A

Dissertation Report

On

# "Performance Evaluation Of Dairy Waste Water Treatment By Electro coagulation Using Vertical Rotating Cylindrical Aluminum electrode."

By
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Environmental Engineering
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Submitted In the partial fulfilment for the Award of degree of
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# *CERTIFICATE*

This is to certify that the dissertation report on "**Performance Evaluation Of Dairy Waste Water Treatment By Electro coagulation Using Vertical Rotating Cylindrical Aluminum e**lectrode" which is submitted by Amit Kumar (2014PCE5435), in partial fulfilment for the Master of Technology in Environmental Engineering to the Malaviya National Institute of Technology, Jaipur. It is a recorded of a student's own work carried out by him under my supervision and guidance during academic session (2014-2016).This work is approved for submission.

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# Dedication

I would like to dedicate my thesis to my beloved parents

# ACKNOWLEDGEMENT

I owe a great many thanks to a great many people who helped and supported me during this dissertation work.

I take this moment to acknowledge with deep sense of gratitude and honour to express my indebtness to **Dr. Sanjay Mathur**, Associate Professor, Department of Civil Engineering, Malaviya National Institute of Technology, Jaipur for his guidance, precious council and supervision from the initial to the final level enabled me to develop an understanding of the subject and helped me in learning many new things, which will definitely help me in future. I would also like to thank **Prof. A.B. Gupta**, **Dr. Urmila Brighu**, **Prof. Y.P. Mathur** and all the Faculty members at Malaviya National Institute of Technology (MNIT) for their suggestions and helpful discussions.

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**Date:** **AMIT KUMAR**

# ABSTRACT

The dairy industry is among the most polluting of the food industries due to its large water consumption. There is a need for efficient treatment technologies which are also energy intensive. In the present study, the vertical rotating cylindrical aluminium electrode has been used for the treatment of simulated dairy waste water(SDW) by electro-coagulation process. Experiments were conducted in a laboratory scale cylindrical mono-polar batch reactor. Full factorial central composite design (CCD) was employed for responses: chemical oxygen demand (COD) and specific electrical energy consumption(SEEC).Four factors namely current density, initial COD, electrolysis time and RPM with each factor at three levels were used for the study. Regression model equations were developed which were validated by high $R^2$ values of 98.26% and 98.29% for COD and SEEC respectively. It was discovered that the COD removal efficiency of the reactor with rotating electrode was more (approx.91%) as compared to other batch reactors with static aluminium or iron electrodes. It consumes appreciably low energy (0.170 J/mg COD which is about 92-100% reduction compared with static electrodes) which is important from the point of cost consideration. Also, the requirement of cleaning the electrode is much less than the same with the static electrode.

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# ABBREVIATIONS

| | |
|---|---|
| COD | Chemical Oxygen Demand |
| BOD | Biological Oxygen Demand |
| EC | Electro coagulation |
| Al | Aluminum |
| $e^-$ | Electron |
| Fe | Iron |
| CaCO3 | Calcium carbonate |
| NaCl | Sodium chloride |
| Al(OH)3 | Aluminum hydroxide |
| $OH^-$ | Hydroxide ion |
| Fe | Iron |
| CaCO3 | Calcium carbonate |
| $Cl^-$ | Chloride ion |
| S/V | Surface area to volume ratio |
| D.C. | Direct Current |
| ppm | Parts per million |
| PVC | Poly vinyl chloride |
| ANOVA | Analysis of variance |
| DOE | Design Of Experiments |
| 3-D | Three dimensional |
| CPCB | Central Pollution Control Board |

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# 1.Introduction

## 1.1. Background of dairy industry

The milk is one of the most valuable commodity entering trades and it is required by everybody in everyday life as an article of food. Since the milk is most perishable, basic consumer health and economic consideration are necessary that public should be provided with the comodity which is of better quality, pure, free from pathogenic bacteria. To persevere quality standard, quality control operation criteria have to be performed in all the phases of production of milk which involve maintenances of sanitary conditions at milk production place, milk storage, transportation and handling the milk at the reception site, processing, and packing, etc. whenever the milk is delivered to the purchaser. Due to fast industrialization taking place all over the country, the number of dairy factories and allied industries is steeply rising (Shete & Shinkar, 2013).

The wastewater from dairy industry is generally a mixture of milk or other dairy products which diluted with water. Dairy effluents have a high level of organic materials. Dairy industry effluent is considered to be one of the most contaminated wastewaters and purification of this effluent has always been challenging. Thus, various research studies have been conducted with this aim. Dairy industry wastewater includes industrial waste, flushing waste and waste from aqueous cooling systems. The wastewater from industry may originate from washing milk carrying and storing containers, bottles and glasses, delivery station floors, sterilizing depositories and other installations present, such as pumps, boilers, etc. (Ghahremani, et al., 2012).

## 1.2. Characteristics of dairy wastewater

**Table 1: Characteristics of wastewaters from dairy industry (concentration in mg/l, except pH)**

| Types of waste water | Chemical oxygen demand(COD) | Biological oxygen demand(BOD) | pH | Total suspended solid(TSS) | Total solid(TS) | References |
|---|---|---|---|---|---|---|
| Dairy waste water | 2500-3000 | 1300-1600 | 7.2-7.5 | 72,000-80,000 | 8000-10000 | (Qazi, et al., 2011) |
| Milk & Dairy Products Factory | 10251.2 | 4840.6 | 8.34 | 5802.6 | | (Cristian, 2010) |
| Dairy effluent | 1900 to 2700 | 1200 to 1800 | 7.2-8.8 | 500 to 740 | 900 to 1350 | (Deshannavar, et al., 2012) |
| Whey | 71526 | 20000 | 4.1 | 22050 | 56782 | (Deshpande, et al., April 2012) |
| Dairy industry wastewater | 2100 | 1040 | 7-8 | 1200 | 2500 | (Arumugam & Sabarethinam, Oct 2008) |
| Aavin dairy industry washwater | 2500-3300 | | 6.4-7.1 | 630-730 | 1300-1400 | (Sathyamoorthy & Saseetharan, March 2012) |
| Cheese Whey pressed | 80,000 - 90,000 | 120,000 - 135,000 | 6 | 8000 - 11000 | | (Kabbout, et al., 2011) |
| Bhandara Co-operative dairy industry wastewater | 1400 to 2500 | 800 to 1000 | 7.1 - 8.2 | 1045 to 1800 | 1100 to 1600 | (Monali, et al., 2011) |

Dairy wastewater characteristics are characterised by analyzing physico-chemical characteristics of wastewater in the monthly interval, during the year 2012 (Tikariha & Sahu, 2014).

### 1.2.1. Physical characteristics

#### 1.2.1.1. Colour

Colour is a qualitative characteristic of wastewater that can be used to determine the general condition of wastewater. If dairy wastewater is six hr old, have light brown colour, while wastewater has a light-to-medium gray shade that is undergoing some degree of decomposition, or it is collected for some time. If the colour of dairy wastewater is dark grey or black, the wastewater is septic, having undergone extensive bacterial decomposition under anaerobic conditions. Colour of dairy wastewater is changed with the season as per study i.e. in monsoon season it was light yellow, during winter it was brownish to light blackish and in summer season it becomes almost dark black due to temperature effect (Tikariha & Sahu, 2014).

#### 1.2.1.2. Turbidity

The turbidity of dairy waste water was varying form 35.9-97.1 NTU. The turbidity of wastewater depends on the strength of wastewater. If the wastewater is stronger or more concentrated, the turbidity is higher (Tikariha & Sahu, 2014).

#### 1.2.1.3. Salinity

Salinity value was varying from 0.254-0.639 ppm in wastewater. Due to increase in solubility of solids, the salinity of wastewater is increased, while the value of salinity lowered due to a decrease in temperature which responsible to decreased the solubility of solids (Tikariha & Sahu, 2014).

#### 1.2.1.4. Electrical Conductivity

Electrical Conductivity values of dairy wastewater were varying from 352.7-954.0 µ mhos/cm. Electrical conductivity value of wastewater was obtained higher during the rainy season due to increasing in the concentration of solids and the value of electrical conductivity lowered in winter season due to reducing in the discharge of solids from milk processing plant or industry (Tikariha & Sahu, 2014).

### 1.2.2 Chemical Characteristics

#### 1.2.2.1. Total Dissolved Solids (TDS)

Total dissolved solid values had ranged from 180.2 - 445.4 ppm in waste water. Due to the greater input of dissolved solids in water, the concentration of TDS increases. The minimum level of TDS was observed in the month of October and November due to the lower dissolution of solids in water, because of lower temperature (Tikariha & Sahu, 2014).

#### 1.2.2.2. Hydrogen Ion Concentration(pH)

The pH value of dairy waste water had ranged from 6.1-7.7. The pH of dairy effluent indicated the acidic nature of wastewater in most of the months of investigation. Acidic nature of dairy waste water is due to the breaking of milk lactose in to lactic acid. (Tikariha & Sahu, 2014).

#### 1.2.2.3. Alkalinity

Phenolphthalein alkalinity was calculated nil, throughout the study duration. So that, the value of total alkalinity was similar to the methyl orange alkalinity determined. Total alkalinity values of wastewater had ranged from 198.45-376.80 mg CaCO3/L in wastewater. The value of total alkalinity of wastewater was calculated higher during rainy season due to the addition of buffering material by surface runoff. The value of Carbonate and Hydroxide alkalinity was estimated zero and the value of Bicarbonate alkalinity was similar to the total alkalinity value. (Tikariha & Sahu, 2014)

#### 1.2.2.4. Free Carbon Dioxide

Free $CO_2$ values had ranged from 22.00-108.41 mg/L in dairy waste water. Due to a higher rate of addition of organic matter in to the waste water, the concentration of free CO2 in wastewater was increased and the reduced value of free $CO_2$ in wastewater was due to the addition of a lower quantity of organic matter in to waste water. (Tikariha & Sahu, 2014).

#### 1.2.2.5. Total Carbon Dioxide

Total $CO_2$ value had ranged from 196.63-398.95 mg/L in dairy waste water. Total $CO_2$ of dairy wastewater was comparatively higher in the rainy season due to the addition of higher concentration of bicarbonate ions in wastewater in the rainy season, the total $CO_2$ value of dairy wastewater was relatively higher and lowered during the winter months due to less concentration of bicarbonate ions in dairy wastewater. (Tikariha & Sahu, 2014).

#### 1.2.2.6. Total Hardness

Total hardness values fluctuated from 145.50 - 293.40 mg $CaCO_3$/L for the dairy waste water. A Higher value of total hardness in dairy waste water was calculated in the April month, because of more evaporation during the month of April due to increasing in temperature and the value of total hardness lowered during the December month due to a lower temperature. (Tikariha & Sahu, 2014).

#### 1.2.2.7. Calcium

The range of Calcium values fluctuated from 40.40-83.39 mg/L for dairy waste water. (Tikariha & Sahu, 2014).

#### 1.2.2.8. Magnesium

The range of Magnesium value was found from 10.01- 19.11 mg/L in dairy wastewater. (Tikariha & Sahu, 2014).

#### 1.2.2.9. Protein

Protein was found to vary from 13.78-72.12 in waste water of milk processing unit. The lower value of protein was found in the rainy season due to dilution of wastewater, and higher value of protein in wastewater was observed in summer as well as in winter, because of difference in the rate of decomposition as well as the difference in the influx of protein in to the dairy waste water. (Tikariha & Sahu, 2014).

#### 1.2.2.10. Carbohydrate

Carbohydrate value was vary from 0.1007-0.2958 mg/L in waste water of milk processing unit. Less concentration of carbohydrate was found in months of June due to dilution of waste water, while, a higher level of carbohydrate was obtained in the winter season, because of difference in influx of carbohydrate and rate of breakdown of carbohydrates. (Tikariha & Sahu, 2014).

## 1.3. Problem relates to dairy wastewater

The dairy industry generates large amounts of wastewaters produced in the form of oil/water emulsions which are problematic to treat because of their complex behaviour. Dairy waste effluents are concentrated in nature, and the main contributors of organic charge to these effluents are carbohydrates, proteins and fats originating from milk. These liquid wastes are characterized by high levels of chemiical oxygen demand (COD) and biological oxygen demand (BOD), together with the presence of nitrogen and phosphorus. Because of these polluting features, wastewaters issued from the dairy industry have to be treated before their discharge into the environment. Numerous processes are being for the treatment of dairy wastewaters. They are based either on the revival of valuable components, mainly proteins and lactose or on the degradation of substances that can alter negatively, the environmental quality of the water courses (Bensadok, et al., 2011).

Dairy effluents are normally by using biological and physicochemical methods. Aerobic biological treatment methods require high energy which is the primary drawback of these processes, whereas, dairy wastewater treated by the anaerobic process, reflects indigent nutrient removal. Therefore, further treatment of anaerobically treated waste water is required. Among physico-chemical methods, removal of suspended and colloidal material from the dairy effluents by using coagulation-flocculation have been carried out (Kushwaha, et al., 2010).

## 1.4. Objectives of the study

Most of the studies conducted for the treatment of wastewater have used static electrodes. This configuration causes the appreciable deposit of salts on the electrode surface, which in turn, results in heating of electrodes and loss of efficiency. Moreover, with static electrodes, the possibility of small slugs of wastewater bypassed without getting treatment is also high. The advantages of the rotating electrode is that it ensures uniform mixing in solution, which enhances flocculation and avoids the possibility of untreated waste slug getting bypassed. Therefore, the removal of COD is more for less energy consumption.

Passivation and pitting of anode is also less compared to the mono-polar batch reactor.

In the present study, systematic experimental investigations with vertical rotating aluminum electrode were carried out to understand the effect of different operating parameters. The result of the experimental studies was used to develop the numerical relationship between various variables. Central composite design (CCD) and response surface methodology (RSM) have been utilized for the modeling, analyzing and optimization of responses: COD and specific electrical energy consumption for the variables: current density, initial COD, RPM and time. Providing excess energy results in dissolution of aluminium in water which has neuro-toxic effects as well as increases operating cost. Therefore, with the aim of reducing energy consumption for COD removal, the present reactor is compared with various batch reactors of aluminum or iron electrodes for performance evaluation concerning to energy consumption and COD removal efficiency.

**The effect of following four parameters will be studied:**

1.Current density

2.Rotation of electrode (RPM)

3.Time

4.Initial COD variation

**The output responses are:**

1.COD removal

2.Specific electrode energy consumption

# 2. Literature review

## 2.1. Electro-coagulation

Electro-coagulation is the recent application in the treatment of waste waters related to food industries. Electro coagulation is the process in which, coagulants such as iron or aluminium cations are generated in situ by dissolving electrically from iron or aluminium electrodes, respectively. The anode material undergoes oxidation, resulting metal ions generation takes place, and the cathode is subjected to the oxidation reaction, which releases hydrogen gas. The flocculated particles float out of the water with the help of hydrogen gas. The electrode reactions at anode and cathode are given below (Anon., n.d.) (Tchamango, et al., 2010):

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

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

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

$Al + 3H_2O + OH^{-} \rightarrow Al(OH)^{-4} + 3/2H_2$

The Al3+ and OH− ions produced at the electrodes can react to form various mono-nuclear and poly-nuclear species, 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 (Anon., n.d.)

### 2.1.1. Important processes occurring during Electro-coagulation:

Six important processes are occurring during Electro-coagulation-

i. Movement of particles to oppositely charged electrode and accumulation of particle due to charge neutralization

ii. Precipitate has formed with a cation($OH^-$) and pollutant

iii. Formation of hydroxide, which leading to pollutant adsorption also known as ‘Bridge Coagulation.'

iv. Hydroxides forming bigger grille like structures and sweeping through water is also known as Sweep Coagulation

v. Different species are oxidise in to less toxic pollutants

vi. Impurities are removal by sedimentation or electro floatation and their adhesion to bubbles

(Holt, 2006).

## 2.2. Parameters affecting Electro-coagulation operation

**i. The material of electrodes:** Mostly Iron and Aluminum metals are chosen as an electrode material because other materials have high cost or availability issues when used on large scale. Aluminum electrode always dissolves as Al (III) in the solution while Iron electrode dissolves mostly as Fe (II) in solution and then it is oxidized in bulk solution to Fe (III) (Moreno & C, 2007). Aluminum is excellent to Iron if considered the treatment efficiency and when we consider energy consumption also, Iron electrode is better than Aluminum electrode (Sasson, 2009). When we used Fe electrode, it fed a greenish colour to the treated water which then lead to turbid yellow due to oxidation of residual Fe ions to Fe3+ ions and then the subsequent formation of Fe(OH)3 imparting yellow color and turbidity (Diaz, 2003).

**ii. pH of the solution:** - pH of the solution is the most efficient parameter that influences the process of EC. During EC, pH of the solution increases when it as acidic to slightly alkaline and decreases when it is highly alkaline (Vepsalainen, 2012). pH of the solution also affects the conductivity of the solution, electrodes dissolution, potential of colloidal particles and speciation of hydroxides. Effective coagulants are formed in acidic(pH<7), neutral(pH=7) and slightly alkaline pH(pH>7) (Vepsalainen, 2012).

**iii. Current Density: -** Both treatment efficiency and cost of operation are depend on current density. Current density increases the efficiency and also the cost of the process up to a certain limit until the system started to lose energy as heat (Kobya, 2003).

**iv. Hydraulic Retention Time:** HRT is the ratio of the total volume of Electro-coagulation reactor to flow rate of waste water. The residence time of the process varies directly with current density and consumption of energy. It is reported that, when the current density of the solution is held constant at 100A/m2, then the aluminum electrode requires 15 min for better removal efficiency which was 50% more than the iron electrode (Kobya, 2003).

**v. The concentration of anions:** Hydroxyl anions can replace by opposing anions in to precipitate, which affects removal efficiency and optimum conditions of coagulation. Sulphate anions are passivating agents and it reduces the rate of metal cations production. Chloride ions work opposed to pitting corrosion and break down of the passive layer (Kolics & P, 1998).

**vi. Temperature:** Dissolution rate of anodes is directly related to the temperature. The dissolution rate of anode increases with increase in temperature. Increasing temperature also improves the solubility of aluminum (Chen, 2004).

**vii. Conductivity:** Electrolyte such as Sodium Chloride (NaCl) is used to increase the conductivity of waste water due decreasing its internal resistance. NaCl has high efficiency and low environmental impact. The presence of Sodium Chloride in solution also prevents the formation of Aluminum sulfate octadecahydrate sieve layer which acts as a passivating layer on the electrode surface (Gunukula, 2011). At constant current density, the cell voltage decreases with increase in the conductivity of waste water (Kobya, 2003).

## 2.3. Advantages of Electro-coagulation:

1. EC process requires simple equipment and is easy to operate with adequate operational latitude to handle most problems encountered on running

2. Wastewater treated by EC process, and it gives clear, colorless, palatable and odorless water

3. Flocs are similar to chemical floc formed by EC process, except that EC floc tends to be much larger, is acid-resistant and more stable, contains less bound water, and therefore, can be separated faster by filtration

4. Sludge formed by EC process tends to be easy to de-water and readily settable because it is composed of mainly metallic hydroxides/oxides and it is a less sludge producing technique

5. Effluent from EC process consist low concentration of total dissolved solids (TDS) as compared with chemical treatments. If this effluent is reused, the low TDS level contributes to a lower water recovery cost

6. The advantage of EC process, it removed the smallest colloidal particles from wastewater, because the electric field is applied to sets them in faster motion, thereby facilitating the coagulation

7. The EC process avoids uses of chemicals, and so there is no possibility of secondary pollution and no problem of neutralizing excess chemicals caused by chemical substances added at high concentration as when chemical coagulation of wastewater is used

8. During electrolysis, Gas bubbles are formed and They can carries the impurity to the top of the water where it can be more conveniently concentrated, collected and removed

9. The electrolytic processes in the EC cell are controlled electrically with no moving parts, thus requiring less maintenance

10. The EC technique can be comfortably used in rural areas where power is not available, since a solar panel aconnected to the EC unit may be sufficient to carry out the process

(Mollah et al. 2001).

11. EC has Shorter retention time

12. During the EC process, the Small quantity of sludge produced

13. EC has Shorter retention time

14. Easily dewatering

15. EC requires less maintenance, and there is no problem of neutralizing excess chemicals

16. During the EC process relatively large size, more stable and less bound water containing flocs are formed

17. More efficient and rapid removal of organic pollutants from waste water

18. A major improvement of EC process over commercial techniques is that dosage of the coagulant can be controlled just by fixing the current which makes automation of the system very easy.

(Mollah, 2001), (Jiang, 2002), (Sasson, 2009), (Siringi, 2012)**,** (Ghadim, 2013)**,** (Mouedhen, 2008).

## 2.4. Disadvantages of Electro-coagulation:

1. The sacrificial electrodes are dissolved into wastewater streams as a result of oxidation and need to be regularly replaced.

2. The use of electricity may be costly in many places.

3. An oxide impermeable layer may be formed on the cathode leading to reduce the efficiency of the EC unit.

4. The high conductivity of the wastewater suspension is required.

5. Gelatinous hydroxide may tend to solubilize in some cases.

(Mollah et al. 2001)

11. Maintenance of a constant pH is hard as one cannot manage the production of $H^+$, $OH^-$ and $Cl^-$ ions.

12. When Al electrode is used in EC process, a passive oxide layer develops on the surface of anode leading to an increase in the applied potential and also wastage of energy.

13. There is a lack of systemic approach to designing of EC reactor.

14. “A significant difficulty with EC as a technique is that although it has reached a stage of profitable commercialization, yet the amount of scientific attention it has received is still very primitive.”

(Gunukula, 2011) **,** (Mouedhen, 2008)**,** (Zodi, 2013).

## 2.2. Recent study

Series of experimental investigations have been performed out on the electro coagulation treatment of dairy wastewater with aluminum electrodes. However, there is an insufficiency of studies related to rotating electrodes for dairy wastewater treatment. Treatment of dairy waste water using iron electrodes resulted in 98% removal of COD and 99% removal of grease and the optimum current density,

electrolysis time and pH for 18,300 mg COD/L and 4570 mg oil–grease/L were 0.6 $mA/cm^2$, 1 min and 7, respectively (Sengil & Ozacar, 2006). Treatment of dairy effluents by electro coagulation using aluminium electrodes resulted in up to 61% removal of the chemical oxygen demand (COD) while the removal of phosphorus, nitrogen contents, and turbidity were 89, 81 and 100%, respectively (Tchamango et al. 2010). Elimination 98.84% COD, 97.95% $BOD_5$, and 97.75% TSS using aluminum electrodes in the bipolar batch reactor has been reported (Bazrafshan, et al., 2013). Also, abatements of 70% of phosphates, 100 % of turbidity, and 80% of COD using Al electrodes have been carried out (Bensadok, et al., 2011). Electro-coagulation for fluoride removal with a static plate electrode was successfully applied, and 87.16% removal was obtained (Sinha, et al., 2014). Few studies have been carried out on the electro-coagulation treatment with rotating electrodes. Electro-coagulation for fluoride removal with a batch cylindrical electrode has been carried out in which 97.6% fluoride removal was obtained using aluminum cylindrical anode and rotating impeller cathode (Un, et al., 2013). Cr (VI) was efficiently eliminated using electro-coagulation by vertical and horizontal rough cylinder anodes and it was found that the performance of a cell with vertically oriented electrodes is superior to that of a cell with horizontal electrodes for removal of Cr(VI) ions by electro-coagulation (Khalaf, et al., 2016).

There are various recent studies of EC in the treatment of food industry wastewater shown in table 2.

**Table 2: Recent applications of EC in the treatment of food industry wastewater**

| **Water & wastewater type use** | **Genuine (G) & synthetic(S) water** | **Anode and cathode material type** | **Reactor type** | **Volume treated (ml)** | **Initial pollutant level (mg/l)** | **Optimum removal efficiency [%]** | **Research group Publication year** |
|---|---|---|---|---|---|---|---|
| Dairy wastewater | S | Fe | Batch | 1500 | COD:3900<br>Turbidity: 1744 [NTU]<br>TS: 3090<br>TN: 113 | COD: 70<br>Turbidity: 100 [NTU]<br>TS: 48<br>TN: 93 | (Kushwaha et al. 2010) |
| Dairy wastewater | G | Fe | Batch | 650 | COD:18300<br>O&G: 4570<br>TSS: 10200 | COD:98<br>O&G: 99<br>TSS: n.d. | (Sengil & Ozacar, 2006) |
| Almond Industry Wastewater | G | Al/Fe[b]<br>Fe/Al | Batch<br>Continuous<br>(pre-industrial scale-up) | 700-54000[e] | Turbidity: 3200 [FTU]<br>TSS:3400<br>COD: 7500<br>$BOD_5$:3445 | Turbidity: 99/98 [FTU]<br>TSS:100/99<br>COD: 80/90<br>$BOD_5$:n.d/96 | (Valero et al. 2011) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Pasta and cookie processing wastewater | G | Al | Batch<br>Batch+$H_2O_2$<br>(=EF) | 1500 | Turbidity:1153 [NTU]<br>TS:2905<br>Fecal Coliforms, MPN:11000<br>COD:2700-3100<br>BOD: n.d | Turbidity: n.d/97<br>TS: n.d/95<br>Fecal Coliforms: n.d/100<br>COD:80-84<br>BOD: 84-88 | (Roa-Morales et al. 2007) |
| Poultry Slaughterhouse waste water | G | Al<br>Fe[b] | Batch+ Polymer (LPM 9511,10mg/l) | 1700 | O&G: 720-950<br><br>TS:1440-2380 | O&G:98-100<br>TS:58-70 | (Asselin et al. 2008) |
| Poultry manure wastewater (UASB pretreated) | S | Al[b]<br>Fe | Batch | 400 | COD:4120 | COD:90 | (Yetilmezsoy et al. 2009) |
| Egg processing Waste water | S+G | Al<br>Fe<br>SS[b] | Batch<br>Batch+ coagulant (200 mg/l bentonite) | 1000 | COD: 8637-8983/ 4068-4132<br>TSS:1651-1953/930-1086<br>Turbidity: 933-1267/ 1340-2060 [FTU] | COD: 97/(92,95)<br>TSS: 97/(97,97)<br>Turbidity: 99/(99,99) | (Xu et al. n.d.) |
| Baker's Yeast wastewater | G | Al<br>Fe | Batch | 800 | COD:2485<br>TOC:1061<br><br>Turbidity:2075 [NTU] | COD:71/69<br>TOC:53/52<br><br>Turbidity: 90/56 | (Kobya & Delipinar 2008) |
| Tea factory wastewaters | G | steel | Batch | 400 | COD:293/607<br><br>$BOD_5$:42/193 | COD:91/97<br><br>$BOD_5$:84/42 | (Maghanga et al. 2009) |

b= observed as the best electrode configuration of those tested;
e= approximation calculation based on values given in the article as issue;

(Kuokkanen et al. 2013).

# 3. Materials and Methods

This topic describes the research methodology used in detail for the present study. The entire experimental work was carried out in the PHE lab of Civil Engineering Department in Malaviya National Institute of Technology (MNIT), Jaipur. The process electro coagulation process for COD removal was conducted on lab scale in a Batch mode as shown in the figure. This system consists of a power control system, a DC power supply and an electrochemical reactor. The reactor was made up of plexiglass and has a working volume of 5000 ml. The electrodes, anode and cathode were made up of Aluminum and are situated 2 cm apart from each other. The four parameters namely, Treating Time, current density, initial COD and RPM were varied. Other parameters such as pH and conductivity, etc. were kept constant.

The analysis of whole procedure includes the following points:

- Selection of dairy wastewater by the market study.
- Designing of the batch reactor by electrode size, treating time and flow RPM.
- Preparation of simulated dairy wastewater and reagents for use in the experimental study.
- Effect of various current density on COD removal efficiency.
- Effect of treating time on COD removal efficiency.
- Effect of RPM on COD removal efficiency.
- Effect of initial COD concentration on COD removal efficiency.
- Determination of COD by using double beam Spectrophotometer.
- Data analysis and interpretation.

## 2.1. EC apparatus

In this study, a cylindrical reactor of 5L effective volume was used to conduct the batch experiments. Two aluminum electrodes with the vertical rotating cylindrical anode of surface area 346.49 $cm^2$ and stationary cylindrical cathode of the surface area of 284.56 $cm^2$ were used. The anode was kept perforated to ensure better mixing and to avoid short-circuiting of pollutants. The electrode gap was kept as 2 cm for all experiments. Electrodes were connected to a DC power supply (Testronix, 0-30V,0-5A) in mono-polar configuration. The batch EC cell with mono-polar electrode connection is shown in Fig.1.

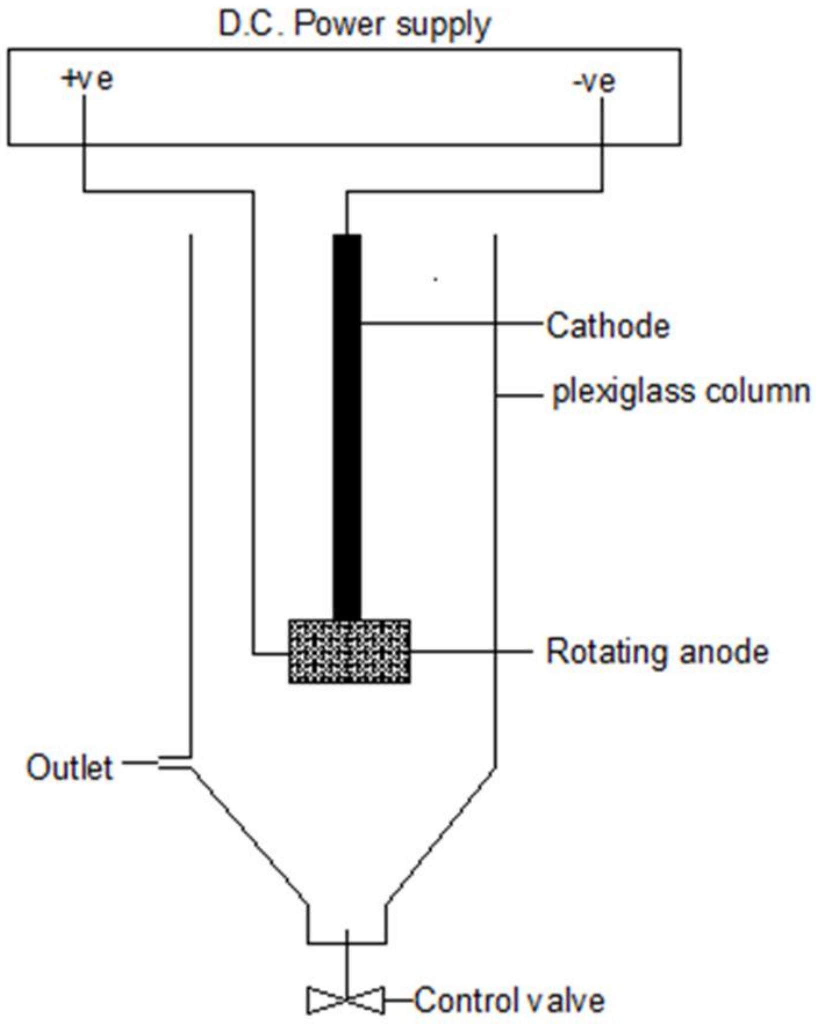


**Figure 1: Experimental setup for batch EC reactor**

## 3.2. Instruments used:

**pH Meter:** A digital auto type pH meter manufactured by LABTRONICS model LT-11 was used for the determination and adjustment the pH of the solution. pH meter is shown in Fig.2.

**Figure 2**: pH meter

**DC power supply:** This instrument used for DC power supply is manufactured by KUSAM-MECO model KM-PS-305-II with 0-30V/0-5A dual output with inbuilt voltmeter and ammeter. It shows in Fig.3.

**Figure 3: DC power supply**

**Conductivity meter:** Conductivity meter manufactured by Lutron of model CD-4302 was used for determining the conductivity of the solution. The range of this conductivity meter is from 2-20 mS. Conductivity meter shows in Fig.4.


**Figure 4**: Conductivity meter

**UV/VIS spectrophotometer:** The UV/VIS, double beam spectrophotometer, is used to calculate the COD of untreated and treated Dairy wastewater has a range of 200-1100 nm. It is manufactured by Schimadzu of model 1800. It shows in Fig.5.


**Figure 5:** UV/VIS spectrophotometer

**Closed reflux apparatus:** The closed reflux apparatus is manufactured by HACH (DRB 200). It is used for digesting the COD sample at 150°c for at least two hrs. Closed reflux apparatus shows in Fig.6.


**Figure 6:** Closed reflux apparatus

**Digital weighing balance:** A Digital weighing balance of CAS series and model no. CAUW 220 D with a range of 1mg to 220 gm. Digital weighing balance shows in Fig.7.

**Figure 7**: Digital weighing balance

**Glass ware:** glass ware such as test tubes, pipettes, COD vials, conical flasks, beakers, funnels, measuring cylinders, WHATMAN filter paper, etc.

## 3.3. Experimental work:

### 3.3.1. Preparation of simulated dairy waste water and characteristics:

Simulated dairy waste water is prepared to serve as a sample for the purpose of the experiment. The different quantity of the milk powder in 1 litre tap water gives different COD levels to the waste water. The amount of milk powder used in our experimental work was 800 mg/l which resulted in a COD level of the range 1000±20 mg/l. If the quantity of milk powder is 1000mg/l which resulted in a COD level of the range 1300±20 mg/l and when the amount of milk powder 1250mg/l milk powder which resulted in a COD level of the range 1600±30 mg/l.

**Table 3: Characteristics of wastewater used for 1 gm/l milk powder**

| Characteristics | Value |
|---|---|
| Chemical oxygen demand(COD)(mg/L) | 1300±20 |
| Total solids(mg/L) | 1791±150 |
| Total dissolved solids(mg/L) | 1062±140 |
| Total suspended solids(mg/L) | 729±10 |
| pH | 7.60±0.20 |
| Conductivity(µS/cm) | 750±10 |

## 3.4. Experimental procedure:

Freshly prepared simulated dairy wastewater(SDW) was used to prevent any change in the composition of wastewater throughout the experiments. 'Nestle Everyday Dairy Creamer' manufactured by 'Nestle India Ltd' was used to prepare SDW. Simulated dairy effluents were prepared by dissolution of commercial milk powder in tap water. 0.1N $H_2SO_4$ and 0.1N NaOH solutions were used to adjust the pH to 7 before the beginning of the experiment. This is because the maximum efficiency of the process is obtained at pH close to neutrality (Bazrafshan, et al., 2013) (Aitbara, et al., 2014). Conductivity was maintained at 1500µS/cm by adding NaCl into the solution so as to ensure minimum conductivity for the flow of electric current. Table 2 gives characteristics of wastewater used for 1gm of milk powder added per litre of wastewater.

The initial COD was decided according to previous studies available in the literature on dairy wastewater which used industrial dairy effluent (Sarkar, et al., 2006) (Kolarski & Nyhuis, 1995) (Yavuz, et al., 2010).The levels of other parameters have been decided through experimental investigations to obtain maximum COD removal efficiency.Table 3 gives variables and their levels.

**Table 4: Variables and their levels**

| Variables | Factor | Level | | |
|---|---|---|---|---|
| | | -1 | 0 | +1 |
| A | Initial COD (mg/l) | 1000 | 1300 | 1600 |
| B | Current density ($mA/cm^2$) | 0.792 | 1.109 | 1.426 |
| C | Time (min) | 20 | 30 | 40 |
| D | RPM | 40 | 50 | 60 |

pH and Conductivity of the samples were determined by using a calibrated conductivity meter (Lutron CD- 4302) and auto digital pH meter ( LABTRONICS), respectively. COD was measured using HACH DRB 200 digestion unit and double beam UV-1800 SCHIMADZU spectrophotometer. Treated water Samples were taken at the end of the experiments from the reactor. All the experiments were accomplished at room temperature. All the samples were filtered with WHATMAN 1.2µm filter paper. The current was maintained constant during the run. The percentage COD removal was calculated using the following relationship:

$$\%\, COD\, removal = \frac{(c_i - c_f) * 100}{c_i}$$

Where $C_i$ and $C_f$ are the initial and final COD concentrations (mg/l) after t (min). Specific electrical energy consumption is known as the amount of electrical energy consumed per unit mass of pollutant removed (Bensadok, et al., 2011).It is calculated using the following relationship:

$$SEEC(J/mg) = \frac{V * I * T + \tau * \omega}{amount\ of\ pollutant\ removed}$$

where I is the current in ampere, V is the voltage, T is a time in minutes, $\tau$ is the torque and ω is the angular velocity of the shaft.

## 3.5. Experimental design and data analysis:

In this study, RSM has been used for designing the experiments. Response Surface Methodology(RSM) is an effective statistical method to understand complex interactions between variables and responses and evaluate their relative significance of several affecting factors. Also, there are reduced the number of experiments required to be performed to obtain sufficient information for optimization of the process (Kushwaha, et al., 2010). RSM allows analysis of linear terms, interaction terms and square terms and gives a mathematical relationship between factors and responses (Un, et al., 2013).The experiments were performed as shown in Table 4. Total 30 experiments were designed based on four factor and three level Central Composite Design(CCD) based on RSM to obtain the design equations for the output parameters. The experimental matrix comprised of 24 factorial runs and six centre point runs. The experiments were performed triplicates and the average value of each response has been presented. Experimental data was analyzed using Design Expert 10.0.0 trial version.

**Table 5: Experimental design matrix**

| Run | A: Initial COD (mg/L) | B: Current density ($mA/cm^2$) | C: Time (min.) | D: rpm |
|---|---|---|---|---|
| 1 | 1300.00 | 0.792 | 30.00 | 50.00 |
| 2 | 1300.00 | 1.109 | 30.00 | 50.00 |
| 3 | 1600.00 | 1.426 | 40.00 | 60.00 |
| 4 | 1000.00 | 0.792 | 20.00 | 40.00 |
| 5 | 1000.00 | 1.426 | 20.00 | 60.00 |
| 6 | 1600.00 | 1.426 | 20.00 | 60.00 |
| 7 | 1300.00 | 1.109 | 40.00 | 50.00 |
| 8 | 1000.00 | 1.426 | 40.00 | 40.00 |
| 9 | 1300.00 | 1.109 | 30.00 | 50.00 |
| 10 | 1300.00 | 1.109 | 30.00 | 50.00 |
| 11 | 1600.00 | 1.426 | 20.00 | 40.00 |
| 12 | 1600.00 | 0.792 | 20.00 | 60.00 |
| 13 | 1600.00 | 1.109 | 30.00 | 50.00 |
| 14 | 1300.00 | 1.109 | 20.00 | 50.00 |

| | | | | |
|---|---|---|---|---|
| 15 | 1000.00 | 0.792 | 20.00 | 60.00 |
| 16 | 1600.00 | 0.792 | 40.00 | 40.00 |
| 17 | 1300.00 | 1.426 | 30.00 | 50.00 |
| 18 | 1300.00 | 1.109 | 30.00 | 50.00 |
| 19 | 1600.00 | 1.426 | 40.00 | 40.00 |
| 20 | 1600.00 | 0.792 | 40.00 | 60.00 |
| 21 | 1000.00 | 1.426 | 40.00 | 60.00 |
| 22 | 1600.00 | 0.792 | 20.00 | 40.00 |
| 23 | 1000.00 | 0.792 | 40.00 | 60.00 |
| 24 | 1300.00 | 1.109 | 30.00 | 40.00 |
| 25 | 1000.00 | 1.426 | 20.00 | 40.00 |
| 26 | 1300.00 | 1.109 | 30.00 | 50.00 |
| 27 | 1000.00 | 1.109 | 30.00 | 50.00 |
| 28 | 1300.00 | 1.109 | 30.00 | 60.00 |
| 29 | 1300.00 | 1.109 | 30.00 | 50.00 |
| 30 | 1000.00 | 0.792 | 40.00 | 40.00 |

# 4.Results and discussion:

## 4.1. Statistical methods used

The design of Experiments (DOE) and statistical models is used to investigate the effect of different factors on the treatment parameters of dairy industry waste water. In the present work, three-level four-factorial central composite design(CCD) which 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 are carried out and data are collected for each run. Literature survey and parametric studies suggested that current density, treating time, initial COD and RPM are effective operational parameters for dairy wastewater treatment by the Electro-Coagulation process. The experimental data was evaluate using Design Expert 10.0.0 trial version for analysis, mathematical modelling and optimization of the process. Model graphs and actual vs. predicted plots were used to describe and show and the effects and interactions.

## 4.1.1 Design of experiments

The design of experiments (DOE) is an analytical method to establish the relationship between factors that influence a process and the output of that process, or it is used to arbitrate cause-and-effect relationships. It is a process of developing the experiment so that the suitable data that can be evaluated by statistical methods will be collected, resulting in relevant and objective conclusions. The purpose of DOE is to decide how a response depends on one or more input variables or predictors so that future data of the response can be predicted from the input variables. The standard one variable at a time method does not account for interactions between variables whereas Design of experiments (DOE) allows the simultaneous study of the effect of various variables on a response in a cost effective manner (Mathews, 2012).

## 4.1.2 Response Surface Methodology

Conventionally, the efficiency of the system is discovered by changing one factor at a time while keeping the other factors constant which disregard complex interactions among the factors. Response Surface Methodology (RSM) is a collection of statistical and mathematical techniques which are valid for the modelling and evaluating of problems in which a response of concern is manipulated by several factors and the objective is to optimize the response. So that, 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. Further, there are few number of experiments needed to be performed to obtain sufficient information for the optimization of the process. It also presented mathematical models defining relationships between responses and factors (Kushwaha, et al., 2010).

### 4.1.3 Central Composite Design

Central Composite Design(CCD) is a most suitable response surface method design. There are three types of design points of CCD as shown in figure 8:

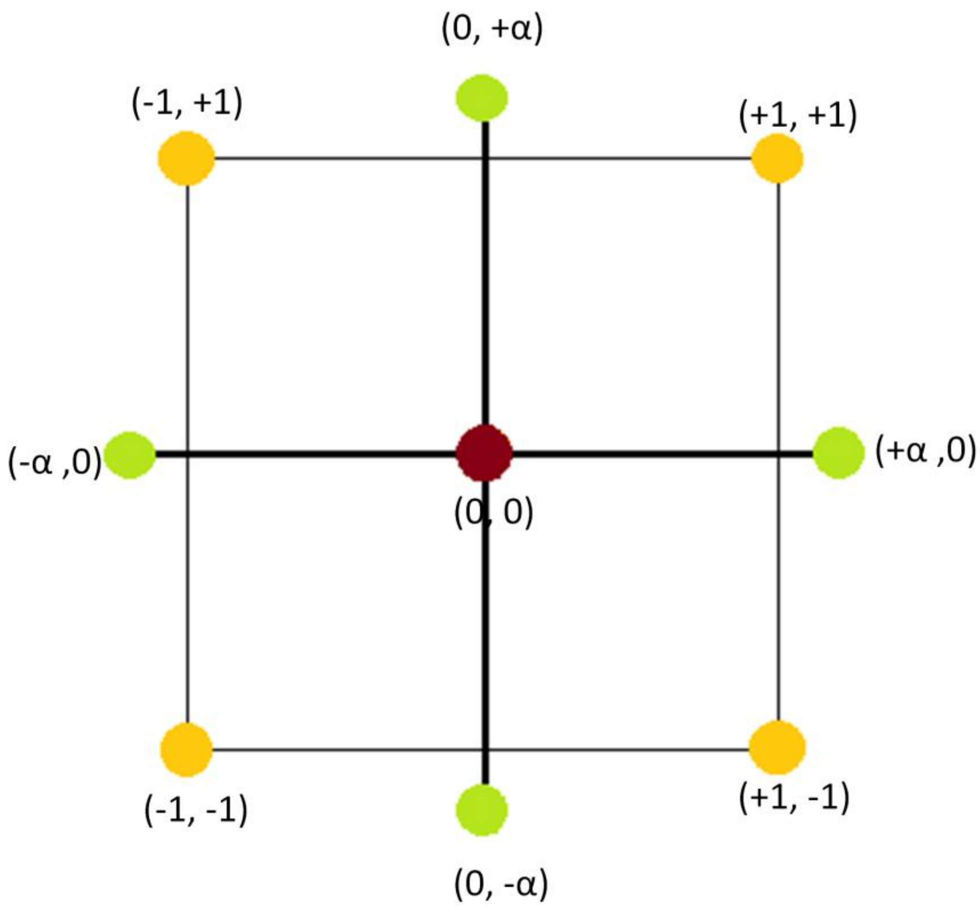


**Figure 8: Design points in central composite design (2-factor problem)**

i. ***Centre points (0,0)***: These points are discovered at the centre and also used to detect curvature in the response. (Expert, 2016).

ii. ***Axial points {(+α, 0), (0, +α), (-α, 0), (0, -α)}***: Axial points are discovered at a distance α from the centre point and are also used to estimate the coefficients of quadratic terms. (Expert, 2016).

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

### 3.5.4. Design Expert Software

In the present work, Design Expert software has been used to design the experiments, optimize and evaluate the system. Design Expert software can manipulate both process variables and also mixture variables. There are three main parts of a design expert. These are as follows:

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

ii. ***Design analysis and mathematical modelling***: once the response data has been entered, then the model analysis can be done. It involves diagnostics of design using ANOVA, Normal Probability Plots, Box-Cox Plot for Power Transformations, Actual vs. Predicted Plots, and Plots of Leverage and Influence Statistics. Design analysis and mathematical modelling also provide model-graphs which include Interaction, 3-D Surfaces, Contours, One-Factor, and Cubes for representation of results.

iii. ***Optimization of the process***: To use optimization, each response is first evaluated to set up an appropriate model. Optimization of one response or the simultaneous optimization of multiple responses can be completed graphically or numerically.

### 3.5.5. The procedure adopted for Design of Experiment

i. A cause and effect analysis of all the process variables (inputs) and responses (outputs) was adapted.

ii. Documentation of the process to be studied which includes a review of process flowcharts, written procedures, etc. was done.

iii. A complete problem statement was written down which included identification of design variables, identification of responses to be studied and possible interaction between them, identification of assumptions, estimation of time and materials required, statement of goals and limitations, etc.

iv. Preliminary Experimentation was done which involved clarifying of the experimental procedure, approving that process was in control and all equipment was operating accurately.

iv. The design of Experiment applied which included a selection of a suitable design with considering opportunities to add a variable if required.

vi. Replicates, Randomization and Blocking: - this involved determination of some replicates which means the number of times each experiment is repeated and it also helps in increases the precision of estimates of effects and estimating errors. Randomization of study variables which reduces the risk of unexpected sources of variation affecting the estimates of effects and helps to meet the assumptions of statistical methods used for analyzing experimental data, and blocking which divides the design into two or more blocks so that some inescapable sources of variation could be corrected.

vii. Experiments were conducted as per the decided procedure.

viii. Data analysis was done to confirm the accuracy of the data through graphing of the data, running ANOVA/ regression, determination of model standard error and $r^2$.

ix. Results were explained which included developing a predictive model for the response, choosing the optimum variable levels without extrapolating outside the range of experimentation.

x. Optimization results were confirmed by running another test at the optimized settings to see if expected results do indeed result. It is always accessible that some factor not examined has a significant impact on the outcome.

xi. Results documentation.

## 4.1. Development of regression model equations and its verification

The results of the responses for the input parameters which are obtained from EC experiments were analysed with design expert software for the determination of mathematical expression for prediction of % COD removal and SEEC. The software suggested quadratic models to obtain regression equations for the responses: %COD removal and SEEC. Eqs (1) and (2) give the regression model equation for COD and SEEC regarding coded factors. The experimental values and values predicted with Eq. (1) and (2) are presented in Table 5.

$$COD = 80.55 + 3.50 * A + 1.32 * B - 1.97 * C + 1.16 * D + 0.75 * A * B + 0.17 * A * C + 1.13 * A * D + 0.56 * B * C - 0.38 * B * D - 3.19 * C * D + 7.22 * A^2 - 18.52 * B^2 - 8.69 * C^2 - 13.19 * D^2$$

(1)

$$SEEC = 0.34 - 0.19 * A + 0.030 * B + 0.052 * C - 0.022 * D - 0.016 * A * \mathrm{B} - 0.022 * A * C - 5.557E - 003 * A * D + 5.696\mathrm{E} - 003 * B * C + 5.500E - 003 * B * D + 0.040 * C * D + 0.012 * A^2 + 0.14 * B^2 + 0.069 * C^2 + 0.096 * D^2$$

(2)

**Table 6: Dairy waste water treatment results**

| Run | %COD removal | | SEEC(J/mg COD) | |
|---|---|---|---|---|
| | Experimental | Predicted | Experimental | Predicted |
| 1 | 58.93 | 60.71 | 0.457 | 0.450 |
| 2 | 83.43 | 80.55 | 0.343 | 0.340 |
| 3 | 49.82 | 50.42 | 0.524 | 0.535 |
| 4 | 43.12 | 42.40 | 0.813 | 0.795 |
| 5 | 48.62 | 48.86 | 0.756 | 0.740 |
| 6 | 62.00 | 59.28 | 0.372 | 0.383 |
| 7 | 67.65 | 69.89 | 0.441 | 0.461 |
| 8 | 47.19 | 46.40 | 0.933 | 0.966 |
| 9 | 83.28 | 80.55 | 0.343 | 0.340 |
| 10 | 83.42 | 80.55 | 0.342 | 0.340 |
| 11 | 47.79 | 49.08 | 0.506 | 0.507 |
| 12 | 56.35 | 57.02 | 0.372 | 0.378 |
| 13 | 89.06 | 91.27 | 0.261 | 0.162 |
| 14 | 70.56 | 73.83 | 0.391 | 0.357 |
| 15 | 50.13 | 49.60 | 0.670 | 0.671 |
| 16 | 47.31 | 46.96 | 0.481 | 0.448 |
| 17 | 59.62 | 63.35 | 0.519 | 0.510 |
| 18 | 83.23 | 80.55 | 0.342 | 0.340 |

| | | | | |
|---|---|---|---|---|
| 19 | 53.72 | 52.98 | 0.513 | 0.499 |
| 20 | 46.31 | 45.92 | 0.473 | 0.506 |
| 21 | 40.00 | 39.32 | 1.042 | 0.980 |
| 22 | 45.87 | 45.30 | 0.477 | 0.480 |
| 23 | 39.23 | 37.82 | 0.896 | 0.887 |
| 24 | 64.89 | 66.20 | 0.451 | 0.458 |
| 25 | 44.07 | 43.18 | 0.888 | 0.886 |
| 26 | 84.31 | 80.55 | 0.339 | 0.340 |
| 27 | 80.98 | 84.27 | 0.457 | 0.542 |
| 28 | 64.32 | 68.52 | 0.436 | 0.414 |
| 29 | 82.12 | 80.55 | 0.346 | 0.340 |
| 30 | 41.88 | 43.38 | 0.878 | 0.851 |

## 4.2 Experimental verification of regression equations

To verify the correctness of regression equations, few experiments were carried out by selecting the input parameters in the range of levels shown in Table 3. The levels were chosen randomly for each factor. Table 6 gives experimental results for the selected operational parameter settings. Actual vs. predicted plots for COD and SEEC is shown in Fig.9 and in Fig.10 indicating a good correlation between predicted and experimental values and hence correctness of developed equations.

**Table 7: Operational parameter settings and their respective actual and predicted responses used for verification of correctness of regression equations.**

| Run | A: Initial COD (mg/L) | B: Current density (mA/cm$^2$) | C: Time (min.) | D: rpm | %COD removal | | SEEC(J/mg COD) | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Experimental | predicted | Experimental | predicted |
| 1 | 1300 | 1.109 | 30 | 40 | 67.45 | 66.20 | 0.451 | 0.458 |
| 2 | 1300 | 1.426 | 20 | 50 | 55.69 | 56.07 | 0.524 | 0.521 |
| 3 | 1600 | 1.109 | 20 | 60 | 74.54 | 76.67 | 0.235 | 0.241 |
| 4 | 1000 | 0.792 | 40 | 50 | 56.86 | 53.79 | 0.770 | 0.773 |
| 5 | 1600 | 0.792 | 40 | 60 | 44.89 | 45.92 | 0.513 | 0.506 |
| 6 | 1600 | 0.792 | 20 | 60 | 59.05 | 57.02 | 0.375 | 0.378 |
| 7 | 1600 | 1.109 | 20 | 40 | 63.77 | 65.71 | 0.357 | 0.353 |
| 8 | 1000 | 0.792 | 40 | 60 | 39.24 | 37.82 | 0.881 | 0.887 |

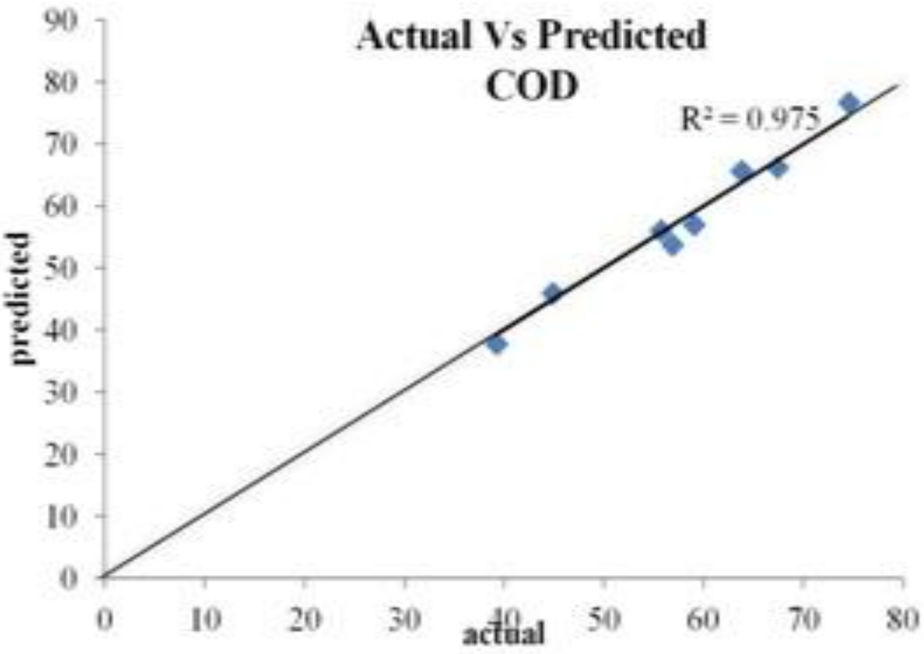


**Figure 9: Actual Vs. Predicted Plots for COD**

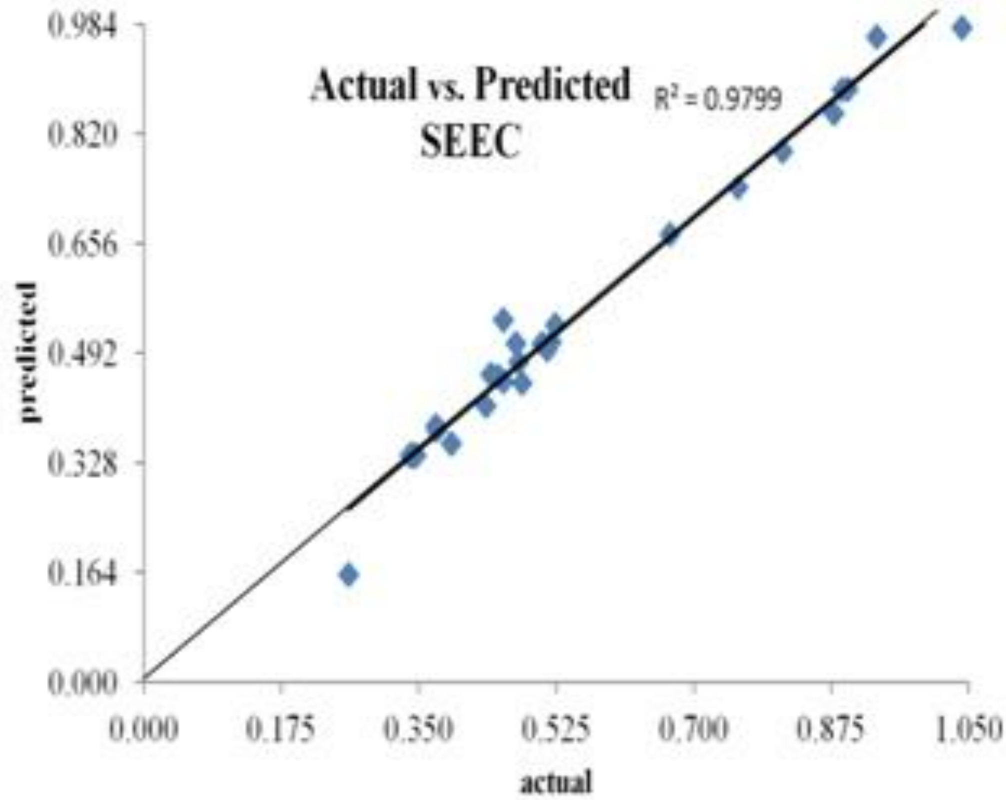


**Figure 10: Actual Vs. Predicted Plots for SEEC**

## 4.3 Validation of the model

ANOVA for the second-order equations fitted for the responses was observed as shown in Table 6. A p-value lower than 0.0001 signifies that the model is statistically significant and that the model terms are significant at 95% probability level (Sinha, et al., 2014). In the present case, $p < 0.0001$ suggested that regression model equations fitted well with the experimental results. Also, high $R^2$ values of 98.26% for COD removal and 98.29% for SEEC, expresses a high correlation value between the actual and predicted values. The ANOVA of the% COD removal by EC using rotating electrode showed F-value of 60.63 for the quadratic model implying that the model is significant. Similarly, F-values of 61.48 for SEEC suggesting that the quadratic model is relevant. "p-values" less than 0.0500 indicate model terms are importantnt. For COD, A,C,CD,$A^2$,$B^2$,$C^2$ and $D^2$ are significant model terms. For SEEC, A, B, C, D, AC, CD, $B^2$, $C^2$ and $D^2$ are significant model terms."Adeq Precision" determines the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 25.327 for COD and 29.971 for SEEC indicates an adequate signal. These models can be used to navigate the design space. According to normal probability plot of externally studentized residuals, the quadratic model well satisfied the ANOVA as shown in Fig.11 and Fig.12.

**Table 8: ANOVA for %COD removal and SEEC**

| | % COD removal | | | | SEEC | | | |
|---|---|---|---|---|---|---|---|---|
| Source | Sum of Squares | Df | Mean Square | F Value | Sum of Squares | df | Mean Square | F Value |
| Model | 7559.45 | 14 | 539.96 | 60.63 | 1.33 | 14 | 0.095 | 61.48 |
| Linear | 345.83 | 4 | 86.46 | 9.70 | 0.062 | 4 | 0.016 | 154.14 |
| Interaction | 199.82 | 6 | 33.30 | 3.74 | 8.414E-003 | 6 | 1.402E-003 | 13.51 |
| Quadratic | 1670.51 | 4 | 417.63 | 46.87 | 1.997E-003 | 4 | 4.992E-004 | 4.81 |
| Residual | 133.59 | 15 | 8.91 | | 0.023 | 15 | 1.545E-003 | |
| Lack of Fit | 131.13 | 10 | 13.11 | 26.66 | 0.023 | 10 | 2.314E-004 | 367.35 |
| Pure Error | 2.46 | 5 | 0.49 | | 3.150E-005 | 5 | 6.300E-007 | |
| Cor Total | 7693.04 | 29 | | | 1.35 | 29 | | |

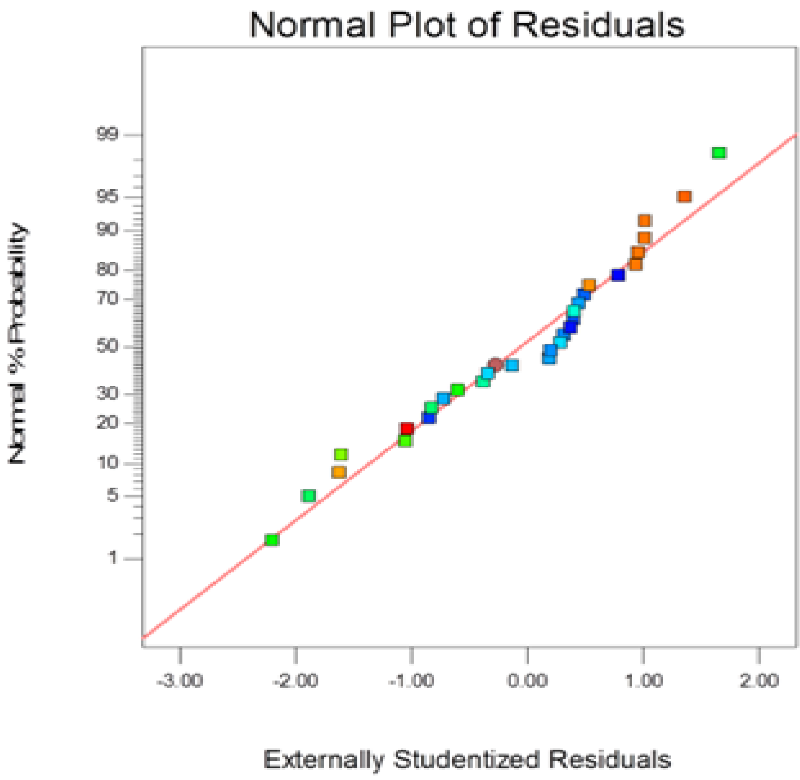


**Figure 11: Normal plot of residuals for COD**

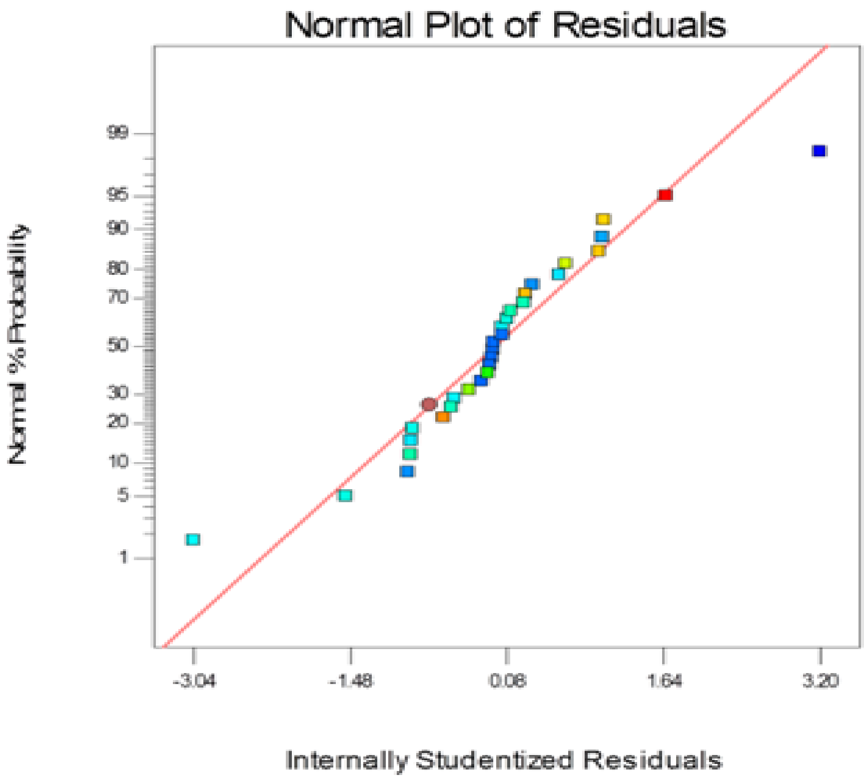


**Figure 12: Normal plot of residuals for SEEC**

## 4.4 Effect of various parameters

### 4.4.1 Effect of parameters on COD removal efficiency

#### 4.4.1.1. Current density

Current density is the most significant operational parameter. As shown in Fig.13 as current density is increased COD removal increases only upto a certain value after which it 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 availability of pollutant becomes a limiting factor. Also, excess energy may break the flocs and increase the TDS of the solution. 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 minimum COD concentration was obtained when the current density was increased from 0.792 to 1.109 $mA/cm^2$ and the retention time was increased from 20min to 30 min for initial COD of 1300 mg/L. According to the regression model Eq. (1), the constant of current density is less than the constant of retention time. Also, the retention time has adverse effect while current density has a positive effect. It can be concluded that retention time is more effective than current density on the % COD removal. Thus, when the retention time is less and the current density is more, there is more COD removal. This is because a sufficient number of pollutants are present initially which leads to an increase in the number of Al hydroxide flocs resulting in the increase in pollutant removal efficiency. But, when the retention time is more than the optimum value, COD removal decreases with increase in current density because of breaking of flocs due to excess energy. When both the retention time and current density are less flocs of aluminum hydroxide formed have small dimension and do not allow to an efficient adsorption of the destabilized milk droplets. These little particles of aluminum hydroxide will remain in suspension (Bensadok, et al., 2011).

#### 4.4.1.2. initial COD concentration

As shown in Fig.13 when the initial COD concentration is increased, % COD removal increases due to the existence of excess colloids for the adsorption in high COD concentrations. Similar results are obtained in the previous studies (Sengil & Ozacar, 2006).

#### 4.4.1.3. RPM and Retention time

When RPM is increased %COD removal increases up to an absolute value of RPM and then decreases as shown in Fig.13. The agitation helps to maintain uniform conditions in solution and avoids the formation of the 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 upto the certain agitation speed, there is an increase in the pollutant removal efficiency. This is because 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 (Khandekar & Saroha, 2013). According to the regression model Eq. (1), the constant of RPM is less than the constant of electrolysis time. Also RPM has a positive effect while retention time has adverse effect. Thus, when the RPM is low and retention time is high %COD removal decreases.

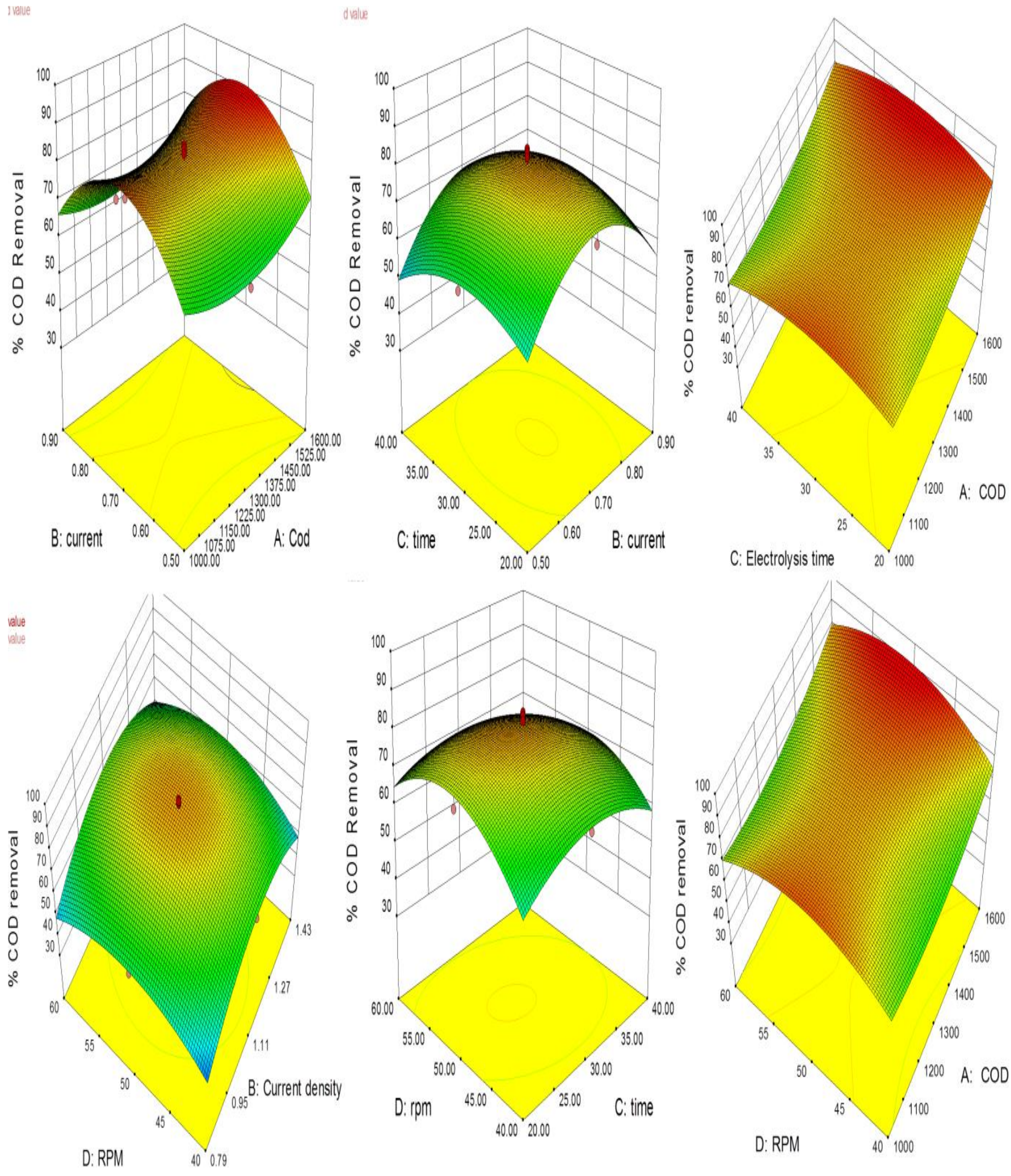


Figure 13: Effect of various parameters on COD removal efficiency

### 4.4.2. Effect of parameters on SEEC

SEEC is an important parameter from the point of cost consideration as it determines the feasibility of any process. Excess energy input can result in the disintegration of flocs which causes loss of COD removal efficiency, excessive dissolution of aluminum in water which has neuro-toxic effects, and loss of energy through heating of electrodes. The major operating cost is due to energy and electrode consumption in this process. From Fig.14, SEEC decreases with increase in initial COD as the availability of pollutant increases. Both, quadratic and linear effect of SEEC are significant for time and current density and RPM. SEEC decreases initially with an increase in current density, time and RPM as COD removal increases. Afterwards, it starts increasing as the COD removal starts decreasing. SEEC increases with time sharply after optimum time. Also, electrode consumption is reduced for lower values of SEEC.

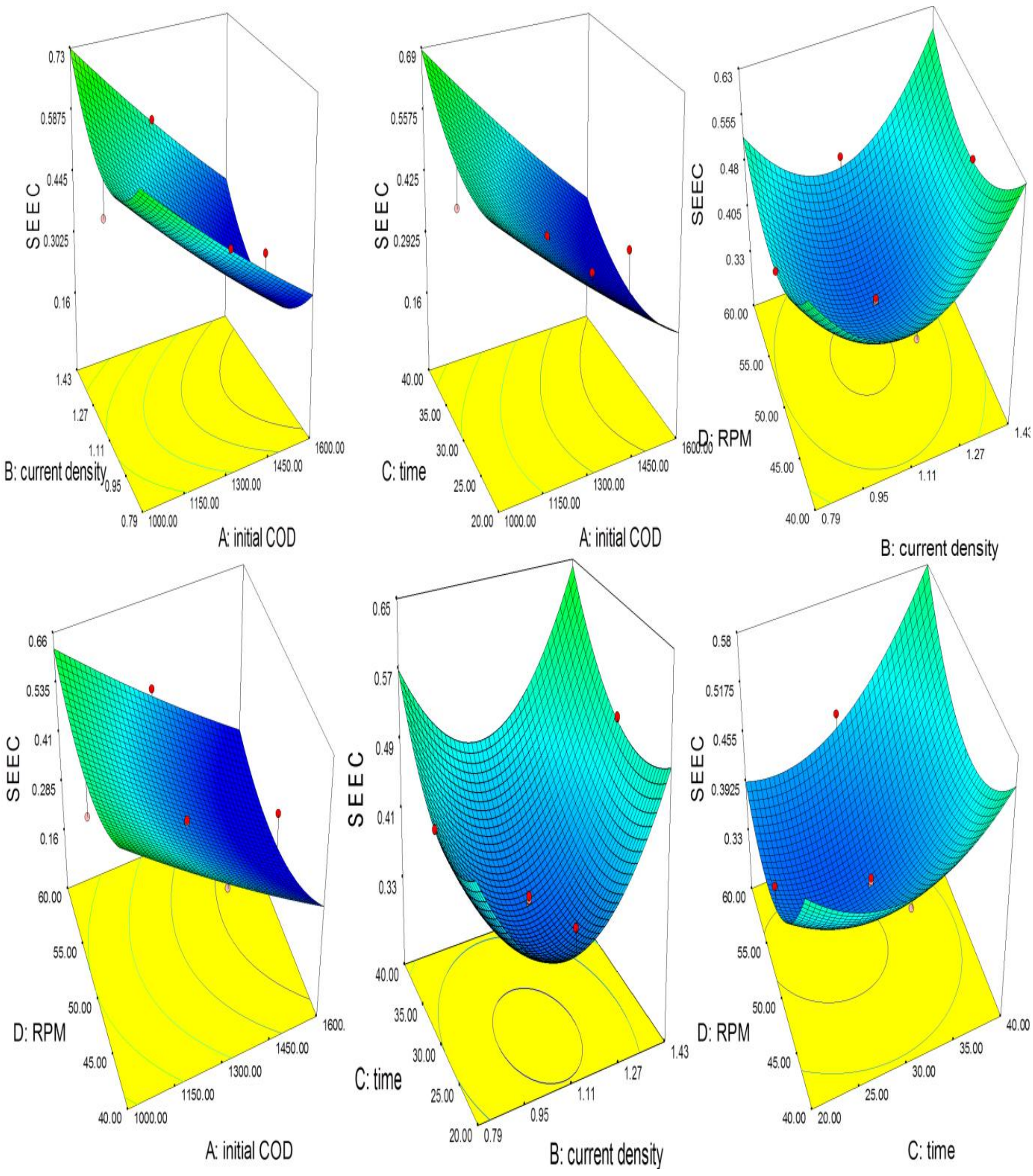


**Figure 14: Effect of various parameters on SEEC**

# 5. Comparison with other batch reactors

The results of the present study is compared here studies on various EC batch reactors using aluminum or iron electrodes. Table 7 shows the comparison between different reactors. For initial COD of 1600mg/L, optimization was targeted for maximum COD removal and minimum SEEC at pH 7 and conductivity 1500µS/cm. Under optimized conditions, COD removal of 91.27% at SEEC of 0.170 J/mg was obtained with desirability value of 1.00. Therefore, there is significant 92-100% reduction in energy consumption when compared with various other reactors. The energy consumption is less as compared to bipolar or hybrid reactors but is more than mono-polar reactor with static Al electrodes. This is because, in the present reactor, power is also required for rotating the anode which increases the energy consumption by 57.40%. However, COD removal is increased by 11% in the present reactor which balances the negative aspect of more energy consumption. Thus, it can be established that the cylindrical mono-polar batch reactor with the vertical rotating aluminum electrode is more efficient in COD removal at very low energy consumption.

**Table 9: Comparison between various reactors in terms of SEEC.**

| | Al electrode Rotating monopole batch reactor (Present reactor) | Al electrode monopolar batch reactor (Bensadok, et al., 2011) | Iron electrode bipolar parallel batch reactor (Kushwaha, et al., 2010) | Al electrode bipolar parallel batch reactor (Bazrafshan, et al., 2013) | hybrid Fe–Al electrodes mono - polar parallel batch reactor (Yavuz, et al., 2010) |
|---|---|---|---|---|---|
| initial COD | 1600mg/L | 7560mg/L | 3900 mg/L | 7855.25±703.05 mg/L | 1200-1900 |
| % COD removal | 91.27 | 80 | 70 | 98.84% | 79.2% |
| SEEC | 0.170J/mg | 0.108J/mg (0.03KWh/Kg) | 9.936J/mg (2.76KWh/Kg) | 44.06(J/mg) (0.095KWh/L) | 6.866J/mg (8.43 KWh/ $m^3$) |
| % reduction in SEEC in the present reactor | | -57.40% | 98.28% | 99.61% | 97.52% |

# 6.Conclusion

In this study, the treatment of dairy wastewater was performed using vertical rotating electrode cylindrical electro coagulation reactor. Four-factor (such as initial COD, Current density, Time and RPM) and three level (+1, 0, -1) 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 and specific electrical energy consumption (SEEC) as major responses for batch EC process. The mathematical expressions were developed to estimate COD removal efficiency and SEEC to navigate in design space. For this purpose, the effect of current density, initial COD, and RPM and retention time was evaluated on output parameters. According to the ANOVA results, the models presents high $R^2$ values of 98.26 and 98.29 for COD and SEEC respectively which indicates that the accuracy of the polynomial models was good. This suggests that central composite design was successfully employed in the present study for experimental design and analysis of results. Finally, the results were compared with the results of other batch reactors which established that the electro coagulation process using vertical rotating electrode is more efficient in COD removal also being energy efficient for the treatment of dairy wastewater.

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