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Comparison of electrocoagulation, peroxi-electrocoagulation and peroxi-coagulation processes for treatment of simulated purified terephthalic acid wastewater: Optimization, sludge and kinetic analysis

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Abstract−This study mainly focuses on a comparative study of electrocoagulation (EC), peroxi-electrocoagulation (PEC) and peroxi-coagulation (PC) processes for the treatment of aqueous solution containing major toxic components of purified terephthalic acid wastewater: benzoic acid (BA), terephthalic acid (TPA), para-toluic acid (p-TA) and phthalic acid (PA). The solution was initially treated by acid treatment method at various pH (2-4) and temperature (15-60 °C). The supernatant was further remediated by EC, PEC and PC methods independently. Process variables such as pH (4-12) and pH (1-5), current density (45.72-228.60 A/m^2), electrolyte concentration (0.04-0.08 mol/L), electrode gap (1-3 cm), H_2O_2 concentration (600-1,000 mg/L) and reaction time (20-100 min) during EC, PEC and PC treatment were effectively optimized through central composite design under Design Expert software. Maximum COD removal of 60.76%, 73.91%, 66.68% with energy consumption (kWh/kg COD removed) of 95.81, 49.58, 69.26 was obtained by EC, PEC and PC treatments, respectively, at optimum conditions. Electrochemical methods were compared by removal capacities, consumption of energy, operating cost, degradation kinetics and sludge characteristics. PEC treatment was found most effective among EC, PEC and PC processes due to its highest removal capacity and lowest energy consumption features.

Keywords: Purified Terephthalic Acid, Electrochemical Treatment, Response Surface Methodology, Optimization, Kinetic Study

INTRODUCTION

Many organic chemical industries use the intermediates and raw materials generated from processing of crude oil and natural gas. Para-xylene, which is an essential raw material for these industries, is also used for the production of PTA. Various waste steams (liquid and gaseous) turn out during PTA production. Industrial PTA wastewater contains several hazardous aromatic compounds like phthalic acid, benzoic acid, terephthalic acid, and para-toluic acid as its major components [1-3]. These aromatic compounds are responsible for liver, bladder and kidney damage as well as also showing carcinogenic effects [4-6]. Their phthalate forms are more hazardous, particularly due to the adverse impact on reproduction capacity of humans [7]. US EPA has mentioned phthalate, its esters and its degradation products as the priority pollutants based on their toxicity. Due to strict environmental regulations, highly efficient and eco-friendly techniques are required to treat these toxic compounds from wastewater before its use or surface discharge. In recent years several bioremediation and physico-chemical processes have been utilized for PTA wastewater treatment. Some of these techniques have operational issues like partial degradation of pollutants, toxic intermediates formation, high sludge formation and generation of secondary phases which affect the economy of the process. Among these wastewater remediation techniques, electrochemical methods have aroused a great deal of interest due to eco-friendly, versatility, automation, high efficiency and cost effectiveness features [8-14]. Recently, more emphasis has been given to the advancement of efficient electrochemical processes for the treatment of aromatic compounds present in petrochemical wastewater. Electrocoagulation (EC) is one of the most famous electrochemical techniques for wastewater treatment. During this treatment, coagulant species form through the dissolution of a sacrificial anode in electrochemical cell. These generated coagulants interact with pollutants present in the solution resulting, solubility reduction or entrapping into growing flocs of precipitates, eventually promoting removal of pollutants by sedimentation and flotation/filtration stage [15,16]. Chemical reactions take place during EC treatment with Fe anode as shown below [17].

At anode:

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{1}$$

In acidic conditions

$$4Fe^{2+} + O_2 + H_2O \rightarrow 4Fe^{3+} + 4OH^- \tag{2}$$

In alkaline conditions

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \tag{3}$$

At cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{4}$$

Electro-Fenton (EF) method is the combination of electrochemical as well as Fenton methods. This method was basically developed for the improvement in oxidation of organic pollutants. Oxidation

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of organic pollutants present in aqueous solution by electrochemical as well as Fenton method has been recognized to be an effective and promising treatment technology among other advance oxidation processes. EF process has different configuration. In type 1, electro-generation of ferrous ions and hydrogen peroxide (H_2O_2) takes place simultaneously by iron anode and oxygen sparging cathode [18]. This is also recognized as peroxi-coagulation (PC) process [19,20]. During PC treatment, H_2O_2 is produced at cathode surface as given below.

$$O_2+2H^++2e^-\rightarrow H_2O_2 \tag{5}$$

In type 2, H_2O_2 is added externally and sacrificial iron anode is treated as Fe^{2+} source [21,22], and is also known as peroxi-electrocoagulation (PEC) process [23]. In type 3, H_2O_2 is produced through oxygen sparging cathode while ferrous ion is externally added [24]. In type 4, Fenton's reagent is used to generate hydroxyl radicals (OH•) and Fe^{2+} ion is regenerated through the reduction of Fe^{3+} ions at cathode [25,26]. During PC and PEC treatments, hydrogen peroxide (H_2O_2) is catalyzed through ferrous ions (Fe^{2+}) to generate hydroxyl radicals (OH•) in acidic medium which favors degradation of organic pollutants. It can be seen by the following reactions [27,28].

$$Fe^{2+}+H_2O_2\rightarrow Fe^{3+}+OH^-+OH^{\bullet} \tag{6}$$

$$RH+OH^{\bullet}\rightarrow R^{\bullet}+H_2O \tag{7}$$

$$R^{\bullet}+Fe^{3}\rightarrow Fe^{2+}+R^{+} \tag{8}$$

$$Fe^{2+}+OH^{\bullet}\rightarrow OH^-+Fe^{3+} \tag{9}$$

where RH is organic pollutant.

Previous studies [12,32,34,37] worked on electrocoagulation and electro-Fenton treatments of single components of PTA wastewater separately and obtained remarkable removal efficiencies. But, it is difficult to predict the overall COD removal efficiency of PTA wastewater by single component treatment. At the same time, removal efficiencies of acids (BA, p-TA, TPA and PA) present in PTA wastewater also differ from single to multi component solution. Actually, the ultimate aim is to treat PTA wastewater which comprises highly toxic aromatic compounds, i.e., BA, p-TA, TPA, PA, etc. together. The contribution of these acids in the overall COD of PTA wastewater is more than 75%. Therefore, we prepared multi component solution of these acids and observed their simultaneous degradation in the aqueous medium by three different electrochemical techniques (EC, PEC and PC). The present work mainly emphasizes the comparative study of EC, PEC and PC treatments of major components (BA, p-TA, TPA and PA) of PTA wastewater from aqueous medium. Initially, acid treatment was conducted. Acid precipitation method is an economical and effective process to remove these aromatics from aqueous solution up to an extent and does not require much electricity. The supernatant obtained after acid precipitation was further subjected to electrochemical treatment. Deeper investigations of previous studies and to the best of the knowledge of authors, there are no studies reported on comparative study of EC, PEC and PC treatments of synthetic PTA wastewater using graphite cathode and iron anode. The aim of this study was to maximize removals from aqueous solution and simultaneously minimize the electrical energy consumption ($EE_{consumption}$).

MATERIALS AND METHODS

1. Materials

All chemicals and reagents were of analytical grade. TPA was provided by Himedia Lab Pvt. Ltd. Mumbai (India). PA was purchased from SRL Pvt. Ltd. Mumbai, India. BA, p-TA, sodium chloride and sodium sulfate were purchased from Loba Chemie Pvt. Ltd. Mumbai, India. Sulfuric acid, sodium hydroxide, hydrogen peroxide (30% w/v), methanol, mercury sulfate, isopropyl alcohol, silver sulfate, acetic acid and potassium dichromate were supplied by RCFL, New Delhi, India.

2. Wastewater Preparation

400 mg/L of each BA, p-TA, TPA and PA was taken according to the previous literature [29-34]. Aqueous solution was prepared with distilled water. To avoid biodegradation well as microorganism's growth, all the samples were preserved at 4 °C. The initial COD of aqueous solution was estimated 2,581 mg/L.

Percent removal and $EE_{consumption}$ were determined by Eq. (10) and Eq. (11), respectively.

$$\%\ \text{Removal}=\frac{C_i-C_f}{C_i}\times 100 \tag{10}$$

where C_i and C_f are initial and final concentration, respectively

$$EE_{consumption}\ (\text{kWh/kgCOD}_{removed}) = \frac{V\times I\times t\times 100}{(\%\ \text{Removal of COD})C_{CDOi}\times V_w}\times 1000 \tag{11}$$

where V, I, t, C_{CODi} and V_w are voltage (volt), current (amp), time (hour), initial COD value (mg/L) and wastewater volume (liter), respectively.

3. Analytical Techniques

COD of aqueous solution was determined by proposed standard method [35] using COD analyzer (Aqualytic, Germany). HPLC (Waters, USA) was used to measure the concentration of BA, p-TA, TPA and PA at wavelength of 240 nm [36-39]. For HPLC analysis, solution for mobile phase was prepared with 2% acetic acid, 7% isopropyl alcohol and 91% water was used. The flow rate was maintained at 1.2 mL/min. Entire HPLC analysis was operated under isocratic mode with C18 column [40-42]. Sludge generated after electrochemical treatments at optimum conditions was analyzed through FE-SEM and DTA/TGA/DTG techniques. FE-SEM analysis of sludge was carried out using FEI, Quanta 200 FEG with resolution: <2 nm and magnification range: 12X - 1000kX, gun type: FEG with Schottky emitter. Initially, samples were mounted on a metal's stub by using adhesive, then gold coating was done on it, and after that analysis was performed. DTA/TGA/DTG analysis involved using an SII 6300 EXSTAR TG/DTA analyzer. During analysis, air flushing rate was maintained at 200 mL/min in the temperature range of 35-1,200 °C with 10 K/min heating rate.

4. Experimental Procedure

The acid treatment was carried out by adding H_2SO_4 (1 N) to the solution at various pH and temperature. Acid treated solution settled for some time. Filtered solution was re-treated by EC, PEC and PC processes independently. Entire electrochemical experi-

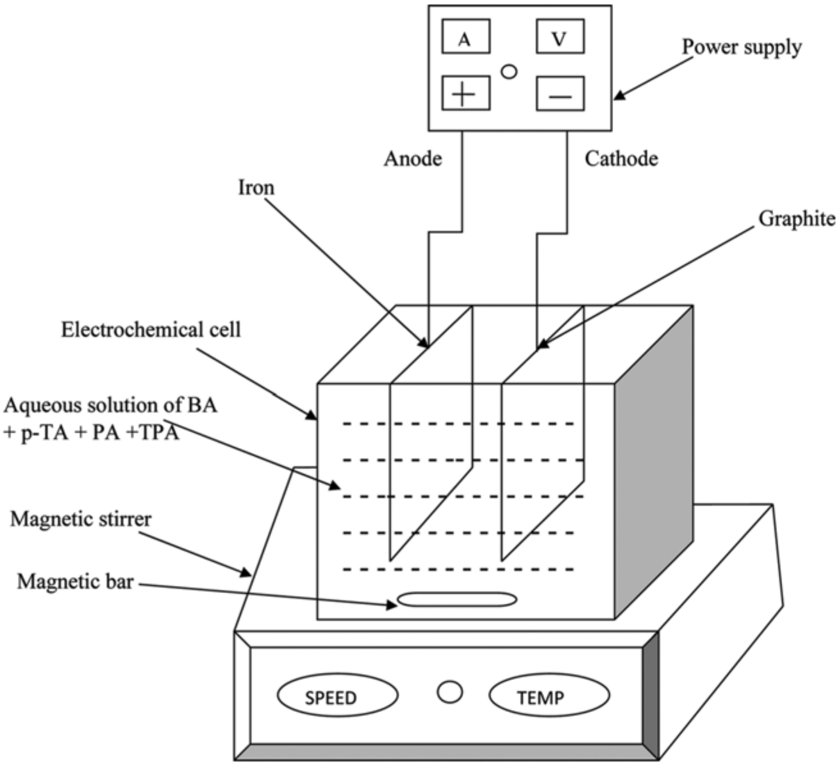


Fig. 1. Schematic diagram of experimental set up for electrochemical treatment.

ments were conducted in a rectangular batch cell of Plexiglas at atmospheric pressure and room temperature. Iron and graphite were used as anode and cathode, respectively (having effective electrode area 131.2 cm^2) during EC, PEC and PC treatments. Fig. 1. shows a schematic diagram of the EC, PEC and PC setup. The electrode distance was fixed at 2 cm during EC and PEC treatments. In PC treatment, a fish aerator was used for the continuous air bubbling to saturate the solution with oxygen. Some random experimental runs were conducted to identify the suitable range of process variables during EC, PEC and PC treatments.

5. Experimental Design

Response surface methodology (RSM) is one of the finest statistical tools used for optimization and designs. In the present work, 4-factor, 5-level full factorial central composite design (CCD) under RSM was applied to optimize different process variables: pH (4-12), current density (45.72-228.60 A/m^2), electrolyte (0.04-0.08 mol/L) and time (20-100 min) during EC treatment, pH (1-5), current density (45.72-228.60 A/m^2), H_2O_2 (600-1,000 mg/L) and time (20-100 min) during PEC treatment and pH (1-5), current density (45.72-228.60 A/m^2), electrode distance (1-3 cm) and time (20-100 min) during PC treatment, as shown in Table 1. Percent removal of COD and $EE_{consumption}$ was taken as two responses of the system. Entire experiments were conducted based on the process conditions given by CCD as shown in Table 2. CCD and actual results for EC, PEC and PC treatments are given in Table 2 and Table 3.

Table 1. Operating parameters and their levels obtained from the statistical software for EC, PEC and PC processes

Central composite design characteristics							
Levels	Parameters (Range)						
	X_1 pH		X_2	X_3			X_4
	$(X_1)_{EC}$ (4→12)	$(X_1)_{PC\ \&\ PEC}$ (1→5)	CD (A/m^2) (45.72→228.60)	$(X_3)_{EC}$ Na_2SO_4 (mol/L) (0.04→0.08)	$(X_3)_{PEC}$ H_2O_2 (mg/L) (600→1000)	$(X_3)_{PC}$ Electrode gap (cm) (1→3)	Time (min) (20→100)
−2(−α)	4	1	45.72	0.04	600	1	20
−1	6	2	91.44	0.05	700	1.5	40
0	8	3	137.16	0.06	800	2	60
+1	10	4	182.88	0.07	900	2.5	80
+2(α)	12	5	228.60	0.08	1000	3	100

Table 2. Actual and CCD predicted COD removal and $EE_{consumption}$ for EC, PEC and PC processes

Run no.	Independent variables						
	X_1		X_2	X_3			X_4
	(X_1) EC	(X_1) PEC & PC		(X_3) EC	(X_3) PEC	(X_3) PC	
1	6	2	91.44	0.05	700	1.5	80
2	10	4	91.44	0.05	700	1.5	40
3	6	2	182.88	0.07	900	2.5	40
4	10	4	182.88	0.08	1000	3	80
5	6	2	91.44	0.07	900	2.5	40
6	10	4	91.44	0.07	900	2.5	80
7	6	2	182.88	0.07	900	1	80
8	10	4	182.88	0.07	900	2.5	40
9	8	3	137.16	0.06	800	2	60
10	8	3	137.16	0.07	900	2.5	60
11	6	2	91.44	0.05	700	1.5	40
12	12	5	91.44	0.05	700	1.5	80
13	6	2	182.88	0.05	700	1.5	80
14	10	4	182.88	0.07	900	2.5	20
15	6	2	91.44	0.07	900	2.5	100
16	10	4	45.72	0.07	900	2.5	40
17	6	2	182.88	0.07	900	2.5	60
18	10	4	182.88	0.07	900	2.5	80
19	8	3	137.16	0.05	700	1.5	60
20	8	3	137.16	0.06	800	2	80
21	4	1	137.16	0.06	800	2	60
22	10	4	137.16	0.06	800	2	60
23	8	3	91.44	0.06	800	2	60
24	8	3	182.88	0.06	800	2	60
25	8	3	137.16	0.05	700	1	40
26	8	3	228.6	0.06	800	2	60
27	8	3	152.44	0.06	800	2	40
28	8	3	91.44	0.06	800	2	80
29	8	3	91.44	0.06	800	2	40
30	8	3	182.88	0.05	700	1.5	60

RESULTS AND DISCUSSION

1. Influence of Operating Variables on Removal Efficiencies

1-1. Influence of pH at Various Temperatures During Acid Precipitation Treatment

In the aqueous solution BA, p-TA, TPA and PA remains in ionized state as pKa value are 4.2, 4.36 3.51 and 2.89, respectively. By reduction of pH, acids present in the solution become deionized and hydrogen ion concentration increases, which favors conversion of dissociated weak acid ions to into undissociated molecules. Because of the common ion effect, the ionic product values of these acids cross their solubility product values [43,44], resulting in precipitation of acids in aqueous solution. After precipitation, settling was allowed for almost 4 hours and then supernatant was filtered. Influence of pH (2-4) on COD removal at various temperatures (15-60 °C) was observed in acid treatment process and

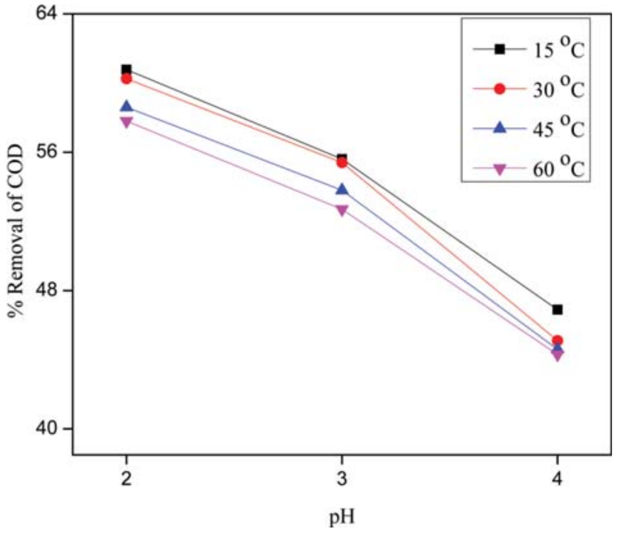


Fig. 2. Effect of pH on removal of COD at different temperatures during acid precipitation treatment.

60.78% COD removal obtained at optimum conditions (pH -2 and temperature- 15 °C) as displayed in Fig. 2. At this optimum condition, removal of BA, p-TA, TPA and PA was 41.6%, 44.8%, 80.9% and 19.8%, respectively. Concentrations of BA- 233.6 mg/L, p-TA- 220.8 mg/L, TPA- 76.4 mg/L, PA- 320.8 mg/L and COD- 1,012.2 mg/L were achieved after acid precipitation treatment. The supernatant was further treated by electrochemical methods.

1-2. Influence of pH During EC, PEC and PC Treatments

The pH is an essential and effective operating parameter to influence the performance of electrochemical processes. The solution was fixed to desired pH, 4-12, during EC and 1-5 during PC and PEC treatments to study the effect of initial pH. Influence of pH on COD removal in EC, PEC and PC treatment is indicated in Fig. 3(a), Fig. 4(a) and Fig. 5(a), respectively. In acidic medium, Fe^{2+} ions generated at anode surface bind anionic pollutants in the aqueous solution. Further charge neutralization and solubility reduction take place [45]. With increase in pH, concentration of metal hydroxides ($Fe(OH)_3$) increases, which favors enhancement of pollutant adsorption rate on metal hydroxide precipitates [42,63-65], resulting in higher removal. At very high pH, formation of $Fe(OH)_4$ flocs takes place which are highly soluble and have poor binding nature with pollutant ions, resulting in lower removal. During PC and PEC treatments, removals are higher at low pH due to greater amount of metal hydroxide flocs and $OH^{\bullet}$ radicals formation through H_2O_2 as shown in Eq. (6) [47,48]. Under high acidic condition, formation of oxonium ion ($H_3O_2^+$) occurs instead of hydroxyl radicals, and under high basic condition decomposition of H_2O_2 ($H_2O_2 \rightarrow H_2O + \frac{1}{2} O_2$) occurs, resulting in lower removal in both the cases [28,49].

1-3. Influence of Current Density (CD) and Reaction Time (T) During EC, PEC and PC Treatments

CD and T, which are key operational parameters during electrochemical treatment, strongly influence the dominant mode of removal. Anodic dissolution of Fe^{2+} ions increases with CD, accelerating formation of Fe^{2+} and $Fe(OH)_{n(s)}$ during treatment [50,51]. Greater amounts of Fe^{2+} ions could increase the reaction rate and

Table 3. Actual and CCD predicted COD removal and EEconsumption for EC, PEC and PC processes

Run no.	% Removal of COD: (R_1)						$EE_{consumption}$ (kWh/kg $COD_{removed}$): (R_2)					
	EC		PEC		PC		EC		PEC		PC	
	Actual (Exp.)	CCD Pre.	Actual (Exp.)	CCD Pre.	Actual (Exp.).	CCD Pre.	Actual (Exp.)	CCD Pre.	Actual (Exp.)	CCD Pre.	Actual (Exp.)	CCD Pre.
1	30.58	29.52	37.34	38.62	34.96	36.33	116.71	120.90	95.58	92.41	107.72	103.29
2	28.25	33.21	36.55	41.57	35.01	40.26	63.17	53.73	48.82	42.93	50.79	43.25
3	39.51	35.18	48.11	47.53	45.89	48.75	116.34	130.66	95.54	96.71	98.61	92.34
4	41.66	39.94	49.56	48.12	48.12	46.27	220.67	230.17	185.49	191.04	193.5	201.34
5	28.98	32.65	38.11	36.99	36.02	38.17	61.58	54.66	46.83	48.24	49.2	45.95
6	45.01	42.21	54.06	58.16	51.21	59.65	79.29	84.55	66.02	61.37	71.64	60.52
7	58.56	62.04	66.59	65.36	64.06	60.23	156.98	148.18	138.05	140.65	143.87	153.25
8	47.31	49.86	56.02	55.34	52.79	51.68	57.15	54.23	48.27	48.86	49.09	50.13
9	57.26	56.66	66.41	65.5	63.28	66.63	79.33	80.17	68.40	69.35	70.62	66.63
10	57.26	54.82	64.91	64.84	63.12	63.47	79.33	82.86	69.98	70.06	70.81	70.25
11	23.12	31.76	30.25	29.46	27.47	31.52	77.19	56.19	58.99	60.57	66.37	56.94
12	25.23	27.94	32.69	29.13	30.22	28.5	141.46	127.74	109.18	122.52	125.55	133.35
13	47.65	50.46	58.29	58.51	55.87	58.59	192.93	182.18	157.71	157.12	165.83	157.72
14	25.54	29.61	33.61	36.91	32.14	35.72	89.99	77.62	68.38	62.27	68.69	61.07
15	41.79	44.47	49.58	50.11	48.26	46.15	106.76	100.32	89.98	89.03	96.98	101.54
16	30.62	32.75	41.26	38.61	39.58	38.16	10.60	9.91	7.86	8.40	7.35	7.71
17	41.31	37.39	51.13	59.03	48.97	53.31	166.90	184.40	134.85	116.80	141.04	128.93
18	40.16	32.43	48.74	54.69	47.29	50.67	228.91	283.47	188.61	168.09	197	183.32
19	58.62	56.15	65.89	63.36	64.56	63.98	77.49	80.90	68.94	71.69	69.1	69.64
20	57.39	54.44	68.12	65.71	66.1	61.99	105.53	111.25	88.91	92.17	91.79	98.13
21	26.68	27.74	34.52	35.12	34.2	32.19	170.26	163.75	131.59	129.34	135.74	144.45
22	53.1	46.46	61.54	60.2	59.26	58.77	85.54	97.77	73.81	75.46	75.82	76.36
23	49.53	47.55	57.78	57.03	56.34	57.26	54.04	56.29	46.33	46.94	46.94	45.95
24	58.08	57.41	70.26	67.27	68.95	64.75	118.71	120.10	98.13	102.49	98.44	105.07
25	51.28	50.02	60.06	58.55	58.16	57.14	59.05	60.54	50.42	51.72	49.58	50.44
26	56.16	54.99	65.67	62.4	64.2	59.61	155.99	159.31	133.40	140.39	135.22	145.95
27	55.05	55.94	63.26	58.55	61.24	55.98	55.01	54.13	47.87	51.72	46.79	51.61
28	49.26	48.42	57.22	58.27	56.16	55.4	72.45	73.71	62.37	61.25	64.8	65.63
29	40.54	39.38	48.61	49.09	47.1	45.94	44.02	45.32	36.71	36.35	36.22	37.15
30	45.69	52.46	54.61	66.71	52.51	64.58	150.90	131.43	126.25	103.35	131.13	100.41

generation of hydroxyl radicals, resulting in high removal efficiencies. Here, we studied CD (45.72-228.60 A/m^2) and T (20-100 minutes) during electrolysis. Effects of CD and T on removal of COD during EC, PEC and PC treatments are indicated in Figs. 3(a), (b), 4(a), (b) and 5(a), (b), respectively. It can be seen that initially the removal efficiencies increase with current density and time and reach maximum level at optimum value of CD and T. Beyond optimum values (for EC: CD- 140.11 A/m^2 and T- 66.51 min, for PC: CD-131.54 A/m^2 and T- 60.18 min and for PEC: CD-116.65 A/m^2 and T-56.12 min), removal starts to decrease due to generating less amount of charges and $^{\bullet}OH$ radicals as well as consumption of charges through side reactions. It was clearly observed from the obtained results that the high CD and T may not be the most efficient mode for treatment.

1-4. Influence of Electrolyte Concentration, Electrode Gap and H_2O_2 Concentration During EC, PEC and PC Treatments

Influence of supporting electrolyte concentration, electrode gap and H_2O_2 concentration on COD removal was studied during EC, PEC and PC treatments, respectively. Supporting electrolyte increases conductivity and electron transfer rate in the aqueous solution. Various concentrations of sodium sulfate (0.04-0.08 mol/L) were used during EC treatment, and 0.06 mol/L was obtained as an optimum value, as displayed in Fig. 3(b). The optimum amount of electrolyte obtained during EC treatment was further used in PC and PEC treatments. It is important to keep the electrodes at optimum gap during electrolysis. Influence of electrode distance (1-3) was investigated as given in Fig. 5(b) and got an optimal value: 2 cm. The same optimum distance was fixed during EC and PEC treatments. Lower electrode gap increases solid and fluid transfer, favors accumulation of bubbles and solid particles between electrodes, resulting in an increase in electrical resistance [52]. Short electrode gap may also be the reason for short circuit because of high current density [53]. Removal starts to increase with electrode gap up to an optimal value. This is because slower move-

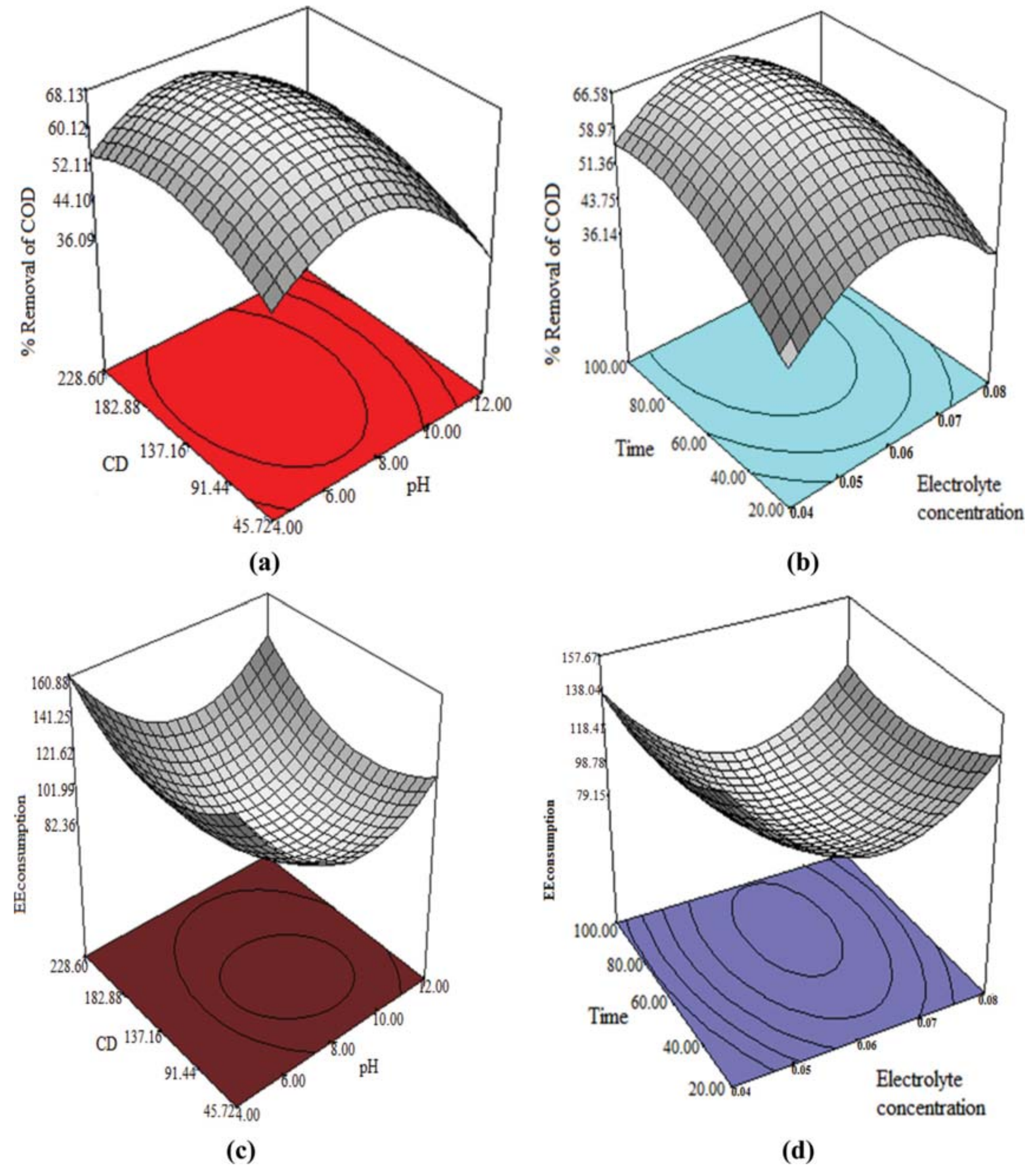


Fig. 3. (a)-(d) Effect of pH, CD, electrolyte concentration and time on percent removal of COD and EEconsumption during EC treatment.

ment of produced ions favors high opportunity to produce flocs. Removal starts to decrease beyond the optimum distance, due to weaker interaction between flocs and pollutants [54]. During PEC treatment, different amount of H_2O_2 (600-1,000 mg/L) was added to the solution prior to the power supply as shown in Fig. 4(b). It is very important to obtain an optimum concentration of H_2O_2 for maximum removal. Fe^{2+} ions catalyze hydroxyl radicals formation at low pH as shown in Eq. (6). It was observed that, beyond optimum H_2O_2 concentration (826.62 mg/L), removal efficiency decreased. This is due to the excess concentration of H_2O_2 which leads the scavenging effect on hydroxyl radicals and producing hydroperoxyl radicals ($HO_2^{\bullet}$) having lower oxidizing power than $HO^{\bullet}$ radicals [55-57].

$$H_2O_2+HO^{\bullet}\rightarrow HO_2^{\bullet}+H_2O \tag{12}$$

2. Influence of pH, CD, Electrolyte Concentration, H_2O_2 Concentration and Time on $EE_{consumption}$ During EC, PEC and PC Treatments

CD and time strongly affect the $EE_{consumption}$ during electrochemical treatment. It can also be seen in Eq. (11) that energy consumption depends on COD removal. Initially, due to low COD removal energy consumption was high at a particular CD and time. It was observed that the $EE_{consumption}$ was minimum at optimum operating conditions: at pH- 8.3, CD- 140.11 A/m², electrolyte- 0.06 mol/L, time- 66.51 min during EC treatment, at pH- 3.2, CD- 116.65 A/m², H_2O_2 -826.62 mg/L, time- 56.12 min during PEC

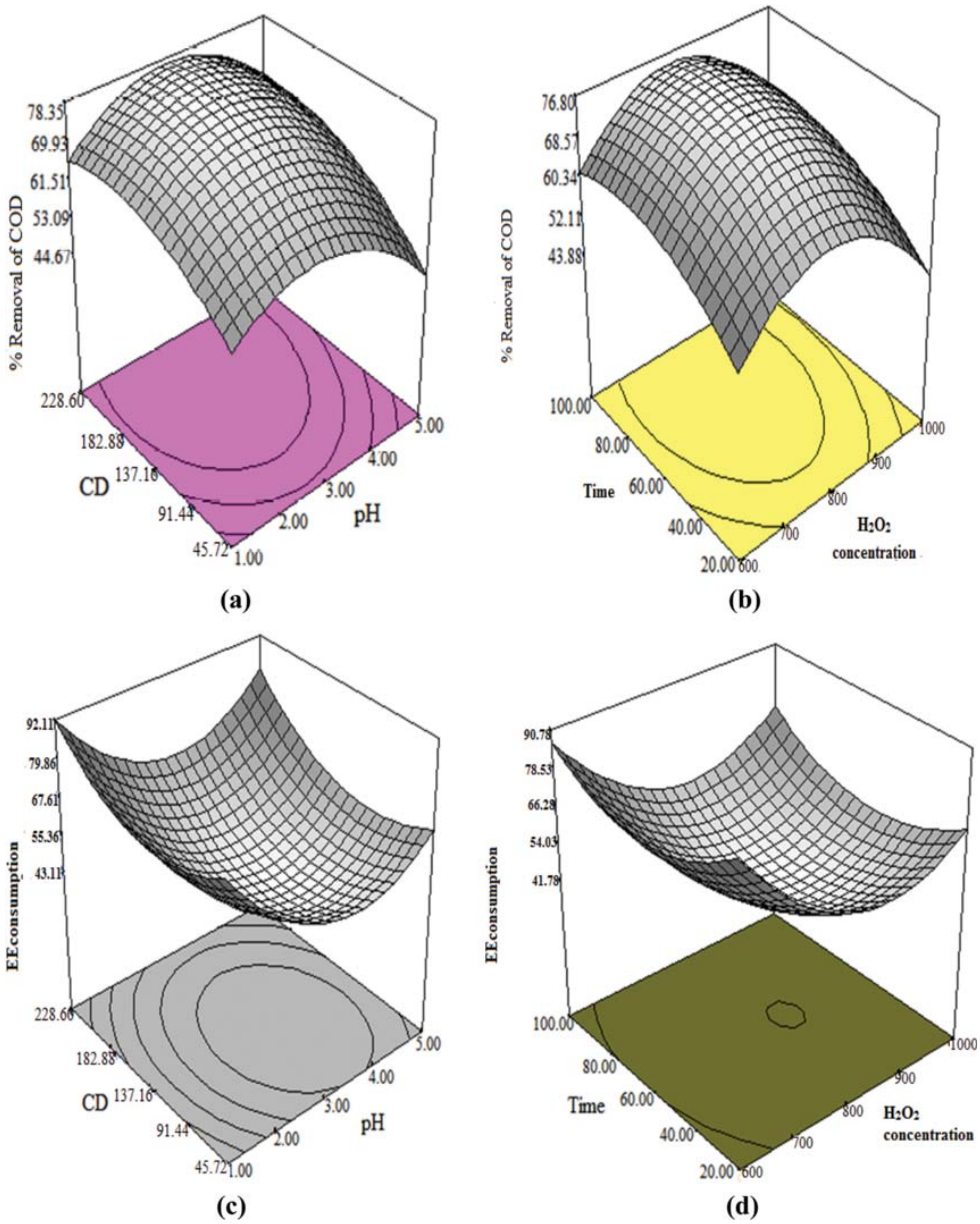


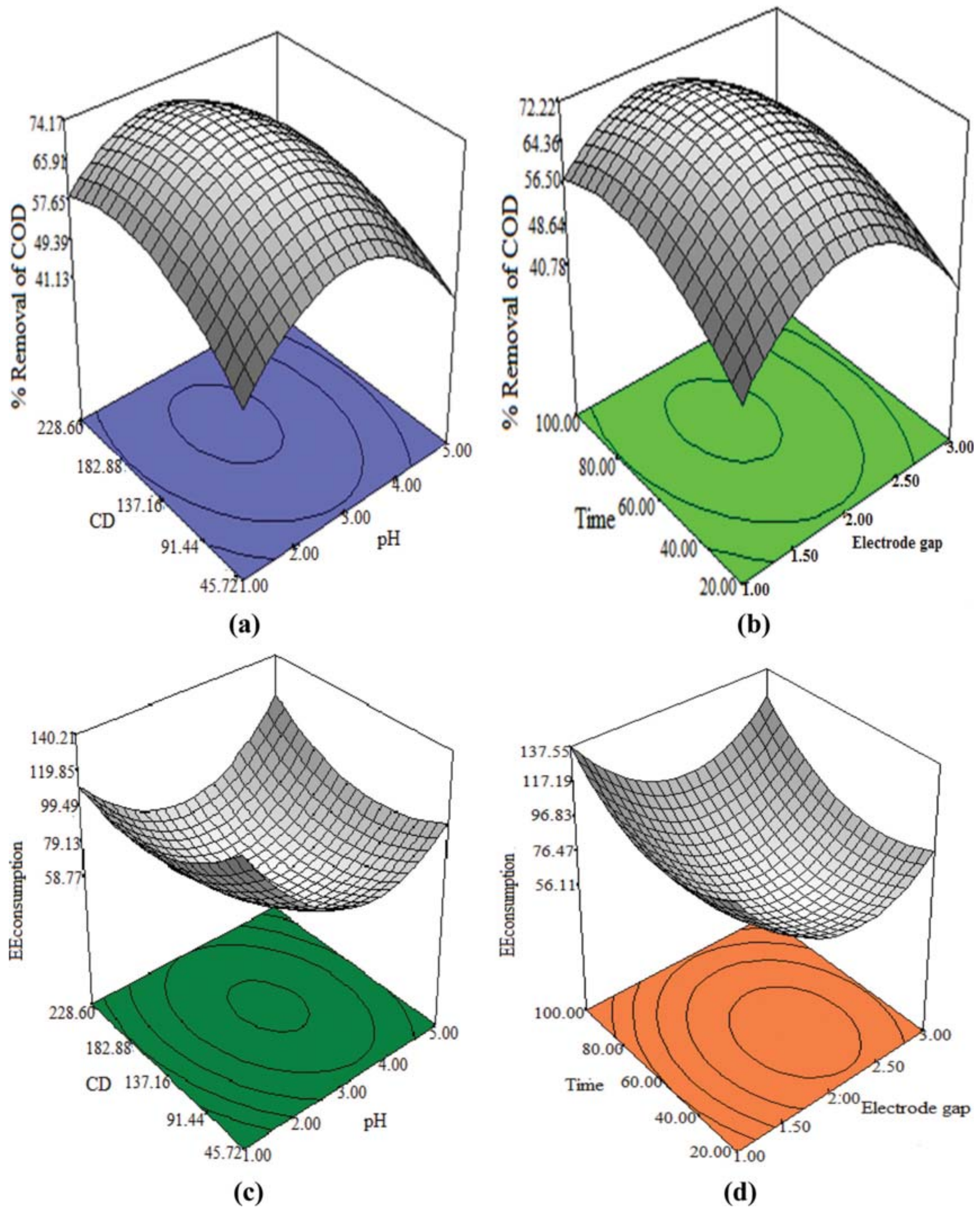
Fig. 4. (a)-(d) Effect of pH, CD, H_2O_2 concentration and time on percent removal of COD and EEconsumption during PEC treatment.

treatment and at pH- 3, CD- 131.54 A/m^2, electrode gap- 2 cm, time- 60.18 min during PC treatment. This is because consumption of energy was minimum due to optimum CD and time with high COD removal. Parameters like pH, electrolyte concentration, electrode distance and H_2O_2 concentration have direct impacts on COD removal, which influences $EE_{consumption}$. Energy consumption was found minimum at optimum pH, electrolyte concentration, electrode distance and H_2O_2 concentration because of high COD removal during EC, PEC and PC treatments as can be seen in Figs. 3(c), (d), 4(c), (d) and 5(c), (d), respectively. Increment in $EE_{consumption}$ was found beyond the optimum conditions due to high CD, longer time and low COD removal.

3. RSM Analysis

3-1. Optimization

To study the combined effect of operating parameters--pH, CD, time, electrolyte amount, electrode distance and H_2O_2 concentration--several experiments were conducted using statistically designed experiments. Statistical design of experiment, as is known, is used to consider the interaction among the variables for optimizing the parameters for multivariable systems and develop statistically sig-



(a) (b)

(c) (d)

Fig. 5. (a)-(d) Effect of pH, CD, electrode gap and time on percent removal of COD and EEconsumption during PC treatment.

nificant models by performing minimum number of experiments. The optimum operating conditions were obtained through CCD, based on experimental runs by taking percent removal of COD (maximum) and electrical energy consumption (minimum) within the ranges of parameters. Entire electrochemical treatments were optimized to get maximal removal of COD and minimal $EE_{consumption}$. Table 2 and Table 3 represent operating conditions with experimental results during EC, PEC and PC treatments. CCD-predicted conditions were checked by conducting experimental runs and optimized values were obtained as given in Table 4. Maximum removal of BA- 66.16%, 70.12%, 75.24%; p-TA- 59.15%, 63.28%, 68.11%; TPA- 64.07%, 68.22%, 73.49%; PA- 65.14%, 69.36%, 74.25% and COD- 60.76%, 66.68%, 73.91% was found at optimum conditions (as mentioned in Table 3) during EC, PC and PEC treatments, respectively. From Table 4, the difference between CCD predicted and experimental results was very little, indicating adequacy of the model.

3-2. ANOVA Analysis

3-2-1. Coefficient of Regression (R^2), Adjusted R^2, Predicted R^2, Coefficient of Variation (CV) Adequacy of Precision, PRESS, P-

Table 4. CCD predicted optimum operating conditions and their experimental and CCD results during EC, PEC and PC processes

	pH	CD (A/m^2)	Na_2SO_4 (mol/L)	H_2O_2 (mg/L)	Electrode gap (cm)	Time (min)	% Removal of COD		$EE_{consumption}$ (kWh/kg $COD_{removed}$)	
							CCD (Pre.)	Test Run	CCD (Pre.)	Test Run
EC	8.3	140.11	0.06	-	-	66.51	60.76	59.16	95.81	102.52
PEC	3.2	116.65	-	826.62	-	56.12	73.91	71.82	49.58	52.23
PC	3	131.54	-	-	2	60.18	66.68	64.14	69.26	73.65

Table 5. Quadratic model ANOVA analysis for COD removal and EEconsumption during EC, PEC and PC processes

Variable	COD			EEconsumption		
	EC	PEC	PC	EC	PEC	PC
Standard deviation	5.87	5.64	5.77	6.30	6.01	5.98
Mean	49.88	52.64	52.06	100.5	87.06	88.64
Coefficient of variance (CV)	8.46	8.12	8.24	9.11	8.71	8.56
R^2	0.90	0.91	0.90	0.89	0.94	0.92
Adjusted R^2	0.89	0.89	0.91	0.87	0.92	0.90
Predicted R^2	0.85	0.86	0.86	0.86	0.89	0.91
Press	2189.54	2041.09	1989.54	2511.81	2217.31	2070.56
Adequacy of precision	22.08	27.31	24.56	17.43	20.61	21.45
F-value	20.62	19.15	18.16	24.17	21.34	22.32
P-value	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001

value and F-value

Coefficient of regression is used to investigate the adequacy of model. For a good fitting model, R^2 should be more than 0.80 [58]. In this study, R^2 for COD: 0.90, 0.91 and 0.90 and $EE_{consumption}$: 0.89, 0.94 and 0.92 were achieved for EC, PEC and PC processes, respectively. Variation in model predicted values is measured by predicted R^2. Significance of the model and signal to noise ratio are indicated by adjusted R^2 and adequacy of precision, respectively. The model is highly significant for high value of adjusted R^2 and for signal to noise ratio >4 [59,60]. CV indicates the variation in actual and model predicted values. For a good model, the value of CV should not be greater than 10. PRESS stands for "predicted residual error sum of squares," defined as sum of the squared differences between actual and estimated values over all the points, which measures fitting quality of a model. The value of PRESS should be low. The F-value indicates distribution of actual data around the fitted model. The P-values are used to check the significance of the each coefficient and necessary to understand the pattern of the mutual interaction between the test variables. P-value <0.05, shows that model is significant, and <5% model term values are not significant. P-value >0.100 shows that model terms are insignificant. Coefficients become very significant for model at larger magnitude of F-value and smaller P-value [61]. Some researchers have also found the significant model term within required range of F and P-values [62,63]. In the present study, all F-values and P-values are in satisfactory range for all responses. This implies that all the operating parameters during EC, PEC and PC processes are significant for the treatment.

4. Kinetic Study

Degradation kinetic during EC, PEC and PC treatments at optimum parametric conditions was studied as shown in Table 5. First-order, second-order and power law model were applied to find best fit reaction order. It is already known that pollutant degradation rate is directly proportional to COD removal rate during wastewater treatment [45,66,67]. Therefore, first-order, second-order and nth-order kinetic models are represented as

$$\text{For 1}^{\text{st}}\text{ order: } \frac{-d(COD)}{dt}=k_1(COD) \text{ or } \ln\frac{COD_i}{COD_t}=k_1t \tag{13}$$

$$\text{For 2}^{\text{n}}\text{ order: } \frac{-d(COD)}{dt}=k_2(COD)^2 \text{ or } \frac{1}{COD_t}-\frac{1}{COD_o}=k_2t \tag{14}$$

$$\text{For n}^{\text{th}}\text{ order: } \frac{-d(COD)}{dt}=k_n(COD)^n \tag{15}$$

By solving Eq. (16) with limits, at t=0, $COD=COD_i$ and at t=t, $COD=COD_t$

$$\frac{1}{COD_t^{n-1}}-\frac{1}{COD_i^{n-1}}=(n-1)k_nt \tag{16}$$

where, k_1- 1st order rate constant, k_2- 2nd order rate constant, k_n- nth order rate constant and t- time (in sec).

Regression method was used for the error minimization during kinetic analysis. The error minimization function is given below.

$$ARE=\frac{100}{n}\Sigma_{i=1}^{n}\left|\frac{(COD_{t,\,exp}-COD_{t,\,cal})}{COD_{t,\,exp}}\right|_i \tag{17}$$

where, $COD_{t,exp}$ - experimental COD and $COD_{t,cal}$ - calculated COD at time t.

The experimental results found at optimum conditions were used to determine the rate constants and orders of reaction, Values of

Table 6. Kinetic study for EC, PEC and PC treatments at optimum operating conditions

Treatment method	Rate constant (k)	Order of reaction	Relative error (%)
1st Order			
EC	0.0113	1	5.6
PEC	0.0180	1	11.1
PC	0.0141	1	8.5
2nd Order			
EC	1.91×10^{-5}	2	4.1
PEC	3×10^{-5}	2	10.4
PC	2.48×10^{-5}	2	7.4
nth Order			
EC	1.49×10^{-4}	1.68	4.5
PEC	4.20×10^{-4}	1.61	9.7
PC	2.51×10^{-4}	1.70	7.5

rate constants for first- (k_1), second- (k_2) and nth (k_n)-orders and reaction order for power law model are given in Table 6. The relative error during second-order was found minimum as shown in Table 6. Fig. 6(a) and Fig. 6(b) indicate first- and second-order plots for EC, PEC and PC treatments. Higher rate constant (k) values indicate higher degradation rate; hence from the observed results it can be concluded that COD degradation rate during PEC treatment was highest among EC, PEC and PC treatments. In the present study, COD degradation during EC, PC and PEC treatment favors second-order rate kinetics due to high R^2 value as shown in Fig. 6(a) and Fig. 6(b).

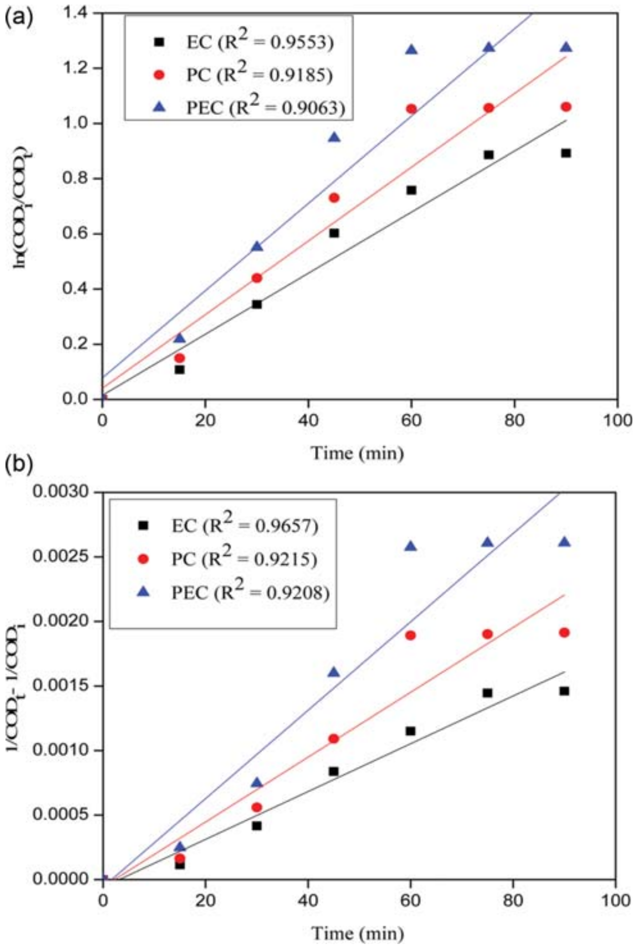


Fig. 6. (a) 1st order (b) 2nd order kinetic plots for EC, PEC and PC processes at optimum operating conditions.

5. Sludge Study

5-1. FE-SEM

The FE-SEM analysis of sludge was performed to identify sample morphology. FE-SEM images of EC, PEC and PC produced sludge are indicated in Fig. 7(a), Fig. 7(b) and Fig. 7(c), respectively. FESEM characterization was carried out to identify the surface structure. It was observed from the high magnification FESEM images that PEC produced sludge is more porous as compared to EC and PC generated sludge. Therefore, particle size of EF produced sludge remains smaller than EC and PC sludge.

5-2. DTA/TGA/DTG

DTA/TGA/DTG plots for EC, PEC and PC produced sludge are shown in Fig. 7(d), Fig. 7(e) and Fig. 7(f) respectively. In this study, TGA plot of EC generated sludge indicates more weight loss or higher oxidation capacity as compared to PC and PEC sludge. This may be due to CO_2 and CO formation during reaction. Approximately 9.18%, 1.85% and 1.51% at 200 °C and 23.06%, 8.59% and 7.34% near 500 °C of weight reduction was found by EC, PC and PEC produced, respectively. This is because of the evaporation of water or solution present in pore which could not remove during drying [33]. DTG study of EC, PEC and PC sludge indicates maximum amount of weight loss: 0.269 mg/min at 191 °C, 0.0168 mg/Cel at 313 °C and 0.0069 mg/Cel at 283 °C. DTA analysis shows endothermic characteristics with 80.0 μV·s/mg at 887 °C for PC sludge, exothermic characteristics with −144 μV·s/mg at 377 °C and −206 μV·s/mg at 373 °C for EC and PEC produced sludge. Endothermic and exothermic natures are due to the decomposition with early oxidation of fragments and carbon chain fragmentation.

6. Operating Cost Study

The cost analysis during electrochemical treatments was estimated as follows.

$$OC=EE_{consumption}\times EEC+Electrode_{consumption}\times ELC+H_2O_2\times HC \qquad (18)$$

where, OC, EEC, ELC and HC are operating cost, energy cost, electrode material cost, and H_2O_2 cost, respectively. Cost analyses for both processes are shown in Table 7. At optimum conditions, operating cost was found lowest during PEC treatment as compared to EC and PC treatments. This is because of the low consumption of electrode material as well as electrical energy in case of PEC treatment.

CONCLUSIONS

The treatment of simulated purified terephthalic acid wastewater containing BA, TPA, p-TA and PA was investigated by EC, PEC and PC methods. Acid precipitation treatment was conducted ini-

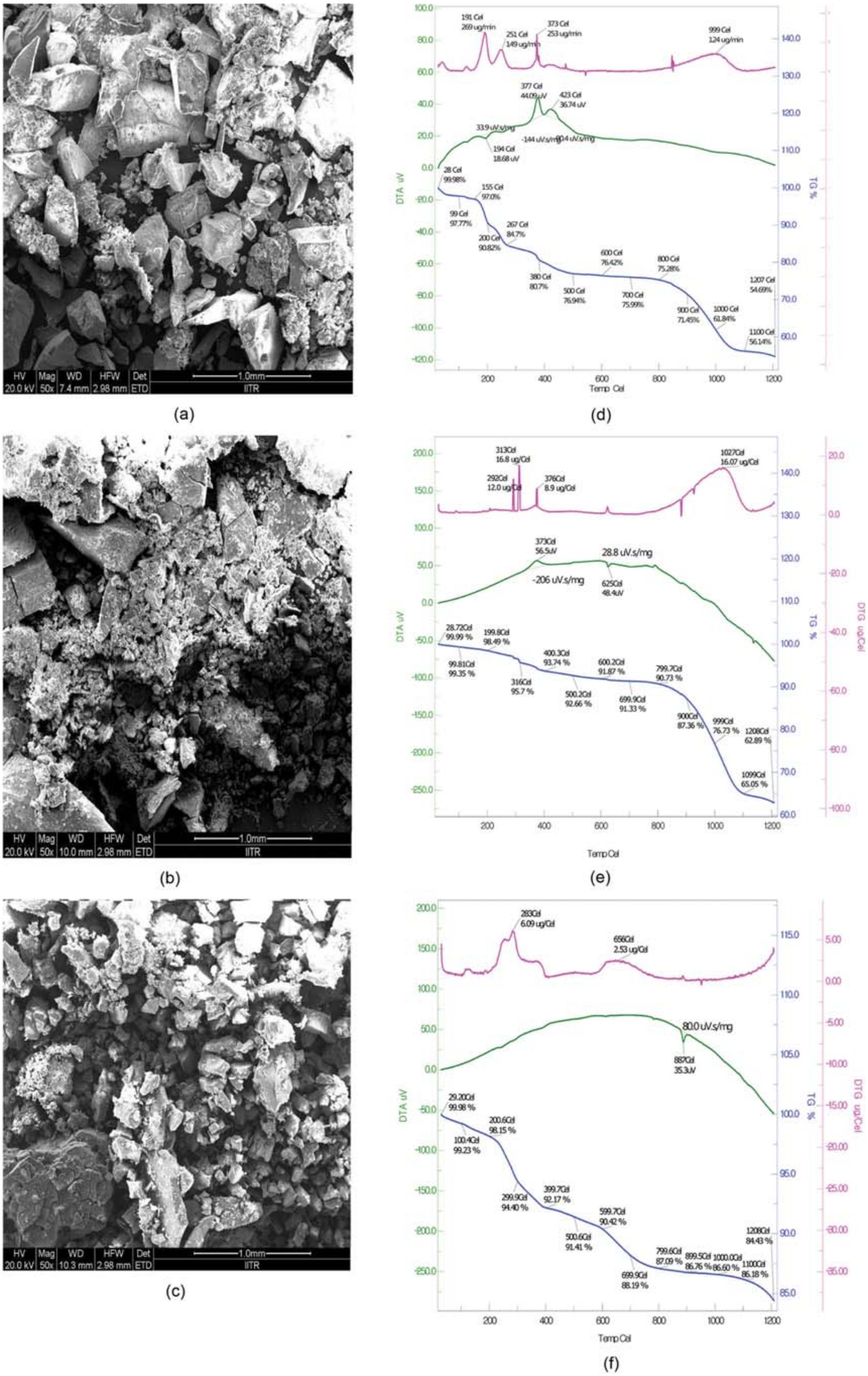


Fig. 7. (a)-(c) SEM images (d)-(f) DTA/TGA/DTA graphs obtained for EC, PEC and PC generated sludge.

Table 7. Operating cost during EC, PEC and PC treatments at optimum operating conditions given by CCD and experimental test runs

Treatment method		$EE_{consumption}$ (kWh/kgCOD$_{removed}$) (Rs. 5.75/kWh)	Electrode consumed (kg/kg COD$_{removed}$) (Rs. 55/kg for iron)	H_2O_2 consumed (kg/kg COD$_{removed}$) (Rs. 22/kg (30%w/v))	Operating cost ($) 1 $=65 Rs.
EC	CCD	95.81	4.81	-	12.54
	Test run	102.52	4.92	-	13.23
PEC	CCD	49.58	3.56	1.10	8.49
	Test run	52.23	3.71	1.14	9.19
PC	CCD	69.26	4.32	-	9.78
	Test run	73.65	4.66	-	10.45

tially at various pH and temperature and 41.6%, 44.8%, 80.9%, 19.8% and 61.78 removal of BA, p-TA, TPA, PA and COD, respectively, was obtained at optimum pH -2 and temperature- 15 °C. Acid-treated aqueous solution was further subjected to EC, PEC and PC treatments independently. Influence of various parameters such as pH, CD, electrode distance, electrolyte concentration, H_2O_2 concentration and electrolysis time was investigated for EC, PEC and PC treatment, and maximum removal was achieved of BA- 66.16%, 75.24%, 70.12%; p-TA- 59.15%, 68.11%, 63.28%; TPA- 64.07%, 73.49%, 68.22%; PA- 65.14%, 74.25%, 69.36% and COD- 60.76%, 73.91%, 66.68% with $EE_{consumption}$ (kWh/kgCOD$_{removed}$)- 95.81, 49.58 and 66.68, respectively, at optimum conditions. Proximity of experimental and CCD estimated results shows optimized and effective CCD developed model. COD degradation during EC, PEC and PC processes obey second-order kinetics under low error range and high R^2 values. In the present research, PEC treatment was found most efficient on the basis of removal efficiencies, $EE_{consumption}$ and operating cost.

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