Equations (4.1), (4.2), (4.3), (4.4) respectively.

$$\% \ COD \ removal = 76.99 + 1.50 * A + 0.45 * B + 5.98 * C + 0.24 * A * B - 0.57 * A * C - 0.97 * B * C - 5.85 * A^2 - 6.40 * B^2 - 2.16 * C^2 \tag{4.1}$$

$$\% \ BOD \ removal = 79.87 + 2.11 * A + 0.84 * B + 4.78 * C - 0.45 * A * B - 0.24 * A * C - 0.19 * B * C - 5.56 * A^2 - 6.51 * B^2 - 1.75 * C^2 \tag{4.2}$$

$$Anode \ Consumption = 0.086 + 0.023 * A + 8.600E - 003 * B - 0.014 * C + 3.750E - 004 * A * B + 2.125E - 003 * A * C + 3.125E - 003 * B * C + 4.005E - 003 * A^2 + 0.012 * B^2 + 4.005E - 003 * C^2 \tag{4.3}$$

$$SEEC = 0.098 + 0.042 * A - 1.600E - 003 * B - 0.053 * C - 7.500E - 004 * A * B - 0.012 * A * C + 2.250E - 003 * B * C + 0.012A^2 + 0.011B^2 + 0.033C^2 \tag{4.4}$$

The coefficient of first-order terms indicates the main effects while second- and third-order terms indicate the interactions among the concerned factors. The main effects can be observed from the Equations (4.1), (4.2), (4.3), (4.4) which show that current density, pH and conductivity show a positive effect on %COD and %BOD removal, while current density, pH show positive effect and conductivity show a negative effect on anode consumption. Current density show positive effect while pH and conductivity show a negative effect on SEEC. Also, it can be seen that conductivity and current density show the greatest effect on the COD & BOD removal and SEEC. Similarly, current density has the greatest effect on anode consumption.

4.3 Verification of regression equations

To verify the correctness of the equations obtained by the Design Expert 10.0.0, 12 set of random experiments, as shown in Table 9, were performed. The experimental results were plotted against predicted response and their graphs, and respective R^2 values are displayed in Figure 12. R^2 value for % COD removal, % BOD removal, anode consumption and SEEC are 0.9355, 0.8859, 0.9853, 0.9958 respectively.

Table 9: Operational parameter settings and their respective actual and predicted responses used for verification of correction of regression equations.

A: Current density (mA/cm^2)	B: pH	C: Conductivity (μS/cm)	%COD removal		% BOD removal		AC(mg/mg COD)		SEEC(J/mg COD)	
			Exp.	Pred.	Exp.	Pred.	Exp.	Pred.	Exp.	Pred.
2.40	6	1000	60.44	61.03	65.23	65.80	0.107	0.111	0.196	0.199
1.92	7	1000	58.08	60.93	62.19	65.43	0.089	0.087	0.144	0.142
2.88	7	1000	62.98	65.07	67.05	70.13	0.133	0.129	0.249	0.250
2.40	8	1000	64.31	63.87	68.67	67.86	0.119	0.121	0.184	0.191
1.92	6	1500	61.28	63.03	65.98	64.40	0.073	0.071	0.084	0.080
2.88	6	1500	62.66	65.55	66.76	69.52	0.116	0.116	0.166	0.165
1.92	8	1500	63.34	63.45	66.95	66.98	0.082	0.087	0.081	0.078
2.88	8	1500	66.13	66.93	70.28	70.30	0.131	0.134	0.159	0.161
2.88	7	2000	73.87	75.89	76.76	79.21	0.111	0.105	0.124	0.120
2.40	6	2000	71.58	74.93	74.95	75.74	0.079	0.076	0.093	0.088
1.92	7	2000	71.31	74.03	74.09	75.47	0.055	0.055	0.065	0.060
2.40	8	2000	74.83	73.89	78.12	77.04	0.096	0.100	0.089	0.090

Exp.=Experimental values, Pred.= Predicted values
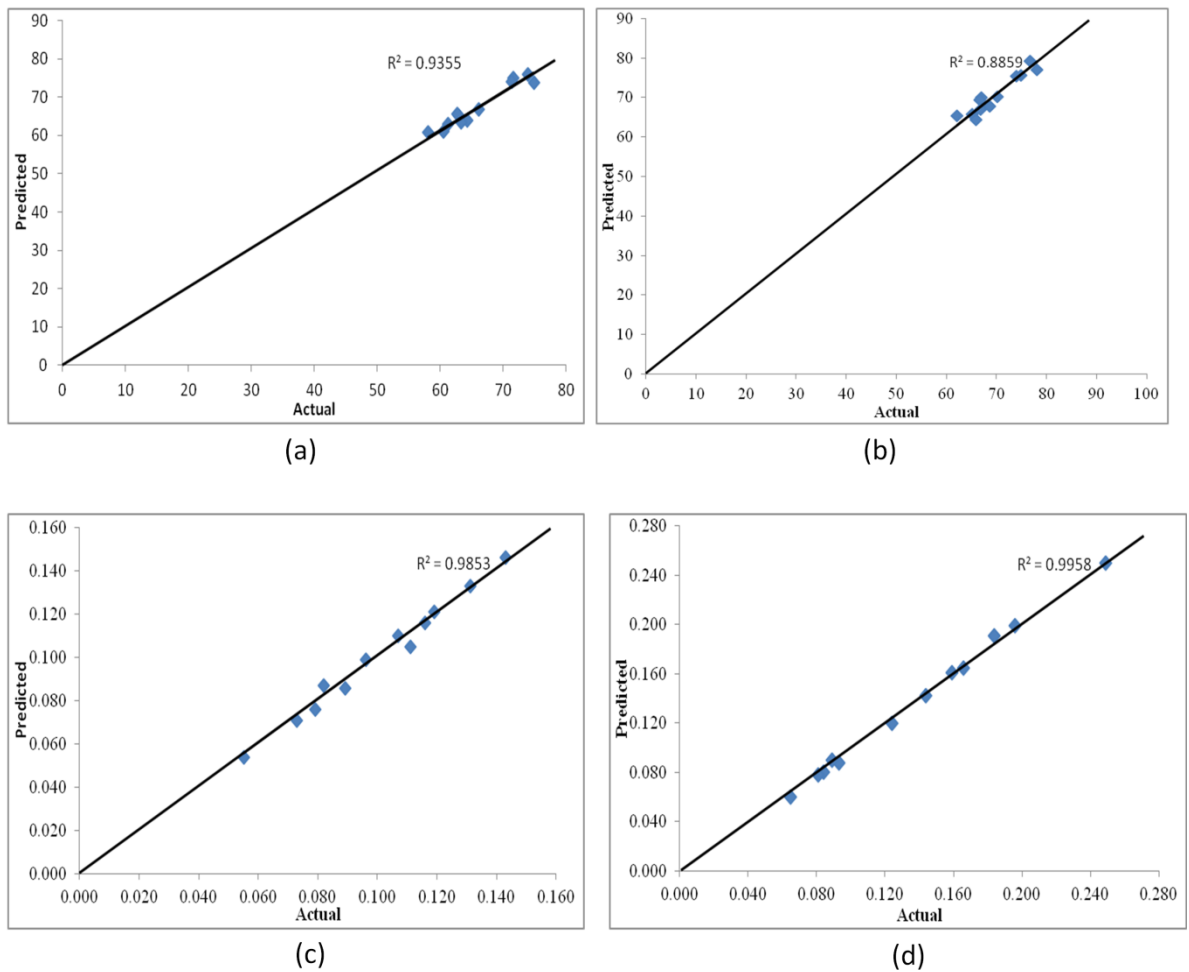
Figure 12: Actual v/s predicted plot (a) % COD removal (b) %BOD removal (c) anode consumption (d) SEEC for verification of regression equations.

4.4 Validation of the model

4.4.1 Analysis of variance(ANOVA)

ANOVA for the second-order equations fitted for the responses was observed to assess the "**goodness of fit**" as shown in Table 10-13. Analysis of ANOVA gives an insight into the linear, quadratic and interaction effects of the factors. This analysis was carried out at 5% significance level, i.e., for 95% level of confidence. The p-value should be less than 0.05 to be strongly significant. Between 0.05 and 0.10 it is marginally significant (Expert, 2016). A model p-value lower than 0.0001 indicates that the model is statistically significant and that the model terms are significant at 95% probability level (Sinha, et al., 2014). In this case, p-value < 0.0001 suggests that regression model equations fitted well with the experimental results.

Regression coefficient R^2 was also used for validating the model. R^2 is the fraction of the overall variance. It establishes how closely a certain function fits a particular set of experimental data. R^2 values range from 0 to 1, with 0 representing no statistical correlation between the data and the line and 1 representing a perfect fit between the data and the line drawn through them. High R^2 values of 96.05% for COD removal, 94.60% for BOD removal, 97.45% for anode consumption and 99.65% for SEEC, expresses a high correlation value between the actual and predicted values.

The ANOVA of the % COD removal by EC using aluminum electrode showed F-value of 24.34 for the quadratic model implying that the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. Similarly F-values of 17.53, 38.27, 285.74 are obtained for % BOD removal, anode consumption and SEEC implying that the quadratic model is significant. Further, the critical F-value ($F_{0.05,9,9}$=3.19) calculated at 95% confidence interval and degree of freedom equal to 9, is much less than the calculated F-values.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 16.728 for COD, 14.247 for BOD, 23.965 for anode consumption and 57.351 for SEEC indicates an adequate signal. These models can be used to navigate the design space.

For COD, factors with strongly significant model terms in the descending order include the linear effect of conductivity, pH quadratic factor, and current density quadratic factor. For BOD, linear effect of conductivity, pH quadratic factor and current density quadratic factor and linear effect of current density are strongly significant model terms in the descending order. From Equation (4.1) and Equation (4.2), as the level changes from -1 to 0, pH is more effective than current density or conductivity in COD/BOD removal. Also, conductivity is slightly more effective than the current density in COD/BOD removal. This is because the coefficient of the quadratic term of pH is more followed by the coefficient of the linear term of conductivity. Similarly, when the level changes from 0 to +1 quadratic coefficients of current density and pH remain negative while the linear coefficient of conductivity becomes positive. Therefore, conductivity is more effective than pH or current density in COD/BOD removal.

Table 10: ANOVA for COD

Source	Sum of Squares	DF	Mean Square	F Value	p-value Prob > F
Model	1121.10	9	124.57	24.34	< 0.0001 (significant)
A	22.65	1	22.65	4.43	0.0647
B	2.01	1	2.01	0.39	0.5467
C	357.13	1	357.13	69.79	< 0.0001
AB	0.46	1	0.46	0.090	0.7709
AC	2.58	1	2.58	0.50	0.4960
BC	7.49	1	7.49	1.46	0.2572
A^2	93.49	1	93.49	18.27	0.0021
B^2	112.07	1	112.07	21.90	0.0012
C^2	12.80	1	12.80	2.50	0.1482
Residual	46.06	9	5.12		
Lack of Fit	31.55	5	6.31	1.74	0.3059 (not significant)
Pure Error	14.51	4	3.63		
Cor Total	1167.16	18			
R^2=0.9605, adjusted R^2=0.9211					

Table 11: ANOVA for BOD

Source	Sum of Squares	DF	Mean Square	F Value	p-value Prob > F
Model	956.84	9	106.32	17.53	0.0001 (significant)
A	44.69	1	44.69	7.37	0.0238
B	7.02	1	7.02	1.16	0.3099
C	228.48	1	228.48	37.67	0.0002
AB	1.64	1	1.64	0.27	0.6158
AC	0.45	1	0.45	0.074	0.7912
BC	0.29	1	0.29	0.048	0.8321
A^2	84.34	1	84.34	13.91	0.0047
B^2	115.65	1	115.65	19.07	0.0018
C^2	8.33	1	8.33	1.37	0.2713
Residual	54.58	9	6.06		
Lack of Fit	39.63	5	7.93	2.12	0.2432 (not significant)
Pure Error	14.95	4	3.74		
Cor Total	1011.42	18			
R^2=0.9460, adjusted R^2=0.8921					

For anode consumption, linear effect of current density, conductivity with p-value < 0.0001, linear effect of pH and pH quadratic factor are strongly significant model terms in the descending order. Interaction effects of factors on COD, BOD and anode consumption, are not significant as the p-value > 0.1. For SEEC, strongly significant model terms are the linear effect of conductivity, current density, and quadratic effect of conductivity, interaction effect of current density*conductivity with p-value < 0.0001 followed by quadratic effects of current density and pH in the decreasing order. From Equations (4.3) and Equation (4.4), as the level changes from -1 to 1, linear effect of current density is more responsible for anode consumption and SEEC because its coefficient is highest. If a term is not significant, then it can be removed from the model unless it is needed to satisfy hierarchy (i.e. it is a parent term of a significant interaction) (Expert, 2016).

Figure 13 shows the actual *vs.* predicted plots for all the four responses.

Table 12: ANOVA for anode consumption

Source	Sum of Squares	DF	Mean Square	F Value	p-value Prob > F
Model	9.311E-003	9	1.035E-003	38.27	< 0.0001 (significant)
A	5.153E-003	1	5.153E-003	190.60	< 0.0001
B	7.396E-004	1	7.396E-004	27.36	0.0005
C	1.932E-003	1	1.932E-003	71.47	< 0.0001
AB	1.125E-006	1	1.125E-006	0.042	0.8429
AC	3.612E-005	1	3.612E-005	1.34	0.2775
BC	7.813E-005	1	7.813E-005	2.89	0.1234
A^2	4.383E-005	1	4.383E-005	1.62	0.2348
B^2	3.617E-004	1	3.617E-004	13.38	0.0053
C^2	4.383E-005	1	4.383E-005	1.62	0.2348
Residual	2.433E-004	9	2.703E-005		
Lack of Fit	2.141E-004	5	4.282E-005	5.87	0.0556 (not significant)
Pure Error	2.920E-005	4	7.300E-006		
Cor Total	9.555E-003	18			
R^2=0.9753, adjusted R^2=0.9491					

Table 13: ANOVA for SEEC

Source	Sum of Squares	DF	Mean Square	F Value	p-value Prob > F
Model	0.058	9	6.471E-003	285.74	< 0.0001 (significant)
A	0.018	1	0.018	786.31	< 0.0001
B	2.560E-005	1	2.560E-005	1.13	0.3154
C	0.028	1	0.028	1226.29	< 0.0001
AB	4.500E-006	1	4.500E-006	0.20	0.6663
AC	1.201E-003	1	1.201E-003	53.01	< 0.0001
BC	4.050E-005	1	4.050E-005	1.79	0.2140
A^2	4.119E-004	1	4.119E-004	18.19	0.0021
B^2	3.476E-004	1	3.476E-004	15.35	0.0035
C^2	2.936E-003	1	2.936E-003	129.62	< 0.0001
Residual	2.038E-004	9	2.265E-005		
Lack of Fit	1.778E-004	5	3.557E-005	5.47	0.0623 (not significant)
Pure Error	2.600E-005	4	6.500E-005		
Cor Total	0.058	18			
R^2=0.9965, adjusted R^2=0.9930					
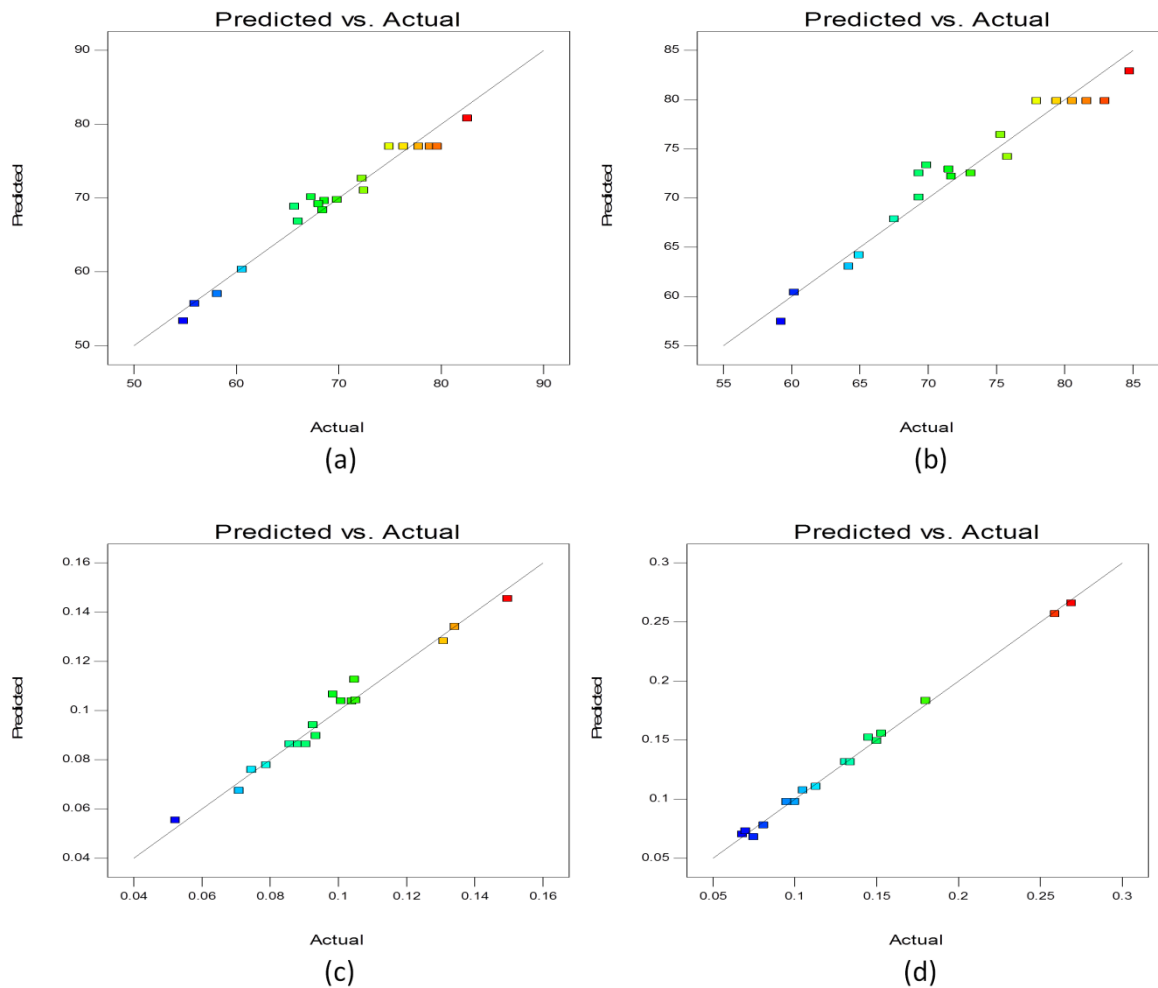
Figure 13: Actual v/s predicted plot (a) % COD removal (b) %BOD removal (c) anode consumption (d) SEEC for experimental runs.

4.4.2 Residuals

The adequacy of the model was also evaluated by residuals. A residual can be defined as the difference between observed value and its fitted response value (Montgomery, 2005). Normal probability plot can be used to check the normal distribution of residuals. The normal probability plot indicates whether the residuals follow a normal distribution, such that the points will follow a straight line (Expert, 2016). If the model is valid and if the assumptions are satisfied, the residuals should be structureless i.e. they should not be related to any other variable including the predicted response (Ghanim, 2014). This can be validated by plot between the residuals on X-axis and the fitted values on Y-axis. The normal probability plots and plots of residuals versus fitted values for % COD removal, %BOD removal, anode consumption and SEEC are illustrated in Figures 14-17. All the plots fulfil the mentioned criterion and propose towards the adequacy of the model.
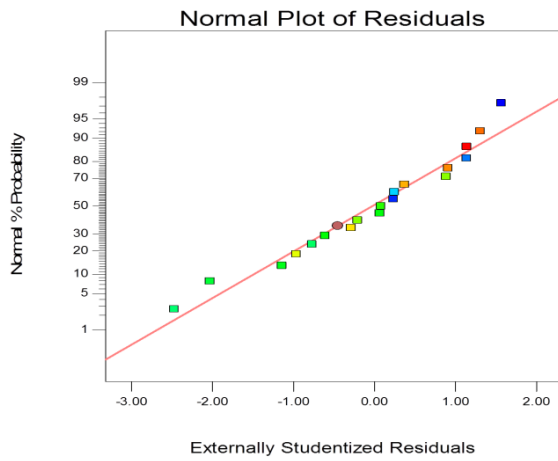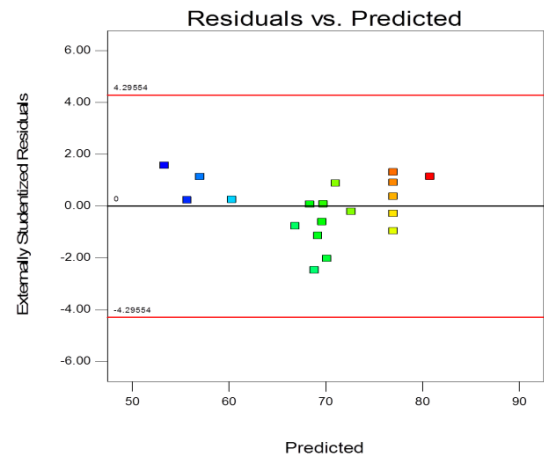
Figure 14: (a) Normal probability plot (b) Residual *vs.* fits for % COD removal
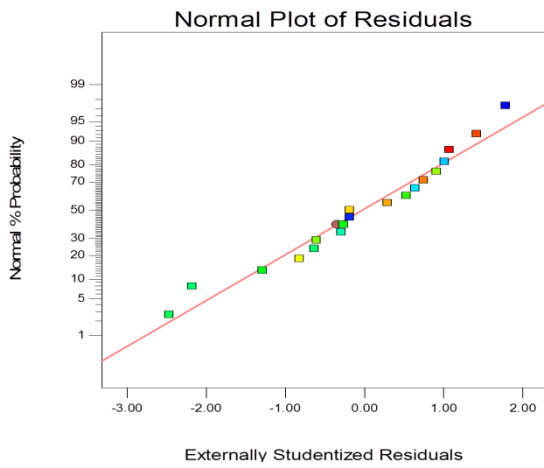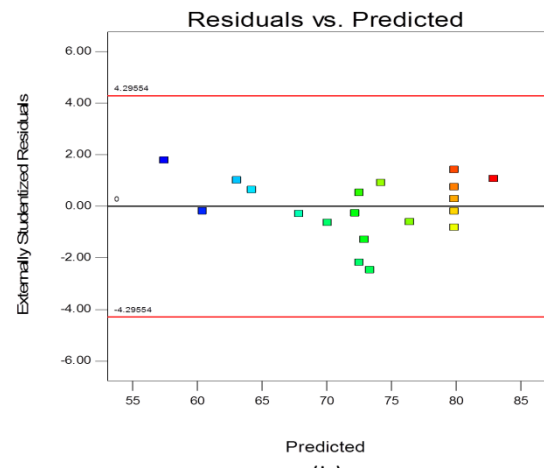
Figure 15: (a) Normal probability plot (b) Residual *vs.* fits for % BOD removal
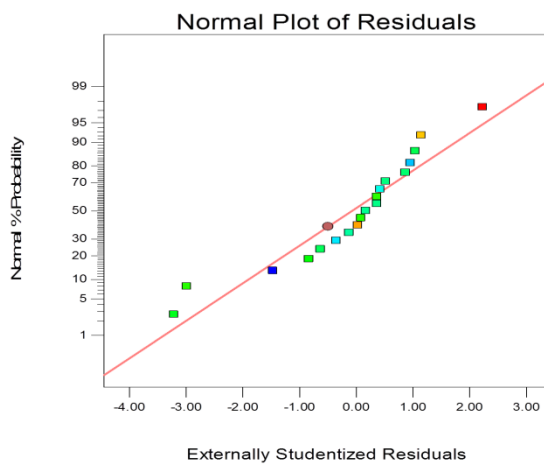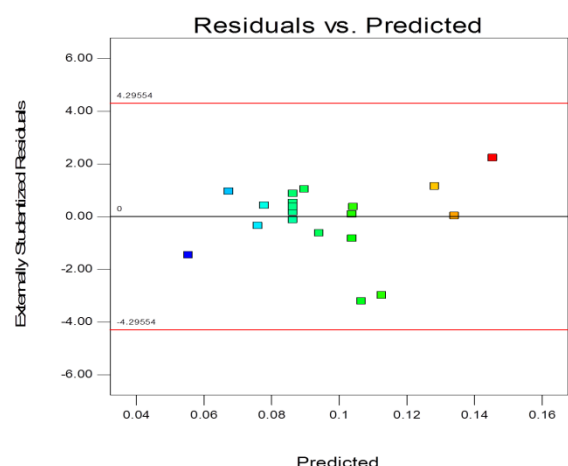
Figure 16: (a) Normal probability plot (b) Residual *vs.* fits for anode consumption
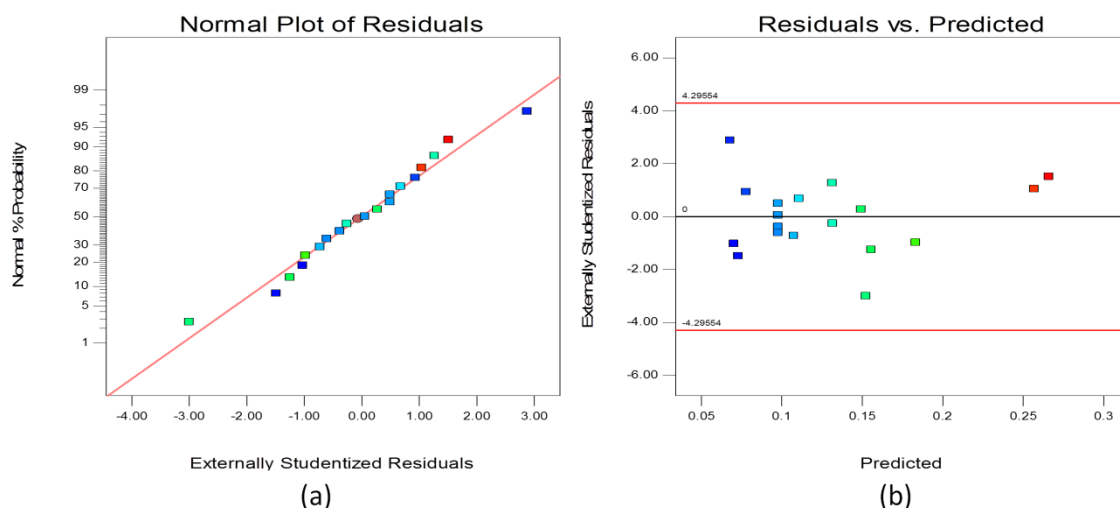
Figure 17: (a) Normal probability plot (b) Residual *vs.* fits for SEEC

4.5 Optimization of the EC process

The numerical optimization of the software has been used to find the specific point that maximizes the desirability function. The desired goal for the factors and responses was selected from the five options: none, maximum, minimum, target, and within the range that might alter the characteristics of a goal. An excess input of energy results in loss of COD/BOD removal efficiency, loss of energy through heating of electrodes, more anode consumption and hence increases the concentration of aluminum in water, which is a neuro-toxic agent. Therefore, the process was optimized for maximum COD removal for minimum energy input. For this maximum importance was given to COD removal efficiency and SEEC. Table 14 shows the criteria for optimization in terms of goal, importance, lower limit and upper limit. Optimization results from Design Expert provided seven numerically optimized solutions which are listed in Table 15. COD removal efficiency of 79.46-79.69% and BOD removal efficiency of 81.01-81.35 was obtained at anode consumption of 0.065-0.066 (mg/mg COD removed) and SEEC of 0.068-0.070 (J/mg COD removed) . The optimization results are presented in Table 15.

Table 14: Criteria for optimization

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
A:current density (mA/cm^2)	is in range	1.92	2.88	1	1	3
B: pH	is in range	6	8	1	1	3
C: conductivity (μS/cm)	is in range	1000	2000	1	1	3
% COD removal (mg/L)	maximize	54.84	82.60	1	1	5
% BOD removal (mg/L)	none	59.24	84.76	1	1	3
anode consumption (mg/mg COD removed)	minimize	0.052	0.150	1	1	3
SEEC (J/mg COD removed)	minimize	0.068	0.269	1	1	5

Table 15: Optimization results for dairy wastewater treatment

current density (mA/cm²)	pH	conductivity (µS/cm)	% COD removal (mg/L)	% BOD removal (mg/L)	anode consumption (mg/mg COD removed)	SEEC (J/mg COD removed)	Desirability
2.209	*6.858*	*1999.996*	*79.46*	*81.03*	*0.065*	*0.068*	*0.924 (selected)*
2.210	6.868	1999.997	79.48	81.06	0.065	0.068	0.924
2.209	6.850	1999.974	79.45	81.01	0.065	0.068	0.924
2.210	6.881	1999.930	79.50	81.10	0.066	0.068	0.924
2.225	6.868	1999.986	79.65	81.26	0.066	0.069	0.923
2.224	6.914	1999.981	79.67	81.35	0.066	0.069	0.923

The experimental verification of these optimum conditions as shown in Table 16 was in good agreement with the predicted results which reaffirmed the applicability of the model.

Table 16: Experimental verification of the optimum conditions

current density (mA/cm²)	pH	conductivity (µS/cm)	% COD removal (mg/L)	% BOD removal (mg/L)	anode consumption (mg/mg COD removed)	SEEC (J/mg COD removed)	Desirability
Design Expert							
2.21	6.86	2000	79.46	81.03	0.065	0.068	0.924
Experimental Verification							
2.21	6.86	2000	78.85	81.20	0.065	0.068	-

4.6 Effect of operating parameters

4.6.1 Effect on COD & BOD

Current is the most sensitive parameter as it can significantly affect the effectiveness of EC treatment. The range of current density selected is very important as formation and breaking of flocs depends on applied current density. It determines the amount of coagulant, as well as the rate and the dimension of the bubbles, produced at the electrodes (Aitbara, et al., 2014). As shown in Figure 18 and Figure 19, when the current density is increased % COD removal increases. This is because when the current density increases, the formation of the aluminum ions takes place more rapidly, compared to the processes of coagulation. The density of the bubbles increases and their dimension decreases with the increase of current density, leading to the speedy removal of the aluminum hydroxide in the solution by flotation and decreasing the probability of collision between the pollutants and the coagulant. The increase in the rate of generation of H_2 bubbles with the rise of the density of current is favourable when the phase separation is carried out by flotation (Aitbara, et al., 2014). When the current density approaches towards $2.88 mA/cm^2$, COD removal starts decreasing. This is because an increase in current above the optimum current does not result in an increase in the pollutant removal efficiency as the sufficient number of metal hydroxide flocs are available for the sedimentation of the pollutant (Khandekar & Saroha, 2013). Thus, availability of pollutant becomes a limiting factor. Also, excess energy can break the flocs and increase the TDS of the solution. This is because when COD concentration in the solution starts increasing, the conductivity of the solution also starts increasing and hence increases the TDS in the solution.

The pH of the solution is an important operational parameter in electro-coagulation. As shown in Figure 18 and Figure 19, COD removal increases with increase in pH up to optimum and then it starts decreasing. Thus, from the optimization results and from Figure 18 and 19, the maximum COD/BOD removal efficiency is achieved at pH close to neutrality. Similar results are obtained by (Bensadok, et al., 2011), (A.S.Koparal, et al., 2008), (Aitbara, et al., 2014). During the startup process the pH of the medium changes, especially for the lower values. This evolution is due to the production of OH^- at the electrode. This particularly prevents the abrupt change of pH in alkaline medium (Aitbara, et al., 2014).

The conductivity of the solution is a key parameter in electrolysis process as the pollutant removal efficiency and operating costs are directly related to the solution conductivity. COD removal increases with increase in conductivity with only a small increase in COD removal beyond 1500 µS/cm. When chlorides are presents in the solutions the products from the anodic discharge of chlorides are Cl_2 and OCl^-. The OCl^- itself is a strong oxidant which is capable of oxidizing organic molecules present in wastewater. So, added $NaCl$ not only increases the conductivity but also contributes strong oxidizing agents (Sengil & Ozacar, 2006). However, a large excess of chloride can also form the $AlCl_4^-$ anion, contributing to the dissolution of aluminum species. Consequently, the aluminum species available for coagulation are lower, involving a limitation of the effectiveness of the treatment (Aitbara, et al., 2014).
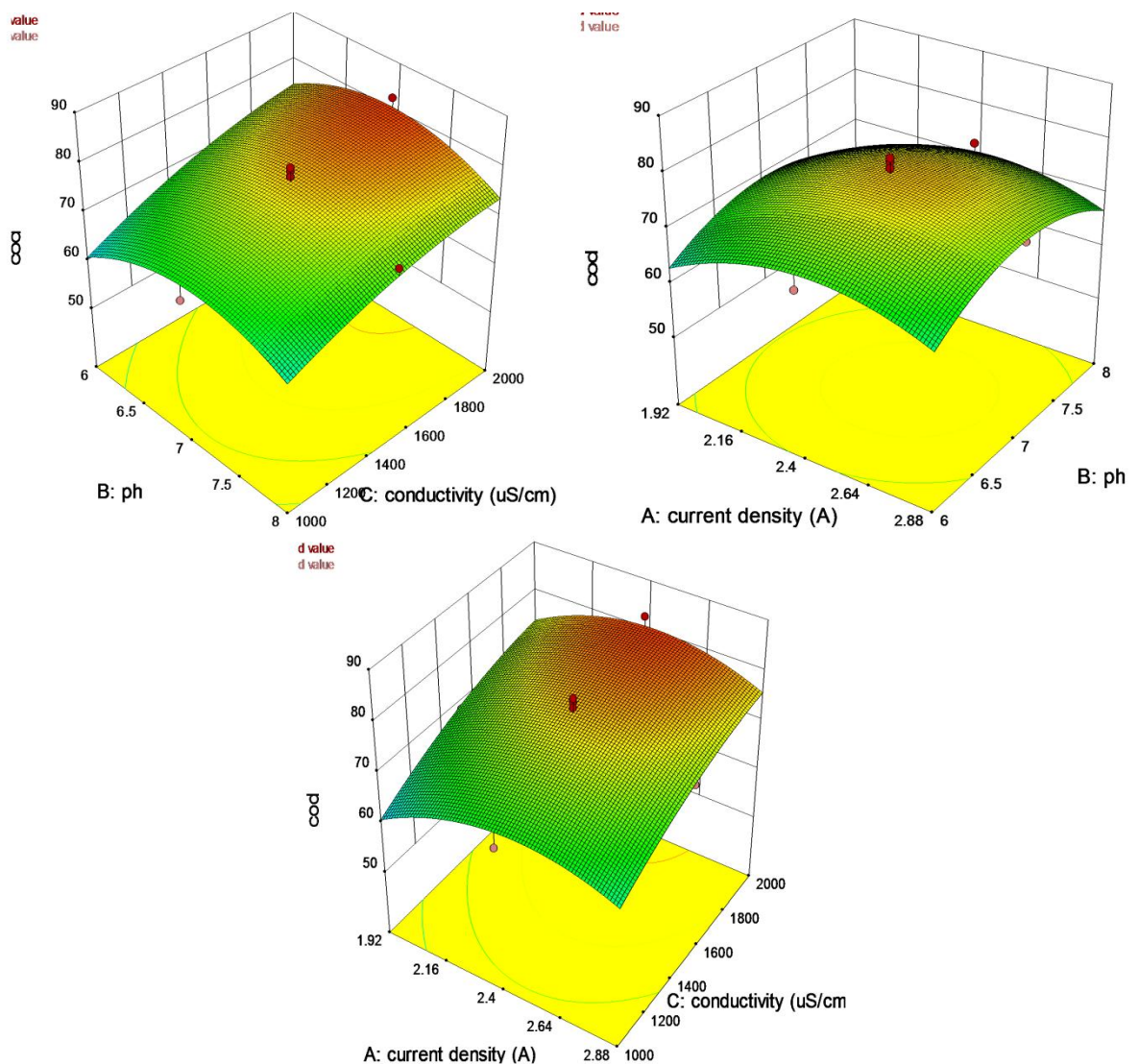
Figure 18: Effect of input parameters on COD removal efficiency
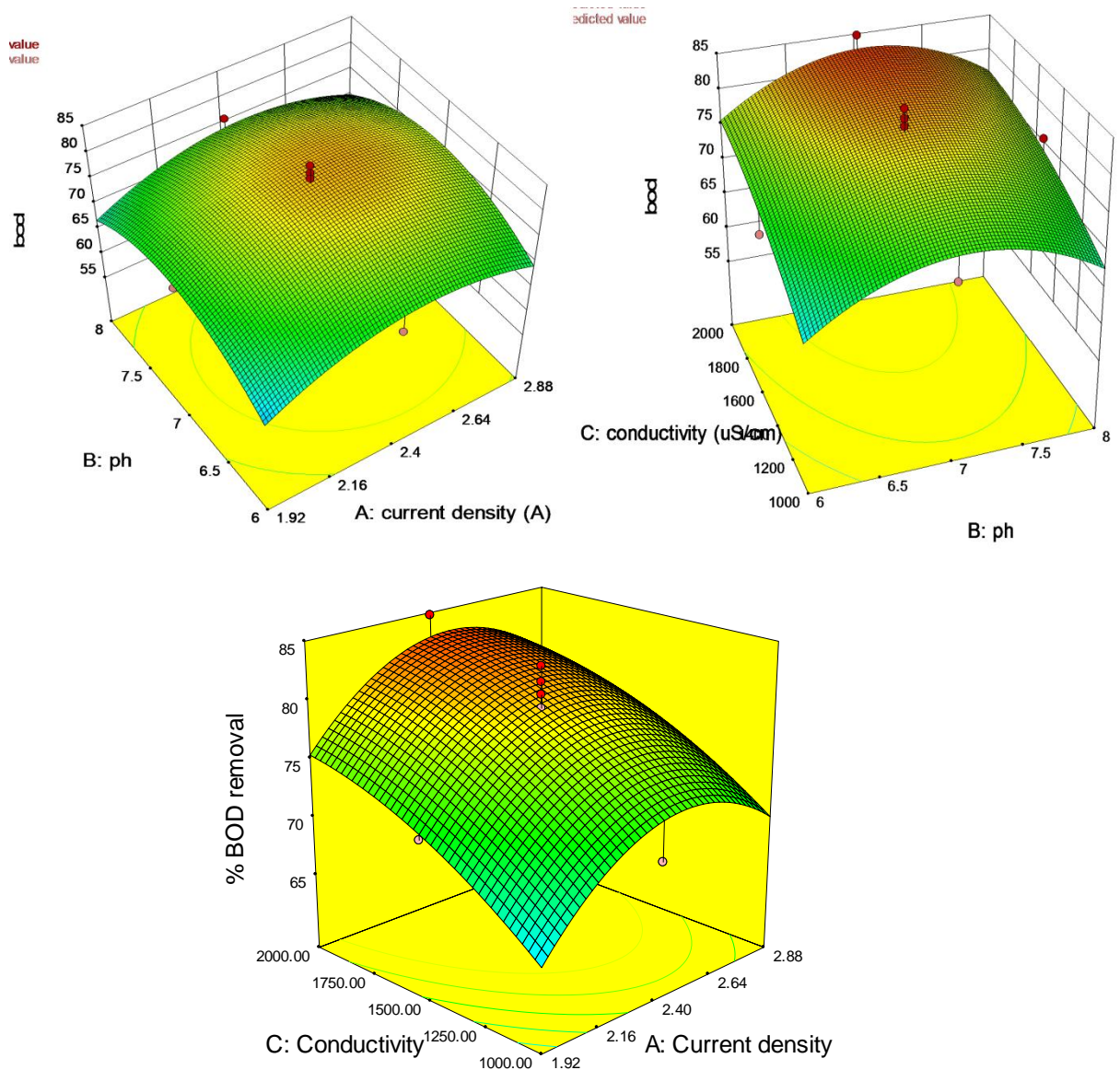
Figure 19: Effect of input parameters on BOD removal efficiency

4.6.2 Effect on anode consumption and SEEC

The anode consumption was calculated in terms of mg/mg of COD removed by weighing the electrodes before and after the run. From Figure 20, as expected when the current density is increased anode consumption increases as more Al^{+3} ions are dissociated into the solution. The anode consumption varied from 0.052-0.150 mg/mg of COD removed.

SEEC is important from the point of cost consideration as it determines the feasibility of any process. As depicted in Figure 21, SEEC(J/mg of COD removed) increases linearly with increase in current density, decreases non-linearly with an increase in conductivity and is slightly affected by pH.

The major operating cost is due to both anode consumption and SEEC. Anode consumption and SEEC decreases with increase in conductivity. This is also evident from Equation (4.3). This is because of reduction in cell voltage at the constant current density (Khandekar & Saroha, 2013). As the applied voltage of the system is reduced, the amount of electrode consumed is also reduced (Bazrafshan, et al., 2013).
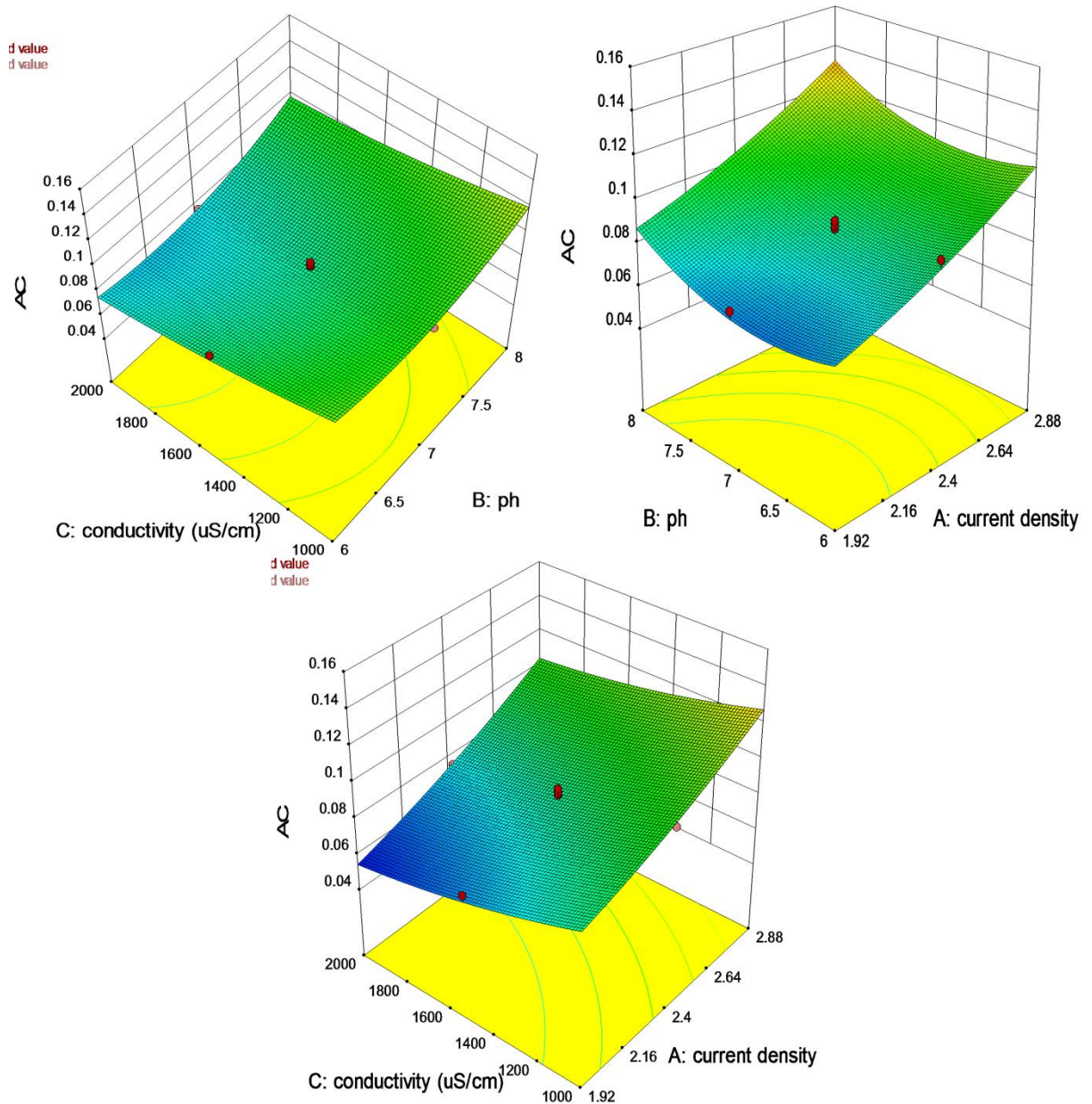
Figure 20: Effect on various parameters on anode consumption
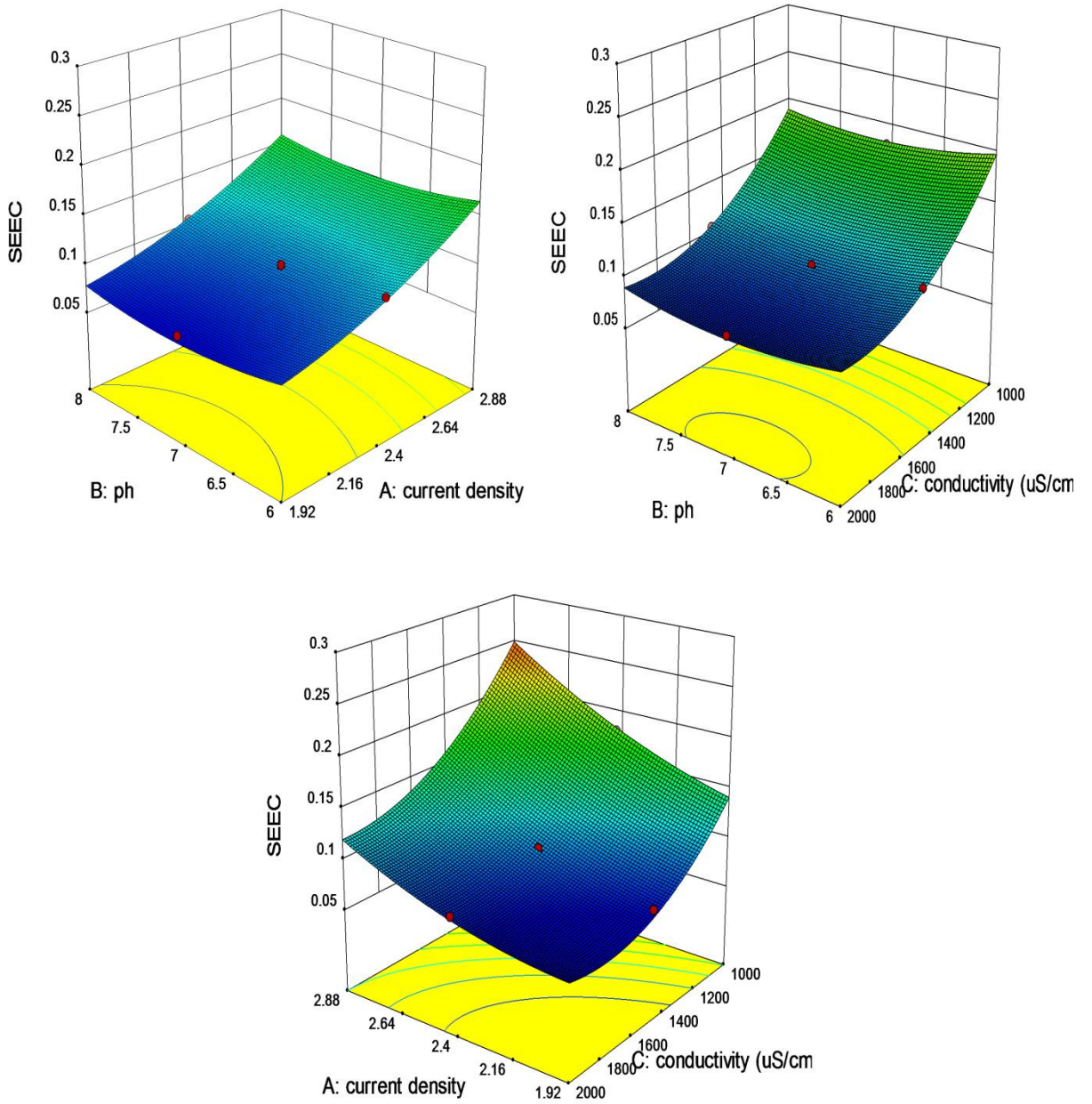
Figure 21: Effect on various parameters on SEEC

5.0 Adsorption kinetics

The dynamics of the adsorption process can best be understood by the processing of adsorption kinetics data. It helps in the prediction of adsorption rate, which gives information for designing and modelling of the process (Nemr, 2009). The kinetics of adsorption was evaluated by the pseudo-first order, pseudo-second order, and elovich model. The validity of the models were verified by linear equation analysis $\log$ (q_e-q) *vs.* t, (t/q_t) *vs.* t and q_t *vs.* $\ln$ t, respectively. For the study, the plots were made for three initial COD concentrations (1300-1700 mg/L) at the current density of 2.21mA/cm^2, pH 6.86 and conductivity 2000 µS/cm. The electrolysis time was between 5-30 min. The value of C_e is known experimentally. The value of q_e is calculated using Equation (5.1) (Kumar, et al., 2010).

$$q_e = \frac{V(C_0 - C_e)}{W} \qquad (5.1)$$

where,

q_e is COD adsorbed per unit mass of adsorbent (mg/g),

C_e is COD concentration in solution (mg/L),

C_o is initial COD concentration in solution

V is the volume of solution.

W is the mass of anode dissolved (adsorbent) (gm)

5.1. Pseudo-first order kinetic model

The adsorption kinetic data are analyzed using Lagergran rate equation. The first-order Lagergran model is given by Equation (5.2) (Khatibikamala, et al., 2010):

$$\frac{dq}{dt} = k_1(q_e - q) \tag{5.2}$$

The integrated form of the above equation is given by Equation (5.3) (Ramachandran, et al., 2008):

$$\log(q_e - q) = \log(q_e) - \frac{k_1 t}{2.303} \tag{5.3}$$

where,

q is the amount of COD adsorbed on the adsorbent at time t (min)

q_e is the amount of COD adsorbed at equilibrium

k_1 (min^{-1}) is the rate constant of the first-order adsorption.

The plot of the $\log (q_e - q)$ as a function of t provides the k_1 and q_e values. A straight line is obtained from the plots suggests the applicability of this kinetic model. It was found that the calculated q_e values are not well-matched with the experimental values as shown in Figure 22. There is variation between $q_{e.exp.}$ and $q_{e.pred.}$ values at higher electrolysis time. Also, the correlation coefficient is low (0.8942-0.9068). Hence, the adsorption not obeys the pseudo-first-order kinetic model.
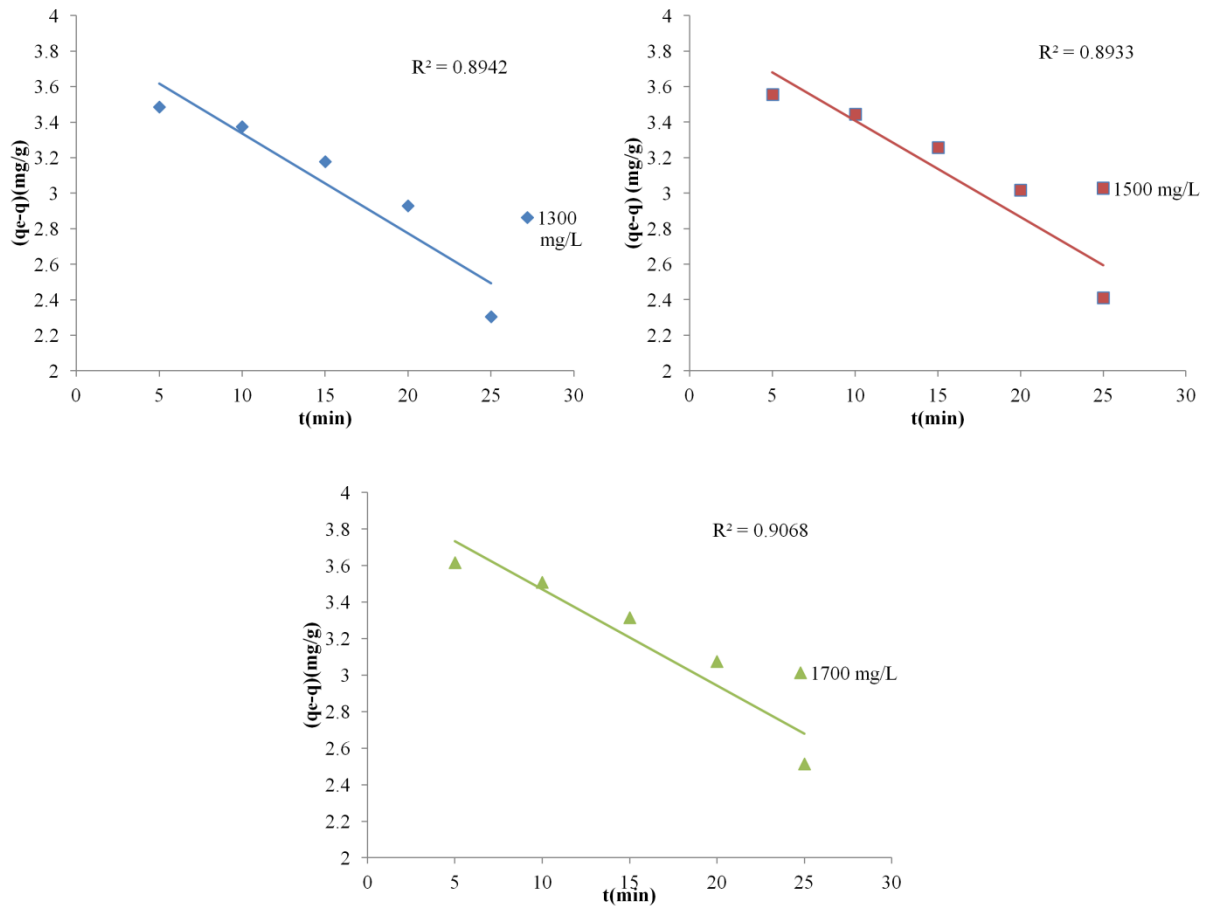
Figure 22: Pseudo first order kinetic model plot

5.2.Pseudo-second order kinetic model

The second-order kinetic model is expressed as shown in Equation (5.4) (Khatibikamala, et al., 2010):

$$\frac{dq}{dt} = k_2(q_e - q) \qquad (5.4)$$

The integrated form of the above equation is given by Equation (5.5) (Ramachandran, et al., 2008):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (5.5)$$

where k_2 is the rate constant of the second-order adsorption.

The plot of t/q_t *vs.* t will be a linear relationship if the second order kinetics is applicable. k_2 and predicted q_e can be determined from the slope and intercept of the plot respectively. The pseudo second order rate constant ranges from $9.00*10^{-6}$ mg/g/min to $10.00*10^{-6}$ mg/g/min for 1300 to 1700mg/L COD concentration. The adsorption is well explained by the high correlation coefficient (R^2=0.9812-0.9824) as shown in Figure 23. Hence, the adsorption obeys the pseudo-second-order kinetic model.
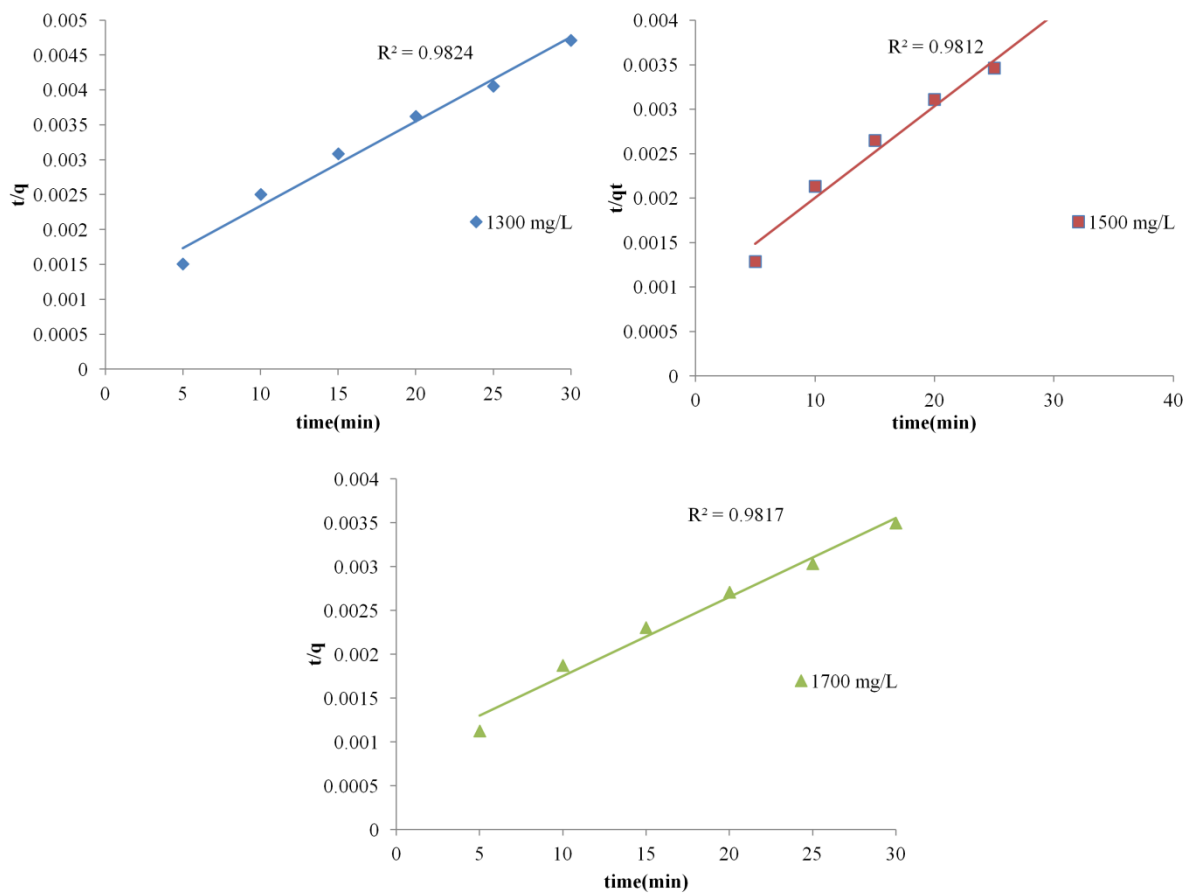
Figure 23: Pseudo second order kinetic model plot

5.3. Elovich model

The Elovich equation is mainly applicable for chemisorptions kinetics. The equation is often valid for systems in which the adsorbing surface is heterogeneous. The model is given by Equation(5.6) (Ramachandran, et al., 2008):

$$q_t = \frac{1}{\beta}(ln\alpha\beta) + \frac{1}{\beta}lnt \qquad (5.6)$$

where,

α is the initial adsorption rate (mg g^{-1} min)

β is related to the extent of surface coverage and the activation energy for chemisorptions (g mg^{-1})

A plot of q$_t$ *vs.* ln t gives a linear trace with a slope of (*1/β*) and an intercept of *1/β* ln (*α β*). The plot has the good correlation coefficient (R^2=0.9653to 0.9669) as shown in Figure 24 which indicates that the rate-limiting step is the surface adsorption that involves chemisorption. The surface of the adsorbate is heterogeneous.
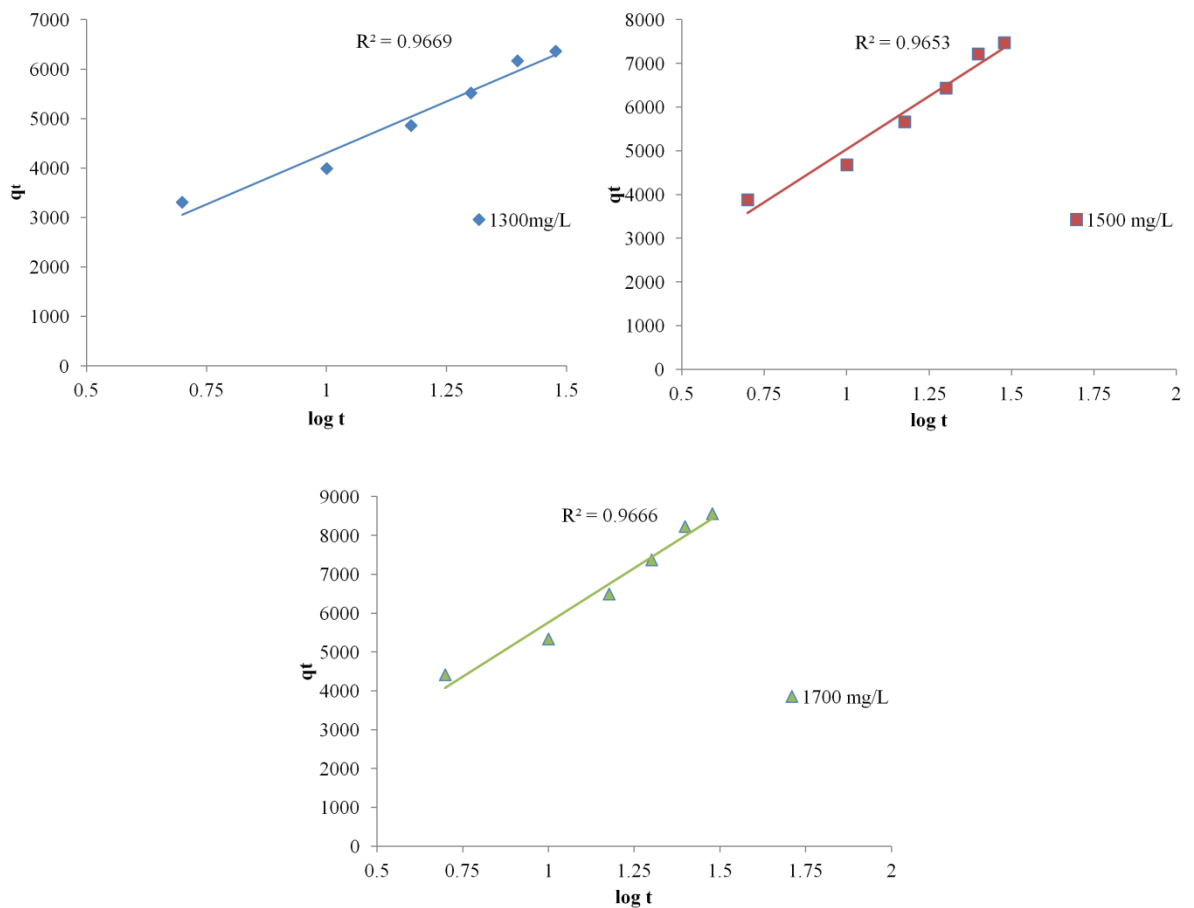
Figure 24: Elovich model plot

The detailed results for the Figures 22-24 have been presented in the Appendix B. Parameters for reaction order kinetics are presented in Table 17. The various parameters were calculated by plotting the graphs as explained above.

The average R^2 value for pseudo first order kinetic model is 0.8981, for pseudo second order kinetic model it is 0.9818 and for the elovich model it is 0.9663.These results indicate that the adsorption system belongs to the pseudo second order kinetic model, and the rate-limiting step is the surface adsorption that involves chemisorption.

Table 17: Calculated kinetic parameters for the adsorption COD at various concentrations

Initial COD conc. (mg/L)	$q_{e.exp.}$ (mg/g)	Pseudo first order kinetics			Pseudo second order kinetics		
		K_1 (min^{-1})	$q_{e.pred.}$ (mg/g)	R^2	K_2 (mg/g/min)	$q_{e.pred.}$ (mg/g)	R^2
1300	6369.876	0.1294	7894.052	0.8942	$9.09*10^{-6}$	10000	0.9824
1500	7473.907	0.1250	8961.898	0.8933	$10.00*10^{-6}$	10000	0.9812
1700	8565.453	0.1216	9956.347	0.9068	$9.00*10^{-6}$	11111.1	0.9817

Initial COD conc. (mg/L)	$q_{e.exp.}$ (mg/g)	Elovich model		
		α (mg/g/min)	β (mg/g)	R^2
1300	6369.876	1979.873	0.000550	0.9669
1500	7473.907	2303.066	0.000475	0.9653
1700	8565.453	2601.374	0.000412	0.9666

6.0 Adsorption isotherm

At a constant temperature, an adsorption isotherm describes the relationship between the amount of adsorbate adsorbed by the adsorbent (q_e) and the adsorbate concentration remaining in solution after equilibrium is reached (C_e). The parameters from the adsorption equilibrium models provide useful pieces of information on the surface properties, adsorption mechanism and interaction between the adsorbent and adsorbate (Lima, et al., 2015).

Depending on the pH of the aqueous medium various types of $Al_n(OH)_{3n}$ complexes may be present in the system. These gelatinous charged hydroxo cationic complexes can effectively remove pollutants by adsorption to produce charge neutralization, and by enmeshment in a precipitate (Mollah, et al., 2001).

The objective of this study is to examine the adsorption isotherms of $Al(OH)_3$ for COD removal from dairy wastewater. The initial COD was varied from 900-1700 mg/L. The experimental data were fitted with Langmuir, Freundlich, and Redlich–Peterson isotherms. Set of seven experiments varying initial COD concentrations(C_o) and their respective COD removal responses after EC (C_e) were used for calculations. The amount of COD adsorbed was determined using a mass balance equation expressed in Equation (5.1). Optimized values of current density 2.21 mA/cm^2 ,conductivity 2000 µS/cm and pH 6.86 were used. The predicted q_e is obtained from the non-linear expressions of Langmuir, Freundlich, and Redlich–Peterson (Langmuir, 1918) (Freundlich, 1906) (Redlich & Peterson, 1959) isotherms as shown in Table 18. In the case of the non-linear method, a trial-and-error procedure was developed to determine the isotherm parameters using an optimization routine to maximize the coefficient of determination between the experimental data and isotherms (Kumar, 2007). This was performed in the solver add-in with Microsoft's spreadsheet, Microsoft Excel. The protocol which has been used is, experimental data was manually entered in MS-Excel, the formulated algorithm was carried out, and the predicted curve was overlaid on the experimental data curve, and goodness of fit was observed (Sinha & Mathur, 2015).

Table 18: Data used to determine highest fitted isotherm

Final COD in the aqueous phase (mg/L)(C_e)	Amount of COD adsorbed(mg/g) ($q_{e.exp}$)	$q_{e.pred}$(mg/g)		
		Langmuir $q_e = \dfrac{q_{max}K_L C_e}{1 + K_L C_e}$	Freundlich $q_e = K_F C_e^{\frac{1}{n}}$	Redlich-Peterson $q_e = \dfrac{AC_e}{1+BC_e^g}$
212.13	4272.48	5117.433	4141.935	5169.767
246.51	5301.18	5946.704	5382.374	6007.605
274.45	6369.88	6620.641	6490.836	6688.520
285.32	6923.87	6882.902	6945.930	6953.502
296.70	7473.91	7157.342	7436.177	7230.791
309.12	8017.90	7456.840	7987.383	7533.401
320.96	8565.45	7742.514	8528.744	7822.047

where,

q_{max} is the maximum adsorption capacity (mg/g).

K_l is the Langmuir constant (L/mg).

K_f is the Freundlich constant that indicate the adsorption capacity of the adsorbent (L/gm).

n is an empirical constant related to the magnitude of the adsorption driving force.

A and B are the Redlich-Peterson constants.

g is an exponent which lies between 0 and 1.

6.1.Goodness of fit

The goodness of fit is an essentially important parameter that estimates how well the curve (i.e. the prediction) pronounces the experimental data. The goodness of fit is judged on following parameters:

(i) Coefficient of determination(R^2)

The coefficient of determination represents the percent of the experimental data that is the closest to the line of best fit. The coefficient of determination is such that $0 < R^2 < 1$,

and denotes the strength of the linear association between 'experimental data ($q_{e.\exp}$)' and 'prediction data ($q_{e.\text{pred}}$)'. R^2 is described by the expression in Equation (6.1) (Hossain, et al., 2013).

$$R^2 = 1 - \left[\sum_{n=1}^{n}(q_{e.exp.n} - q_{e.pred.n})^2 / \sum_{n=1}^{n}(q_{e.exp.n.} - q_{e.exp.n.avg})^2 \right] \qquad (6.1)$$

where,

$q_{e.\exp}$ is the equilibrium sorption capacity found from the batch experiment

$q_{e.\text{model}}$ is the prediction from the isotherm model for corresponding to C_e

n is the number of observations

(ii)Standard error(S.E.) and Chi-square test(χ^2)

Smaller values of S.E. and χ^2 indicates the better model fitting and that predicted values resembles the experimental values. Standard error and χ^2 are computed by Equation (6.2) and Equation(6.3) respectively (Hossain, et al., 2013).

$$S.E. = SS/df \qquad (6.2)$$

where,

SS is Sum of Squares

df is degrees of freedom.

$$\chi^2 = \sum_{n=1}^{n}(q_{e.exp.n} - q_{e.pred.n})^2 / (q_{e.exp.n}) \qquad (6.3)$$

The results for the goodness of fit for the three isotherms have been presented in Table 19. The R^2 values of Redlich–Peterson and Langmuir isotherms are almost similar. Redlich–Peterson isotherm has features of both Langmuir and Freundlich. The model has a linear dependence on concentration in the numerator and an exponential function in the denominator to represent adsorption equilibria over a wide concentration range, which can be applied either in homogeneous or heterogeneous systems due to its versatility. It approaches Freundlich isotherm model at high concentration (as the exponent g tends to zero) and is in agreement with the low concentration limit of the ideal Langmuir condition (as the g values are all close to one) (Sinha & Mathur, 2015).

In the present case, the Freundlich isotherm has the best fit if compared with Langmuir and Redlich- Peterson as shown in Figure 25. This suggests that features of Freundlich isotherm are applicable to the present adsorption. A similar result has been validated by Sengil & Ozacar, 2006. The amount adsorbed is the summation of adsorption on all sites (each having bond energy), with the stronger binding sites occupied first until adsorption energy is exponentially decreased upon the completion of adsorption process (Adamson & Gast, 1997). The slope ranges of Freundlich isotherm, between 0 and 1, is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. Whereas, a value below unity implies chemisorptions process, where *1/n* above one is an indicative of cooperative adsorption (Haghseresht & Lu, 1998). The slope in the present study is 0.57, which is indicative of chemisorptions taking place. The chemisorptions of COD onto the aluminium hydroxide flocs is multilayer at the current density of $2.21 mA/cm^2$.

Table 19: Isotherm parameters

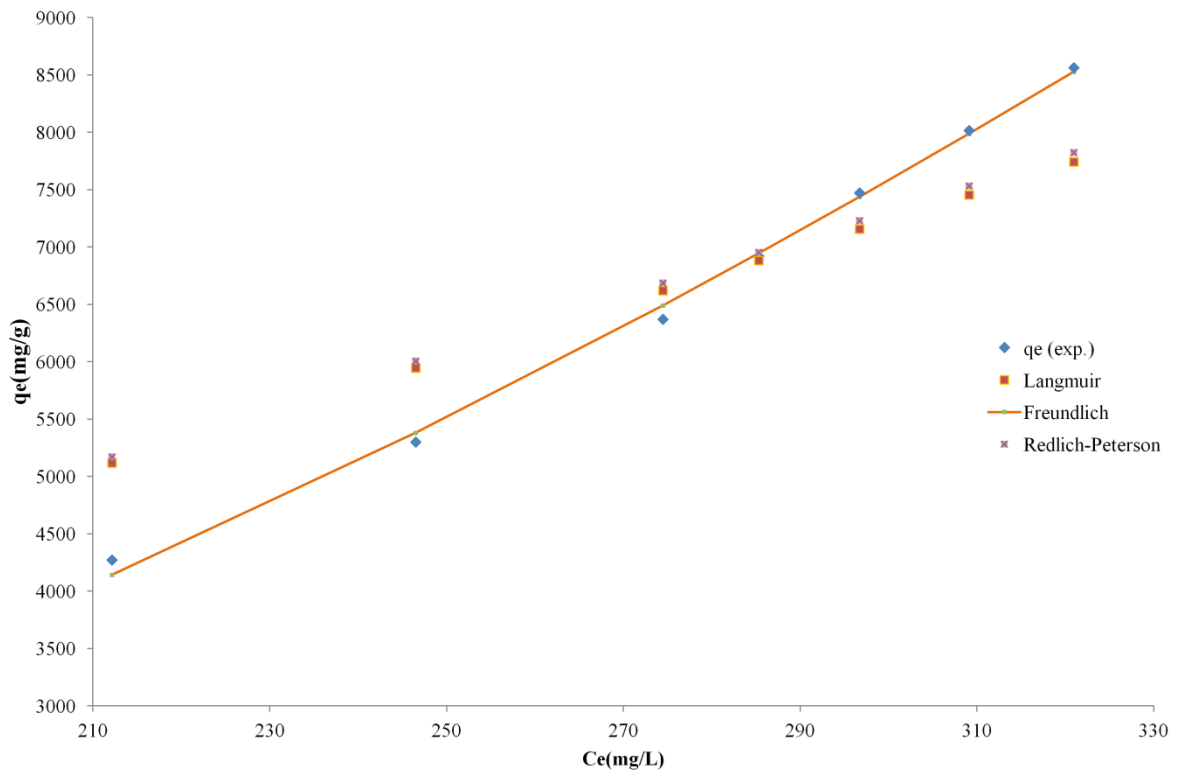| Isotherm	Parameter	Values
Langmuir	q_{max}(mg/g)	58018193.93
	K_l(L/mg)	4.15836E-07
	SE of $q_{e.exp}$	676.374
	χ^2	387.554
	R^2	0.8346
Freundlich	K_f(L/g)	0.362
	n	1.744
	SE of $q_{e.exp}$	92.166
	χ^2	8.607
	R^2	0.9969
Redlich-Peterson	*A*(L/g)	33480.96
	B(L/mg)	1372.824
	g	0
	SE of $q_{e.exp}$	671.2819
	χ^2	400.358
	R^2	0.8370

Figure 25: Adsorption isotherms of COD (pH=6.86, current density=2.21mA/cm^2, electrolysis time 30 min., conductivity=2000 μS/cm)

7.0 Conclusion

In the present study, EC process has been used to simulated dairy wastewater with initial COD of 1300 mg/L, which is in the range of industrial dairy wastewaters. Experimental investigations were carried out to remove COD/BOD of wastewater at low operating cost using aluminum electrodes.

    A. Parametric studies shows that:

     i. Up to 55-65% COD removal occurs in initial 15 minutes of the EC process

    ii. %COD removal decreases at and above 2.56 mA/cm^2 for constant electrolysis time of 30 minutes.

  iii. Lower current density and higher retention time in the reactor causes less electrical energy consumption as compared to higher current density with lower electrolysis time. However, former combination increases the pH in the reactor which reduces removal efficiency and increases the size of the reactor. Therefore, a balance has to be made between the two.

  iv. Increasing the current density and the electrolysis time increases the anode dissolution while increasing conductivity in the solution decreases the anode consumption. Anode consumption is in the range of 0.052-0.150 mg/mg COD removed.

   v. SEEC is affected by the applied voltage, current, electrolysis time, and conductivity. SEEC is in the range 0.075-0.270 J/mg COD removed.

    B. The EC process is a complex technique which is affected by various operating parameters. Design of experiments (DOE) and response surface methodology(RSM) are useful for the analysis and modelling of problems in which a response is influenced by several factors that also involves complex interactions. Literature review and experimental investigations shows that current density, pH, and conductivity are important operational parameters for dairy wastewater treatment.

    C. Three-factor and three level Central composite design based on RSM was employed as an experimental design tool to explain the effect of main operating parameters and their interactions on the removal of COD, BOD, anode consumption and specific electrical energy consumption(SEEC) as major responses for batch EC process. According to the ANOVA results, the models

presents high R^2 values of 96.05, 94.60%, 97.45% and 99.65% for COD, BOD, anode consumption and SEEC respectively which indicates that the accuracy of the polynomial models was good for the models. An experiment was done in optimum conditions which confirmed that the model and experimental results are in close agreement. This suggests that central composite design was successfully employed in the present study for experimental design and analysis of results.

D. Optimization results shows that COD removal efficiency of 79.46-79.69% and BOD removal efficiency of 81.01-81.35% was obtained at anode consumption of 0.065-0.066 (mg/mg COD removed) and SEEC of 0.068-0.070 (J/mg COD removed).

E. COD/BOD removal increases with increase in current density and pH up to an optimum value beyond which it starts decreasing while with an increase in conductivity, removal efficiency increases. There is only a small increase in COD removal efficiency beyond 1500μS/cm.

F. The average R^2 value for pseudo first-order kinetic model is 0.8981, for pseudo-second order kinetic model it is 0.9818 and for the elovich model it is 0.9663.These results indicate that the adsorption system belongs to the pseudo second-order kinetic model, and the rate-limiting step is the surface adsorption that involves chemisorption.

G. The adsorption isotherm study reveals that the Freundlich adsorption isotherm model(R^2=0.9969) fits well with the experimental data and indicate multilayer adsorption taking place.

8.0 Recommendations

Dairy wastewater is generally treated by biological methods. Thus, there is vast scope available for research regarding EC process for dairy wastewater treatment. Some of the recommendations which may improve the treatment process are given below:

- Efficient reactor designs which provide cost-effective treatment need to be developed.
- Scale -up issues should be addressed for its industrial applications. For this, there is a need to identify key scale-up parameters to ensure the dimensional consistency while scaling up the process.
- Thorough economical and environmental comparison of chemical coagulation and EC is suggested as these methods seem to be comparable to metal consumption, pollutant destabilisation mechanisms and removal efficiency in most applications.
- There is a need to work up on new technological innovations and studies to prevent passivation and fouling of electrodes and to further optimise treatment parameters.
- Aluminium is a potential neuro-toxicant and has ill-effects on human health. Therefore, use of other electrode materials which are cheap and readily available requires research.
- An area that requires a great deal of research is the use of hybrid electrodes, different electrode configurations and placement of electrodes. Also, electrode geometry is required to be worked up on to maximize the area available for reactions.
- For further treatment of dairy wastewater, use of bentonite and charcoal as a coagulant could be explored.
- EC process can also be coupled with the biological treatment methods for further efficiency.
- Use of solar energy as a source of power for running the EC process should be explored.

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Appendix A

Table A.1: Variation of % COD removal with electrolysis time at different current densities(pH=7,conductivity=1500μS/cm)

Electrolysis time	Current density(mA/cm^2)					
	1.60	**1.92**	**2.24**	**2.40**	**2.56**	**2.88**
5	33.77	38.12	39.53	40.45	44.15	46.55
10	38.24	42.95	46.26	48.82	53.75	54.98
15	45.85	52.45	57.81	59.42	62.89	63.61
20	54.97	60.04	64.56	67.48	70.06	71.29
25	61.29	65.26	71.91	75.38	75.29	72.88
30	63.85	68.62	73.45	77.81	74.69	72.14
35	64.9	67.68	73.04	76.84	74.17	71.63
40	64.24	66.56	72.95	75.44	73.56	71.25
45	63.93	66.23	72.64	74.95	73.21	71.16

Appendix B

Table B.1: Data for pseudo first-order kinetics and elovich model plot (C_0=1300 mg/L)

Electrolysis time (min)	log t	C	q	q_e-q
5	0.6990	767.121	3309.807	3.4857
10	1.0000	656.857	3994.677	3.3757
15	1.1761	517.498	4860.261	3.1789
20	1.3010	411.034	5521.528	2.9286
25	1.3979	306.962	6167.938	2.3052
30	1.4771	274.450	6369.876	0.0000

Table B.2: Data for pseudo first-order kinetics and elovich model plot (C_0=1500 mg/L)

Electrolysis time (min)	log t	C	q	q_e-q
5	0.6990	875.048	3881.689	3.5554
10	1.0000	745.731	4684.901	3.4454
15	1.1761	504.366	6184.062	3.1105
20	1.3010	396.443	6854.391	2.7920
25	1.3979	338.202	7216.137	2.4112
30	1.4771	296.701	7473.907	0.0000

Table B.3: Data for pseudo first-order kinetics and elovich model plot (C_0=1700 mg/L)

Electrolysis time (min)	log t	C	q	q_e-q
5	0.6990	988.282	4420.609	3.6175
10	1.0000	841.012	5335.329	3.5092
15	1.1761	654.012	6496.820	3.3157
20	1.3010	512.689	7374.602	3.0759
25	1.3979	373.689	8237.957	2.5152
30	1.4771	320.962	8565.453	0.0000

Table B.4: Data for pseudo second-order kinetics

Electrolysis time (min)	t/q_t(min.g/mg)		
	C_o=1300 mg/L	C_o=1500 mg/L	C_o=1700 mg/L
5	0.0015	0.0013	0.0011
10	0.0025	0.0021	0.0019
15	0.0031	0.0024	0.0023
20	0.0036	0.0029	0.0027
25	0.0041	0.0035	0.0030
30	0.0047	0.0040	0.0035