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Treatment of multicomponent aqueous solution of purified terephthalic acid wastewater by electrocoagulation process: Optimization of process and analysis of sludge

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ABSTRACT

The present research work is based on degradation of major pollutants of purified terephthalic acid (PTA) wastewater by electrocoagulation (EC) process. Terephthalic acid (TPA), benzoic acid (BA) and *para*-toluic acid (*p*-TA) are the major pollutants of PTA wastewater. A central composite design (CCD) has been developed for maximum removal of TPA, BA, *p*-TA, COD and minimum consumption of energy. Effects of various process parameters *viz.* pH: (5–13), current density: (49.5–255.5 A/m^2), supporting electrolyte concentration, NaCl: (0.25–2.25 g/L) and electrolysis time: (15–95 min) are studied on removal efficiencies of responses. Aluminium (Al) and iron (Fe) were selected as electrode materials. Maximum percentage removal of TPA: 56.21, 54.10; BA: 59.52, 53.84; *p*-TA: 45.71, 39.91, and COD: 49.91, 42.95 are achieved at optimum operating conditions by Al and Fe electrodes respectively. Operating cost of the process was calculated based on energy consumption, electrode consumption, sludge disposable, and transportation costs and found $13.64 and $14.46 per kg of COD removed by Al and Fe electrodes respectively. Sludge residues obtained after EC treatment at optimum operating conditions are analyzed by settling, sludge volume index (SVI), XRD, SEM/EDX, point of zero charge (PZC), FTIR and DGA/TGA.

1. Introduction

Purified terephthalic acid (PTA) wastewater mainly consists of terephthalic acid (TPA), benzoic acid (BA) and *para*-toluic acid (*p*-TA). These compounds contribute about 75% of the COD of PTA wastewater. High reproductive toxicity is exhibited by PTA wastewater on male mice and public health [1–2]. Aromatic compounds in PTA wastewater are responsible for damage in kidneys, bladder, testis, and liver [3–6]. Pollutants of PTA wastewater also diminish the density of viable spermatogenic cells, relative testis weights and responsible for histopathological abnormalities. It is also cause of acute toxicity, molecular toxicity, chronic toxicity, and subacute toxicity [2,7]. PTA wastewater is extremely toxic at concentrations higher than 1000 mg/L [8–10]. Toxic nature of PTA wastewater pollutants has been investigated by histopathological observation, hematological analysis and epidemiological investigation [4–5,11].

According to Zhang et al. [12] at lower concentration (15 mg/L at 10 °C), toxicity of TPA becomes very less (Non Toxic) but at higher concentration it is very harmful for human being and microorganisms [7]. According to World Health Organization (WHO) maximum tolerable intake capacity of BA for a human should not be more than 5 mg/kg of body weight per day. Due to toxic nature of BA, some countries have stopped the usage of BA as a food additive even in trace amount [13–14]. *Para*-toluic acid is also a major pollutant of PTA wastewater and characterized in the class of highly hazardous pollutants due to its toxic nature. It can be a cause of decrease in epididymal oligozoospermia. Due to toxic nature of TPA, BA and *p*-TA, USEPA added these pollutants in the list of priority pollutants [15–17].

Precipitating nature of TPA, BA and *p*-TA is similar to arsenic and depends on pH of the solution. The most common methods of removing arsenic from aqueous process streams are by precipitation as calcium arsenate, As(III) sulfide, or ferric arsenate [18–20]. The sulfide As_2S_3 has its lowest solubility below pH = 4, but that solubility is significantly higher than has been generally accepted. Calcium arsenates can be precipitated from As(V) solutions, by addition of lime at high pH (> 8) [20–21]. As(V) can also be precipitated from process solutions below pH = 2 with Fe(III) to form ferric arsenate, $FeAsO_4.2H_2O$. TPA, BA, and *p*-TA containing wastewater shows similar behavior at natural pH (~5.6). These compounds are present in PTA wastewater in the ionized state with these pK_a (TPA: 3.51; BA: 4.2; p-TA: 4.36) constants. These acids are precipitated in the solution at low pH (<5). Solubility of these compounds increases in the solution with increasing OH^- ions in the solution [22–24].

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Table 1
Electrocoagulation reactor specifications and electrodes characteristics.

Electrode characteristics		Reactor specifications	
Material (anode and cathode)	Al, Fe	Reactor type	Batch
Shape	Rectangular	Shape and material	Plexiglass (rectangular)
Size of electrode	11 cm × 6 cm × 0.1 cm	Dimensions	13 cm × 12 cm × 0.5 cm
Affected area of electrode	7 cm × 6 cm × 0.1 cm	Volume (m^3)	0.0016
No. of electrode	6	Stirring mechanism	Magnetic bar
Effective area	259.80 cm^2	Electrode gap (cm)	1 cm (constant)
Electrode arrangement	Parallel connection	Magnetic stirrer speed (RPM)	500–700 RPM (constant)

In India, no discharge limit has been prescribed for these compounds by pollution regulating agencies like Central Pollution Control Board (CPCB) or Ministry of Environment and Forest (MOEF). MOEF has given maximum permissible discharge limit of COD < 250 mg/L for petrochemical wastewater [25]. Hence, it is utmost important to determine the efficient methods for treatment of PTA wastewater to meet requirement of discharge limit.

In recent years, many researchers have worked on the treatment of PTA wastewater by various methods like anaerobic and aerobic biological treatment [26–34], electrochemical [35], adsorption [36–39], coagulation–flocculation [25,33,40], advanced oxidation processes (AOP)–UV assisted ozonation (UV/O_3), photo Fenton oxidation ($UV/H_2O_2/Fe_2SO_4$), ozone assisted photochemical oxidation ($UV/O_3/H_2O_2$), photo catalytic degradation, ozone assisted photo-Fenton oxidation ($UV/O_3/H_2O_2/FeSO_4$), supercritical water oxidation, radiation treatment (using γ-rays) [41–42], oxidation process [43–44], crystallization [45] and thermochemical precipitation [46].

Electrocoagulation (EC) is an important process used for treatment of various industries wastewater. In this process, coagulant ions are generated in-situ by electro-oxidation of anode. In recent years, EC process has been successfully applied for removal of dimethyl phthalate, indium, COD, and turbidity from chemical mechanical polishing (CMP) wastewater, polyvinyl alcohol, and salicylic acid from various industries wastewater [47–53].

Response surface methodology (RSM) is an important tool in Design Expert Software, which is mainly used for optimization of the various processes. In recent years, RSM has been successfully employed for treatment of various industries wastewater like chicken processing, rice mill, pulp and paper, chromium, petroleum refinery, shrimp cooking, tannery, cheese whey, textile, tetra-hydro-furan, electro-less plating industry *etc.* [54–64]. However, being such an important tool of optimization, it has never been used previously for this type of studies. Accordingly in present study, EC process has been employed for treatment of multicomponent aqueous solution of purified terephthalic wastewater using Al and Fe electrodes. RSM in Design Expert Software (8.0.7.1, 2010, Stat-Ease Inc. Minneapolis) was used for optimization of operating parameters (pH, current density, electrolysis time, and NaCl concentration) for maximum removal of TPA, BA, *p*-TA and COD simultaneously with minimum energy consumption. Sludge samples obtained after EC treatment at optimum operating conditions are also analyzed briefly. Operating cost of the process is also estimated based on energy consumption, electrode consumption, and sludge disposal and transportation costs.

2. Materials and methods

2.1. Chemicals and wastewater sample preparation

All the chemicals used in this study were of analytical reagent (AR) grade. Terephthalic acid ($C_8H_6O_4$), benzoic acid ($C_7H_6O_2$) and potassium dichromate ($K_2Cr_2O_7$) were supplied by Himedia Laboratories Pvt. Ltd. Mumbai, India. *Para*-toluic acid ($C_8H_8O_2$) and sodium chloride (NaCl) were supplied by Loba chemical Pvt. Ltd. Mumbai India. Sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), isopropyl alcohol (C_3H_8O), methanol (CH_3OH), acetic acid (CH_3COOH), silver sulfate ($AgSO_4$) and mercury (II) sulfate ($HgSO_4$) were purchased from Ranbaxy Chemical Limited, New Delhi, India.

Stock solutions of TPA (1000 mg/L), *p*-TA (1000 mg/L) and BA (1000 mg/L) were prepared at laboratory scale. Tap water purified by Millipore Milli-Q system was used. All wastewater samples and reagents were always preserved at 4 °C to reduce unwanted microorganism growth and biodegradation. Working concentrations of TPA (400 mg/L), BA (400 mg/L) and *p*-TA (500 mg/L) are chosen according to previous studies [25,28,46,65–67]. Initial COD of wastewater was estimated as 2055 mg/L.

3. Experimental procedure and analysis of samples

The experimental conditions for batch electrocoagulation study for treatment of synthetic multicomponent (TPA + BA + *p*-TA) wastewater are given in Table 1. Fig. 1 shows the schematic diagram of experimental setup. The ranges of operating parameters as determined by conducting initial test runs are given in Table 2. Direct current (DC) power supply with provision of varying voltage (0–24 V) and current (0–10 A) was used to power electrodes connected in parallel mode. All experiments were conducted at room temperature (25 ± 2 °C). Current density (CD) of the electrolytic solution was adjusted by using voltage regulator and variable rheostat (5–9Ω). pH of electrolytic solution was adjusted by (1 N, 2 N and 5 N) solutions of NaOH and H_2SO_4 during the whole experimentation. The collected samples were analyzed by using HPLC System with detector wavelength set to 240 nm [68–70]. HPLC was operated in isocratic mode with a C-18 column at ambient temperature. A solution of 91% Millipore water, 2% acetic acid, 7% isopropyl alcohol was used as a mobile phase [25,43] with 1.2 mL/min flow rate. Eqs. 1 and 2 were used for the calculation of percentage removal of TPA, BA, *p*-TA, or COD and energy consumption ($kWh/kgCOD_{removed}$) respectively.

$$\%\ \text{Removal of TPA, BA, } p-\text{TA and COD} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i and C_f are the initial and final concentrations of TPA, BA, *p*-TA or COD.

$$\text{Energy consumption}\left(\frac{\text{kWh}}{\text{kgCOD}_{\text{removed}}}\right) = \frac{\text{VIt} \times 100}{(\%\ \text{Removal of COD})C_{\text{CODi}} \times V_R} \times 1000 \quad (2)$$

where *V* is voltage, *I* is current, *t* is operating time in hours, VR is the volume of the wastewater treated in L and CCODi is the initial COD of wastewater, mg/L [71].

4. Results and discussion

4.1. Effect of pH, CD, time, and NaCl concentration on % removal of TPA, BA, p-TA and COD by Al and Fe electrodes

All experimental runs were conducted according to sets predicted by central composite design (CCD) as given in Table 3. The removal