A Comparative Study of Electrochemical Treatment of Para-Toluic Acid (p-TA) from Aqueous Solution: Process Optimization and Sludge Analysis

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Received: 7 October 2016 / Revised: 1 February 2017 / Accepted: 2 February 2017 / Published online: 6 March 2017
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Abstract The present study deals with the removal of para-toluic acid (p-TA) as well as chemical oxygen demand (COD) from synthetic solution. Pretreatment of aqueous solution was done by acid precipitation at different pH levels (3–6) and temperatures (15–60 °C). The pretreated solution was further treated by electrocoagulation (EC) and electro-Fenton (EF) treatment technologies using iron anode and graphite cathode. Optimization of various independent operating parameters viz. initial pH (1–9), current density (30.48–152.44 A/m²), electrolyte concentration (for EC) (0.03–0.07 mol/L), H₂O₂ concentration (for EF) (300–700 mg/L), and electrolysis time (10–90 min) was performed using central composite design (CCD) in response surface methodology (RSM). At optimum operating conditions, maximum removal percent of p-TA 64.83, 74.50; COD 61.27, 68.21; and energy consumption (kWh/kg COD removed) 69.71, 41.60 were obtained by EC and EF processes, respectively. In this study, it was observed that the EF process was more efficient than EC process based on percent removal of p-TA and COD with minimum energy consumption (E.consumption). Sludge obtained after EC and EF treatments was analyzed for various physicochemical

characteristics like settling, point of zero charge, XRD, FTIR, SEM/EDX, and DTA/TGA.

Keywords Para-toluic acid · Acid precipitation · Electrocoagulation · Electro-Fenton · Optimization · Sludge characterization

Introduction

Purified terephthalic acid (PTA) is a xylene-based petrochemical product widely used for the manufacturing of polyethylene terephthalate bottles, polyester films, and textile fibers [1, 2]. About 3–4 m³ of wastewater (COD (5–20 g/L)) is generated for per ton of PTA production [3]. Wastewater generated from petrochemical industries contains a number of pollutants with very high values of chemical oxygen demand (COD). The wastewater released from a PTA manufacturing unit usually comprises various aromatic compounds such as benzoic acid (BA), para-Toluic acid (p-TA), phthalic acid (PA), terephthalic acid (TPA), and 4-carboxybenzaldehyde (4-CBA) in high concentration with low concentration of methyl acetate, 4-formylbenzoic acid, and p-xylene [4–8]. The phthalate forms are highly toxic due to their endocrine disrupting ability and adverse effects on reproduction capacity as well as development of human beings [9]. Para-toluic acid is a white crystalline powder having low solubility in water; however, solubility increases in aqueous solution of sodium hydroxide [10, 11]. It is widely used for the production of several products such as medicines, agrochemicals, pigments, pharmaceuticals, dyestuffs, and optical brighteners [12]. Although p-TA has wide applications, intake in high amount is very dangerous for the human body due to its hazardous and toxic nature [13]. It can be a reason for the abatement in epididymal oligozoospermia [14]. Because of the highly toxic

Highlights • Maximum percent removal of p-TA 74.50 and COD 68.21 were achieved by electro-Fenton process.
• Energy consumption was low in electro-Fenton process.
• The amount of sludge generated by electro-Fenton process was lower in volume.
• Proximity of actual and model predicted values was found.
• Removal efficiencies were strongly affected by current density and pH.

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nature of BA, p-TA, and TPA, the US Environmental Protection Agency (USEPA) included these compounds in the list of priority pollutants [14–16]. No specific discharge limit for p-Toluic acid has been proposed by the pollution regulating agencies in India. The permissible discharge limit of COD <250 mg/L has been prescribed by the environmental regulating agencies for petrochemical wastewaters into surface waters [17] in India. Hence, it is very necessary to determine the effective treatment technologies for PTA wastewater to achieve the prescribed discharge standards. In the recent years, numerous treatment technologies like adsorption [18–21], electrochemical methods [22, 23], coagulation-flocculation [3, 24, 25], thermochemical precipitation [26], crystallization [27], and oxidation process [28, 29] have been used for PTA wastewater treatment. Electrochemical technologies like electrocoagulation as well as electro-Fenton are the efficient techniques used for wastewater treatment in the last few years.

In electrocoagulation (EC), generation of coagulant takes place in situ by the electrolytic oxidation of an anode material that neutralizes the pollutants present in wastewater by mutual collision and are agglomerated, followed by sedimentation [30]. The EC process includes the following steps: (a) electrolytic reactions at the surfaces of electrodes, (b) in-situ oxidation of metallic ions and eventual precipitation of metal hydroxides in the electrolytic solution, (c) adsorption of colloidal and soluble pollutants on the coagulant surface [31], and (d) pollutant removal through sedimentation or flotation [32]. The reactions occurring at electrodes are as follows:

At anode:

At cathode:

Electro-Fenton (EF) is one of the most popular electrochemical advanced oxidation processes as well as an eco-friendly method for water remediation based on Fenton's reaction chemistry [33]. EF process has two distinct configurations. Fenton reagents are added to the reactor from outside in the first configuration while in the second design, only hydrogen peroxide (H_2O_2) is added to the reactor from outside, and ferrous ions are generated from sacrificial iron anode [34]. The following chain reactions show the EF process [35, 36]:

where RH is organic pollutant:

In the present study, treatment of p-TA from aqueous solution was done through acid precipitation followed by electrocoagulation and electro-Fenton methods separately using iron as anode and graphite as cathode. The electrochemical studies were done by using the central composite design (CCD) of response surface methodology (RSM) in Design Expert Software (DES). RSM is an efficient statistical tool for the optimization of industrial processes [37]. Here, it was used for the optimization of various electrochemical parameters viz. pH, current density, electrolyte concentration or H_2O_2 concentration, and time for maximum removal of COD and p-TA with minimum electrical energy consumption (E.consumption).

Materials and Methods

Chemicals

All the chemicals used during the entire study were of analytical grade (AR). Para-Toluic acid (99% purity), sodium chloride (NaCl), and sodium sulfate (Na_2SO_4) were purchased from Loba Chemie Pvt. Ltd., Mumbai (India). Hydrogen peroxide (H_2O_2) (30% w/v) was supplied by S.D.Fine-Chem Limited Mumbai (India). Sulfuric acid (H_2SO_4), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), sodium hydroxide (NaOH), methanol (CH_3OH), isopropyl alcohol ($\text{C}_3\text{H}_8\text{O}$), silver sulfate (Ag_2SO_4), acetic acid (CH_3COOH), and mercury (II) sulfate (HgSO_4) were procured from Ranbaxy Fine Chemicals Limited, New Delhi (India).

Wastewater Sampling and Analysis

Stock solution of para-Toluic acid of 1000 mg/L was synthetically prepared at laboratory. All the reagents and wastewater samples were preserved at 4 °C to avoid biodegradation and growth of microorganisms. The initial concentration of p-TA (500 mg/L) was taken according to previous studies [24, 38, 39]. Initially, the COD of wastewater was found to be 1049 mg/L. Wastewater characteristics like pH and COD were determined in accordance with the standard methods [40]. Concentrations of p-TA and COD values were analyzed by HPLC (Waters, USA) using a UV detector (Waters 2487 absorbance detector, USA) set at 240 nm [22, 41, 42] and a COD analyzer (Aqualytic, Germany), respectively. Samples were filtered through nylon syringe filter (0.21 μm) before each analysis. The HPLC system was operated at ambient temperature with C18 column and mobile phase (solution of 91% Millipore water, 7% isopropyl alcohol and 2% acetic acid with 1.2 mL/min flow rate) in isocratic mode [43]. Ferrous ion (Fe^{2+}) concentration was measured through spectrophotometric

Fig. 1 Schematic diagram of experimental setup for electrochemical treatment

method [40]. Percent removal of p-TA, COD, and E.consumption (kWh/kg COD_{removed}) were calculated by the following equations:

$$\% \text{Removal of p-TA and COD} = \frac{c_i - c_f}{c_i} \times 100 \quad (7)$$

where C_i and C_f are the initial and final concentrations of p-TA and COD.

$$\text{E.consumption (kWh/kg COD}_{\text{removed}}) = \frac{VIT \times 100}{(\% \text{Removal of COD}) C_{\text{CODi}} \times V_s} \times 1000 \quad (8)$$

where V , I , T , and V_s are the voltage, current (amp), time (hour), and volume of the solution (liter), respectively [44].

Table 1 Operating parameters and their levels obtained from the statistical software for EC and EF processes

Central composite design characteristics

Levels	Parameter (range)			
	X_1 pH (1 → 9)	X_2 CD (A/m ²) (30.48 → 152.44)	X_3 $(X_3)_{\text{EC}}$ Na ₂ SO ₄ concentration ($\frac{\text{mol}}{\text{L}}$) (0.03 → 0.07)	X_4 Time (min) (10 → 90)
			$(X_3)_{\text{EF}}$ H ₂ O ₂ concentration ($\frac{\text{mg}}{\text{L}}$) (300 → 700)	
−2(−α)	1	30.48	0.03	10
−1	3	60.97	0.04	30
0	5	91.46	0.05	50
+1	7	121.95	0.06	70
+2(α)	9	152.44	0.07	90

Experimental Procedure

Acid precipitation experiment was done through mixing of sulfuric acid (1 N) to the aqueous solution at different temperatures to adjust the initial pH ($pH_0 = 6.2$) of wastewater at pH levels 6, 5, 4, and 3. Precipitated solution was allowed to settle for 4 h. Then, the supernatant was filtered and further treated by electrochemical processes. The entire electrochemical experiments were performed in a rectangular Plexiglas batch cell with a capacity of 1.6 L. Iron anode (100 mm $\times$ 80 mm $\times$ 1 mm) and graphite cathode (100 mm $\times$ 80 mm $\times$ 3 mm) with an effective electrode area into the solution (131.2 cm²) were used during both electrochemical processes for treatment of 1 L of solution. The gap between parallel electrodes was 2 cm. Between each successive runs, electrodes were cleaned with H₂SO₄ solution (5% v/v) for next experiment. The schematic diagram for electrochemical treatment is shown in Fig. 1. Some initial test runs were conducted to determine the operating parameter range for both processes. Table 1 shows the operating parameter range. Direct current (0–4 A) and voltage (0–35 V) were used to power the parallel electrodes. Both the EC and EF processes were conducted at room temperature (25 ± 2 °C) and atmospheric pressure. The desired amount of hydrogen peroxide (H₂O₂) was added to the reactor before switching on the power supply during EF treatment.

Results and Discussion

Effect of Acid Precipitation on Percent Removal of P-TA and COD

p-TA was present in ionized state in the aqueous solution, as the pK_a value for p-TA is 4.36. The acid gets deionized by reduction of the pH (initial pH 6.8) of wastewater. The ionic product value and solubility product constant (K_{sp}) for p-TA are 4.395×10^{-5} and 8.714×10^{-6} , respectively [45]. Hydrogen ion concentration increases in the solution with decrease in pH, and due to the common-ion (hydrogen ions) effect, the ionic product value of p-TA surpasses its solubility product value resulting acid precipitation [46]. The precipitated solution was allowed to settle for 4 h. After settling, supernatant was filtered through Whatman filter paper (11 μ m). Precipitation causes reduction in the concentration of p-TA, and the COD value of the supernatant by 38.2% and 33.1%, respectively, at optimum pH 3 and temperature of 15 °C as shown in Fig. 2a, b. The filtered supernatant was further treated by both electrochemical processes.

Effect of pH on Percent Removal of P-TA, COD, and E.Consumption

pH plays a vital role in influencing the performance of EC and EF processes. The effect of pH on removal efficiencies

depends on the formation of complexes. In EC process, complexes form by conversion of Fe²⁺ and Fe³⁺ to Fe(OH)_n-type structures at basic medium [47] and during EF treatment, iron species form the stable complexes with H₂O₂ at acidic medium, leading to the deactivation of catalysts [48]. Both EC and EF experiments were completed according to the CCD predicted sets as given in Table 2. For EC, the removal efficiencies of p-TA and COD reduce beyond the optimum pH (8.11) as shown in Fig. 3a, c. Hydroxides of metal ions were found in dissolved form at low pH, and concentration of metal hydroxides increase by enhancement of pH. Removal efficiencies decrease due to the weak interaction among metal hydroxide ions and suspension impurities at high pH [49]. For EF, the removal of p-TA and COD are higher in acidic conditions (Fig. 4a, c). This is due to the formation of metal hydroxide flocs and hydroxide radicals ($\cdot$ OH) for the neutralization of pollutant ions. At low pH, the rate of generation of Fe²⁺ and H₂O₂ are high and, consequently, the formation of $\cdot$ OH also increases [50, 51]. In electro-Fenton process, a fixed amount of H₂O₂ (300–500 mg/L) was fed to the reactor, which

Fig. 2 Effect of pH at different temperatures in acid precipitation process **a** on removal of p-TA and **b** on removal of COD

Table 2 Actual and CCD predicted removal efficiencies of p-TA, COD, and E.consumption for EC and EF processes

Run no.	Independent variables				% Removal of p-TA:(R ₁)				% Removal of COD:(R ₂)				Energy Consumption (kWh/kg COD _{removed}): (R ₃)			
	X ₁ (pH)	X ₂ : (CD) (A/m ²)	X ₃	X ₄ : (t) (min.)	(X ₃) _{EC} (Na ₂ SO ₄)		(X ₃) _{EF} (H ₂ O ₂)		EC		EF		EC		EF	
					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	3	60.97	0.04	70	33.44	28.89	72.34	68.54	28.54	23.41	65.97	62.65	79.15	106.03	34.24	35.72
2	7	60.97	0.04	30	60.43	56.97	57.21	56.93	57.90	52.53	51.98	50.99	16.72	8.41	18.62	15.53
3	3	121.95	0.06	600	36.15	32.33	74.89	73.01	33.76	29.38	66.51	65.59	100.37	113.6	50.95	49.55
4	7	121.95	0.07	700	65.14	65.74	61.93	67.14	60.24	61.38	56.28	61.56	131.26	129.74	140.49	135.67
5	3	60.97	0.06	600	28.14	25.61	70.02	65.62	26.01	22.86	67.31	62.27	37.22	26.49	14.38	19.23
6	7	60.97	0.06	600	61.26	58.54	61.02	54.42	57.45	53.64	53.70	46.28	39.32	30.63	42.07	49.8
7	3	121.95	0.06	600	35.34	34.47	76.96	72.69	30.44	29.68	71.20	66.72	259.76	269.19	111.05	118.89
8	7	121.95	0.06	600	64.25	68.31	59.63	55.84	59.35	64.17	51.96	49.61	57.09	28.5	65.21	68.97
9	5	91.46	0.05	500	48.04	48.07	62.05	59.46	43.14	43.55	55.68	53.02	77.15	80.04	59.77	62.3
10	5	91.46	0.06	600	40.25	49.44	56.54	62.41	35.35	44.63	50.98	56.66	94.15	69.69	65.28	58.56
11	3	60.97	0.04	400	26.36	29.81	69.94	63.61	23.49	27.12	63.57	56.63	41.21	27.55	15.23	23.37
12	9	60.97	0.04	400	54.31	58.64	50.86	52.58	49.41	54.49	44.49	46.44	45.72	38.17	50.78	50.46
13	3	121.95	0.04	70	24.41	28.13	74.23	70.76	19.51	23.26	68.65	65.44	405.29	354.98	115.18	120.06
14	7	121.95	0.06	600	62.33	61.49	57.95	60.91	60.30	59.15	53.42	54.91	18.73	27.47	21.14	20.2
15	3	60.97	0.06	600	28.34	30.16	70.23	68.7	23.44	25.65	63.86	62.92	123.92	118.77	45.48	46.62
16	7	30.48	0.06	600	53.31	51.98	54.71	55.72	47.43	46.49	49.02	50.35	6.37	35.62	6.17	3.35
17	3	121.95	0.06	600	37.64	36.85	72.54	70.68	32.74	32.28	66.17	63.81	172.51	171.88	85.35	87.8
18	7	121.95	0.06	600	65.35	61.32	59.94	58.72	62.89	57.76	53.97	53.09	125.73	147.81	146.51	145.06
19	5	91.46	0.04	400	47.94	45.86	61.03	63.16	43.04	41.16	56.29	57.41	77.33	94.55	59.12	58.09
20	5	91.46	0.05	500	41.67	42.64	54.67	63.51	36.77	38.29	49.30	57.75	126.72	148.98	94.51	80.84
21	1	91.46	0.05	500	24.94	24.69	46.89	55.47	21.07	20.81	39.33	47.71	157.96	170.79	84.62	74.93
22	7	91.46	0.05	500	67.42	62.46	61.74	50.66	62.52	57.93	55.37	44.47	53.23	50.03	60.10	72.34
23	5	60.97	0.05	500	41.53	45.46	56.37	59.39	36.63	40.51	50.23	52.92	44.05	16.17	32.12	32.18
24	5	121.95	0.05	500	52.22	50.33	63.61	61.67	48.76	45.99	58.07	55.02	115.83	132.68	97.26	100.01
25	5	91.46	0.04	400	46.14	47.11	58.98	61.59	41.24	43.72	51.31	54.81	48.42	50.63	38.91	35.66
26	5	152.44	0.05	400	49.55	52.25	62.88	66.42	44.65	47.82	57.04	60.34	192.00	174.11	150.29	146.14
27	5	91.46	0.05	500	46.34	46.61	60.34	59.62	43.60	43.34	52.72	53.00	45.80	50.11	37.87	36.61
28	5	60.97	0.05	500	44.02	41.97	57.83	63.01	39.12	37.23	51.46	56.31	57.75	51.86	43.90	39.73
29	5	60.97	0.05	500	39.03	42.05	53.72	60.12	34.13	38.53	46.71	54.25	28.36	19.52	20.72	17.47
30	5	121.95	0.04	400	51.14	48.19	65.02	63.65	47.32	43.68	58.73	57.93	119.37	154.38	96.16	98.32

Fig. 3 Effect of pH, CD, time, and electrolyte concentration on percent removal of p-TA, COD, and E.consumption for EC

Fig. 4 Effect of pH, CD, time, and H_2O_2 concentration on percent removal of p-TA, COD, and E. consumption for EF

enhances the formation of hydroxyl radical and increases the removal efficiencies. The generation of oxonium ions (H_3O_2^+) occur at very low pH [52], and high pH is responsible for the decomposition of H_2O_2 into water and oxygen. As pH influences the COD removal efficiency, energy consumption depends on COD. Hence, energy consumption is low at higher COD removal. E.consumption reaches optimum at pH 8.11 for EC and 3.01 for EF as shown in Figs. 3e and 4e respectively.

Effect of Current Density and Electrolysis Time on Percent Removal of P-TA, COD, and E.Consumption

Current density and electrolysis time are very important operating parameters in electrochemical processes. Current densities of 30.48, 60.97, 91.46, 121.95, and 152.44 A/m^2 with different slots of time, 10, 30, 50, 70, and 90 min, were studied during both the processes. Amount of charges generated during electrochemical reactions increases with current density which results in higher removal of p-TA and COD. Similarly, metal ion concentration and hydroxide radicals increase with electrolysis time. The conductivity of electrolytic solution increases with time due to that the rapid movement of ions and radicals results in higher efficiency. Beyond optimum values (50.42 min for EC and 42.63 min for EF), percent removal decreases due to low generation of metal ions and $\cdot\text{OH}$ radicals. The results are shown in Figs. 4a–d and 5a–d. It was found that, beyond the optimum current density of 103.39 A/m^2 for EC and 88.90 A/m^2 for EF processes, removal efficiencies decrease due to the consumption of considerable amount of charge during electrolysis by some side reactions, and, ultimately, the corrosion of electrodes enhances as discussed below.

Fig. 5 Concentration of ferrous ion (Fe^{2+}) in solution with reaction time at optimum conditions

Table 3 Optimum operating conditions predicted by CCD and experimental test run by EC and EF processes

pH	CD (A/m^2)	Na_2SO_4 Conc. (mol/L)	H_2O_2 Conc. (mg/L)	Time (min)	% Removal of p-TA		% Removal of COD		E.consumption ($\text{kWh/kg COD}_{\text{removed}}$)	
					CCD (Pre.)	Test Run	CCD (Pre.)	Test Run	CCD (Pre.)	Test Run
EC 8.11	103.39	0.05	—	50.42	64.83	60.61	61.27	56.87	69.71	75.11
EF 3.01	88.90	—	522	42.63	74.50	71.86	68.21	63.78	41.60	48.49

Fig. 6 **a** Settling characteristics. **b** Point of zero charge. **c** XRD spectra. **d** FTIR spectra. **e, f** SEM images. **g, h** DTA/TGA graphs obtained by the EC- and EF-generated sludge, respectively

- Self decomposition of H_2O_2 [53]:

- Removal of metals from solution due to metal precipitation on the cathode surface [54].

In addition, higher current density results in temperature rise of electrolytic solution and higher energy consumption [55, 56]. E.consumption strongly depends on current density and electrolysis time. Beyond optimum conditions, removal decreases; therefore, the energy consumption increases. The results are shown in Figs. 3e, f and 4e, f.

Effect of Electrolyte and H_2O_2 Concentration on Percent Removal of P-TA, COD, and E.Consumption

Electrolyte is an important part in electrochemical treatment for the enhancement of solution conductivity and electron transfer rate in electrolysis. Different concentrations of an electrolyte (sodium sulfate) were used in EC process and obtained the optimum value (0.05 M) as shown in Figs 4b, d. This optimum electrolyte concentration (0.05 M) was also used in electro-Fenton process. The optimum H_2O_2 concentration is highly important to get maximum removal efficiency in EF process. In the present study, iron anode was used for EC and EF processes, which increases Fe^{2+} ion concentration during electrolysis. Formation of $\cdot\text{OH}$ radicals are catalyzed through anodic iron in the EF process as can be seen in Eqs. (3) to (6). Depending on wastewater COD (after acid

precipitation), i.e., 661 mg/L, theoretical amount of H_2O_2 required to provide entire O_2 for oxidation was calculated by $(34/16) \times 661 = 1404.63$ mg/L. The H_2O_2 was used in concentration range 300–700 mg/L during treatment and achieved the optimal value (522 mg/L) as shown in Fig. 3b, d. It was found that beyond optimum H_2O_2 concentration, efficiencies decreased due to the presence of excess amount of hydrogen peroxide leading to the scavenging effect on hydroxyl radicals [39, 40]:

E.consumption decreases with increase in electrolyte concentration up to 0.05 M as shown in Fig. 3f, and beyond this optimal value, it starts to increase in the EC process. During EF treatment, E.consumption decreases with H_2O_2 concentration up to optimum value and after that, it increases as shown in Fig. 4g.

Effect of Ferrous Ion (Fe^{2+}) Concentration in EF Process

Fe^{2+} ion concentrations play a vital role in the EF process. The concentration of Fe^{2+} ions accelerates the formation of hydroxyl radicals (main oxidizing agent) in the electrolytic solution resulting in higher removal efficiency [57]. In the presence of H_2O_2 , Fe^{2+} ions convert to ferric ions (Fe^{3+}). The coagulating nature of Fe^{3+} enhances the sludge generation with $\text{Fe}(\text{OH})_3$ [58]. However, the excess amount of Fe^{2+} ions causes consumption of $\cdot\text{OH}$ and affects the removal [59].

Fig. 6 (continued)

Table 4 Elemental composition of sludge based on EDAX results for the EC and EF processes

Element		C K	O K	Na K	S K	Fe K
Weight %	EC (sludge)	11.21	30.44	21.62	7.09	29.64
	EF (sludge)	14.58	26.34	19.64	12.53	26.91

Concentration of dissolved Fe^{2+} ions during the EF process with electrolysis time at optimum operating conditions is shown in Fig. 5.

RSM Study

Optimization

Both electrochemical processes were optimized to achieve maximum removal of p-TA and COD with minimum E.consumption based on CCD results. All the operating conditions with their experimental run data are given in Table 2. The optimum results of CCD predicted and experimental test runs were obtained at optimum operating conditions as shown in Table 3. Proximity of CCD predicted values and experimental run results indicate good competence of model.

Model Equations for Responses Based on ANOVA Result

Second-order polynomial equations have been used for both electrochemical processes to express regression model in terms of independent variables.

Generalized equation:

$$R_i = b_0 + b_1 \times \text{pH} + b_2 \times \text{CD} + b_3 \times C_1 + b_4 \times t + b_{11} \times \text{pH}^2 + b_{22} \times \text{CD}^2 + b_{33} \times C_1^2 + b_{44} \times t^2 + b_{12} \times \text{pH} \times \text{CD} + b_{13} \times \text{pH} \times C_1 + b_{14} \times \text{pH} \times t + b_{23} \times \text{CD} \times C_1 + b_{24} \times \text{CD} \times t + b_{34} \times C_1 \times t \quad (11)$$

Responses (R_1 , R_2 , and R_3) are given below:

p-TA

$$R_1^{\text{EC}} = 49.9 + 4.3 \times \text{pH} + 2.16 \times j + 2.37 \times C_1 - 6.62 \times t + 0.90 \times \text{pH}^2 - 0.39 \times j^2 - 0.41 \times C_1^2 - 3.44 \times t^2 + 1.4 \times \text{pH} \times j + 1.25 \times \text{pH} \times C_1 - 2.29 \times \text{pH} \times t - 0.10 \times j \times C_1 - 2.9 \times j \times t + 2.71 \times C_1 \times t \quad (12)$$

$$R_1^{\text{EF}} = 66.00 - 5.51 \times \text{pH} + 4.30 \times j - 4.93 \times C_2 + 5.56 \times t - 3.57 \times \text{pH}^2 + 2.54 \times j^2 + 3.39 \times C_2^2 + 2.2 \times t^2 - 1.89 \times \text{pH} \times j - 1.35 \times \text{pH} \times C_2 - 0.80 \times \text{pH} \times t + 2.67 \times j \times C_2 + 0.73 \times j \times t - 1.80 \times C_2 \times t \quad (13)$$

COD

$$R_2^{\text{EC}} = 45.52 + 4.7 \times \text{pH} + 2.08 \times j + 2.3 \times C_1 - 6.54 \times t + 1 \times \text{pH}^2 - 0.69 \times j^2 - 0.66 \times C_1^2 - 2.74 \times t^2 + 1.74 \times \text{pH} \times j + 1.18 \times \text{pH} \times C_1 - 1.68 \times \text{pH} \times t - 0.12 \times j \times C_1 - 2.6 \times j \times t + 2.76 \times C_1 \times t \quad (14)$$

$$R_2^{\text{EF}} = 60.79 - 3.29 \times \text{pH} + 4.12 \times j - 6.82 \times C_2 + 8.15 \times t - 3.74 \times \text{pH}^2 + 2.13 \times j^2 + 4.01 \times C_2^2 + 2.4 \times t^2 - 0.72 \times \text{pH} \times j - 2.11 \times \text{pH} \times C_2 + 0.6 \times \text{pH} \times t + 2.23 \times j \times C_2 + 2.03 \times j \times t - 2.57 \times C_2 \times t \quad (15)$$

E.consumption

$$R_3^{\text{EC}} = 180.8 - 6.10 \times \text{pH} + 74.62 \times j - 26.71 \times C_1 + 109.1 \times t + 5.12 \times \text{pH}^2 - 12.6 \times j^2 + 2.09 \times C_1^2 + 19.5 \times t^2 - 38.6 \times \text{pH} \times j + 9.28 \times \text{pH} \times C_1 - 9.09 \times \text{pH} \times t - 10.78 \times j \times C_1 + 49.9 \times j \times t - 14 \times C_1 \times t \quad (16)$$

$$R_3^{\text{EF}} = 129.9 + 11 \times \text{pH} + 75.8 \times j + 5.23 \times C_2 + 33.5 \times t + 5.45 \times \text{pH}^2 + 8.5 \times j^2 - 3.9 \times C_2^2 + 3.58 \times t^2 + 7.88 \times \text{pH} \times j + 1.56 \times \text{pH} \times C_2 + 1.69 \times \text{pH} \times t - 3.78 \times j \times C_2 + 16.5 \times j \times t + 3.26 \times C_2 \times t \quad (17)$$

where CD is current density, C_1 is electrolyte concentration, C_2 is H_2O_2 concentration, and t is time.

Sludge Analysis

Settling, PZC, and XRD

Settling—Figure 6a indicates the settling characteristics of sludge generated by the EC and EF processes at optimum operating condition. Initially ($t = 0$), the position of the sludge interface was 10.9 and 10.1 cm for EC and EF, respectively, and after 30 min, the level (2.2 cm) of the EC-generated sludge was higher than the level of (2 cm) of the EF-generated sludge. The settling levels of EC- and EF-generated sludge were constant at 1.8 and 1.5 cm, respectively, after 70 min. The results show that the settling level of the EF-generated sludge was faster than that of the EC-generated sludge.

Point of zero charge (PZC)—It is basically a pH value at which a solid submerged in the electrolyte shows zero net charge at solid surface [60]. The salt addition method proposed by the American Society for Testing of Materials D-3838-05 was used to determine the PZC in this study [61]. Cross-over point on resulting curve plotted between ΔpH ($\Delta\text{pH} = \text{pH}_0$ (initial pH) – pH_f (final pH)) and initial pH (pH_0) at $\Delta\text{pH} = 0$ gives the PZC value. The PZC values for EC- and EF-generated sludges are 8.67 and 8.0, respectively, as shown in Fig. 6b.

XRD—The XRD spectrum gives an idea about morphological structures and extent of crystallinity of the sample. The spectra of the sludge generated (dried at ambient temperature) by the EC and EF processes are shown in the Fig. 6c. The XRD spectra of both the EC- and EF-generated sludges show broad and shallow diffraction peaks. Broad and lower intensity peaks of Bragg reflection shows that the analyzed phase occupies an order of short range that is poorly crystalline. The XRD spectra of both the EC- and EF-generated sludges show some sharp peak which indicates the amorphous nature of the sludge.

FTIR, SEM/EDX, and DTA/TGA

FTIR—FTIR spectroscopy is used to determine the information about surface chemistry as well as the functional groups present in the sample. Functional groups in the sludge sample show electrolyte interaction between cations and flocs, resulting in colloid removal during treatment. The spectra of the EC- and EF-generated sludges are shown in Fig. 6d. Here, the broad and intense bands of 3203 and 3213 cm^{-1} attributed to the stretching vibrations of the hydroxyl group and characteristics of hydrogen ring. Wavelengths of 1134 and 1448 cm^{-1} show the presence of a carbonyl group in the sludge sample. Peaks are observed in the range from 1600 to 400 cm^{-1} , which depicted aromatic C=C stretching.

SEM/EDX—SEM analysis gives an idea about surface structure, i.e., whether it is crystalline or amorphous. EDX predicts the composition of the elements (weight %) in the sample. SEM images of the sludges generated (dried at ambient temperature) after EC and EF treatments are shown in Fig. 6e, f. It is found that the EF-generated sludge has high porosity as compared to the EC-generated sludge. Hence, the particle size of the EF-generated sludge stays more downcast than that of the EC-generated sludge. Elemental composition (in weight %) for EF- and EC-generated sludges through EDX analysis is given in Table 4.

DTA/TGA—Figure 6g, h shows the DTA/TGA analysis of the EC- and EF-generated sludges, respectively. The analyses were performed in dynamic air atmosphere with 200 mL/min air flow rate and at 10 K/min heating rate by using calcined Al_2O_3 as a reference material. TGA indicates that percent weight loss of the EC-generated sludge was more than that of EF due to the formation of CO_2 and CO. Oxidation of the EC-generated sludge exhibits endothermic reactions at temperatures 182, 629, and 902 °C with 108, 96.4, and 42.3 mJ/mg heat requirements, respectively. The EF-generated sludge shows an exothermic nature at 400 °C with 220 mJ/mg and an endothermic behavior at 650 °C with 18.8 mJ/mg heat requirements. DTG spectrum of the EC-generated sludge shows maximum of 0.285 mg/min rate of weight loss at 177 °C and minimum of 0.085 mg/min at 708 °C where the combustion of volatiles takes place exothermally. DTG spectrum of the EF-

generated sludge shows maximum rate of weight loss of 0.124 mg/min at 1054 °C and minimum of 0.045 mg/min at 377 °C temperatures. TGA graphs of the EC- and EF-generated sludges show that about 0.2 and 0.8% weight were reduced below 100 °C, respectively. This is due to the fact that a small amount of water was not evaporated during drying at ambient temperature.

Conclusion

In this study, acid precipitation of wastewater was done at different pH levels and temperatures, and the effects of various operational parameters on EC and EF treatment methods were evaluated based on removal of p-TA and COD with E.consumption. Approximately 43% of p-TA and 37% of COD from aqueous solution were removed by acid precipitation. The filtered supernatant was further treated by electrochemical processes and obtained maximum removal of p-TA 64.83%, COD 61.27% with E.consumption (kWh/kgCOD_{removed}) 69.71 at pH 8.1, CD 103.39 A/m², Na_2SO_4 concentration 0.05 mol/L, and time 50.42 min by EC process and of p-TA 74.50%, COD 68.21% with E.consumption (kWh/kgCOD_{removed}) 41.60 at pH 3.01, CD 88.90 A/m², H_2O_2 concentration 522 mg/L, and time 58.86 min by EF process. The amount of sludge generated through EC process was more than that through EF process. High proximity of CCD predicted values and test run results shows good adequacy of model in this study. Hence, in the present study, the EF process was found to be more efficient than the EC process based on percent removal and energy consumption.

Acknowledgements The authors are thankful to the Department of Chemical Engineering, Indian Institute of Technology, Roorkee, for providing the necessary technical facilities and the Ministry of Human Resource Development (New Delhi, India) for the financial support.

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