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Comparative study of electrochemical oxidation and electrochemical Fenton processes for simultaneous degradation of phthalic and para-toluic acids from aqueous medium

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ABSTRACT

Degradation of binary component of purified terephthalic acid wastewater viz. phthalic acid and para-toluic acid from aqueous medium was investigated in this study. Aqueous solution was initially subjected to acid precipitation treatment at various pH (2–4) and temperature (15–60 °C). After acid treatment, the solution was further subjected to electrochemical oxidation and electrochemical Fenton treatments using graphite electrodes. During electrochemical treatments, effect of process variables such as initial pH: (1–9), current density: (30.48–91.45 A/m^2), NaCl concentration: (0.5–1.5 g/L), Fe^{2+} concentration: (0.5–1.5 mmol/L) and time: (15–95 min) was studied and optimized through central composite design. Maximum removal efficiencies during electrochemical oxidation treatment were 64.55%, 60.24% and 62.77% for phthalic acid, para-toluic acid and chemical oxygen demand respectively with an electric energy consumption of 28.50 kWh/kgCODremoved at optimum conditions. The removal capacities during electro-Fenton treatment were found 75.21%, 65.19% and 68.15% for phthalic acid, para-toluic acid and chemical oxygen demand respectively with 20.11 kWh/kgCODremoved energy consumption at optimum conditions. Both processes were compared based on removal efficiencies, electric energy consumption, kinetics and sludge characteristics. Sludge generated after electrochemical treatments was analyzed by various characterization techniques. In order to get maximum removal efficiencies and minimum energy consumption, electrochemical Fenton method was found more effective than electrochemical oxidation during this study.

1. Introduction

Purified terephthalic acid (PTA) is an important starting material for the manufacturing of synthetic products mainly polyester fibres and plastics [1–2]. Approximately 3-4 m^3 of wastewater with a COD of 4–10 kgCODm^{-3} is generated during per ton of PTA production [3]. The major aromatic compounds present in PTA wastewater are benzoic acid (BA), phthalic acid (PA), para-toluic acid (p-TA), terephthalic acid (TA), 4-carboxybenzaldehyde, whose contribution to the COD are >75% in the wastewater [4–6]. These aromatics show chronic, acute and molecular toxicity to the organisms and are also known to cause for the damage of liver, bladder, kidneys and histopathological abnormalities [7–9]. Some of these aromatics or its products have adverse impacts on human developmental and reproductive systems. Their intermediate degradation products have also endocrine-disrupting, teratogenic, and carcinogenic properties [10–14]. Due to the high toxicity and adverse effects, United States Environmental Protection Agency (USEPA) has added these aromatics in priority pollutants list [15]. Therefore, it is highly essential to treat the wastewater containing these toxic aromatic acids so as to reduce its pollution load within the prescribed limit. The Central Pollution Control Board, Government of India has proposed the effluent discharge limits from a petrochemical plant into surface waters in terms of COD (≤250 mg/L) [16]. Several biological and physico-chemical treatment methods have been applied for the remediation of wastewater containing these hazardous compounds in the recent years. Compared with these techniques, electrochemical methods emerge as a good option due to their better efficiency, automation, low sludge generation and eco-friendly properties [17–18]. Recently, electrochemical techniques have received much more attention for the treatment of wastewater containing organic pollutants. Electrochemical techniques are becoming a strong alternative

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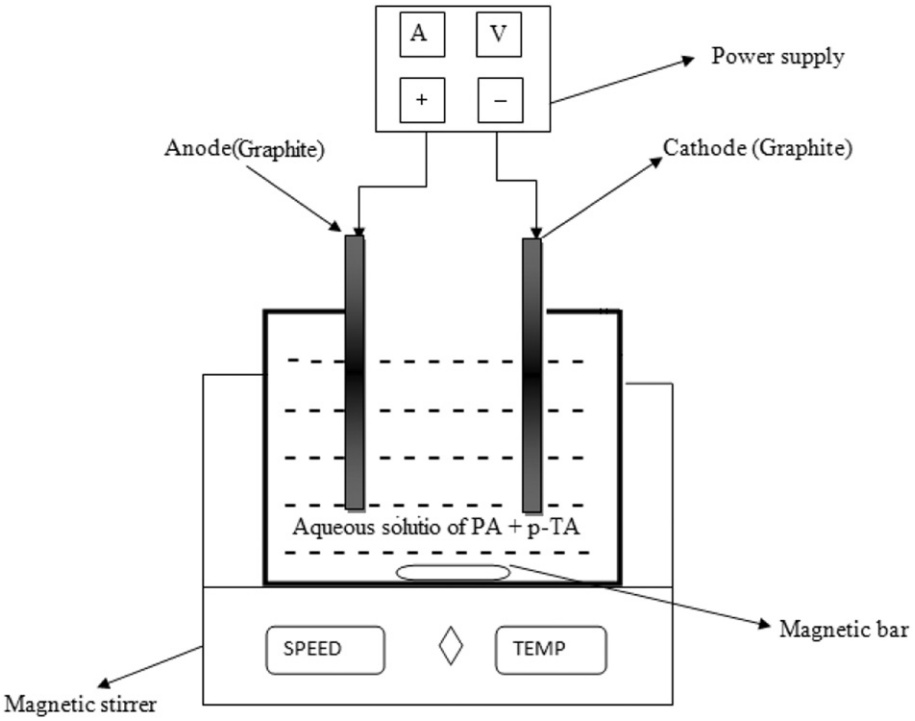

Fig. 1. Experimental set up for EO and EF treatment.

for wastewater remediation due to generation of huge amount of toxic wastewaters through industrial processes which are not easily biodegradable, and need costly physical or physiochemical pretreatments [19].

1.1. Electrochemical oxidation (EO)

EO is one of the most effective electrochemical techniques for degradation of organic pollutants present in wastewater. EO takes place through various oxidants like hydrogen peroxide (H_2O_2), nascent oxygen, free chlorine and radicals viz. Cl, ClO and hydroxyl radicals (OH•). EO can be performed by either indirect or direct ways. Indirect EO use electrochemically generated strong oxidants such as hydrogen peroxide and hypochlorite/chlorine for pollutants degradation. Direct EO or anodic oxidation occurs through physically adsorbed "active oxygen generated on anode surface [20–21]. EO using graphite electrodes occurs through combination of direct oxidation at anode surface and indirect oxidation of in-situ generated oxidizing agents [22–23]. During EO, hydroxyl radicals (OH•) generated at anode as can be seen by following reactions [24].

$$H_2O \rightarrow H^+ + OH^{\cdot} + e^- \quad (1)$$

$$OH^- \rightarrow OH^{\cdot} + e^- \quad (2)$$

However generation of anodic oxygen takes place as a primary reaction by following reaction [20,24].

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \quad (3)$$

In indirect EO, chloride salts of potassium or sodium are added to the wastewater for the generation of hypochlorite ions (OCl^-) and also for better conductivity of the solution [25]. The formation of chlorine by anodic oxidation of chloride is given as

$$2Cl^- \rightarrow Cl_2 + e^- \quad (4)$$

Table 1
Operating parameters and their levels obtained from the statistical software for EO process.

Central composite design characteristics				
Levels	Parameter (range)			
	X_1	X_2	X_3	X_4
	pH (1–9)	CD (A/m^2) (30.48 → 91.44)	NaCl concentration ($\frac{g}{L}$) (0.5 → 1.5)	Time (min) (15 → 95)
−2(−α)	1	30.48	0.5	15
−1	3	45.72	0.75	35
0	5	60.96	1	55
+1	7	76.20	1.25	75
+2(α)	9	91.44	1.5	95