Research article

Comparison of phthalic acid removal from aqueous solution by electrochemical methods: Optimization, kinetic and sludge study

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ABSTRACT

In this work, comparative study between electrochemical processes such as electrocoagulation (EC), peroxi-coagulation (PC) and peroxi-electrocoagulation (PEC) was performed for the removal of phthalic acid (PA) and chemical oxygen demand (COD) from aqueous medium. Initially, acid treatment was studied at various pH (1—3) and temperature (10—55 °C). Subsequently, the supernatant was re-treated by electrochemical processes such as EC, PC and PEC separately. Independent parameters viz. pH, current density (CD), electrolyte concentration (m), electrode gap (g), H_2O_2 concentration and electrolysis time (t) were optimized by Central Composite Design (CCD) for these electrochemical processes. All three processes were compared based on removal, energy consumption, kinetic analysis, operating cost and sludge characteristics. In this study, PEC process was found more efficient among EC, PC and PEC processes in order to get maximum removal, minimum energy consumption and minimum operating cost. Maximum removal of PA- 68.21%, 74.36%, 82.25% & COD- 64.79%, 68.15%, 75.21% with energy consumption - 120.95, 97.51, 65.68 (kWh/kg COD removed) were attained through EC, PC and PEC processes respectively at their corresponding optimum conditions. Results indicated that PA and COD removals are in order of PEC > PC > EC under optimum conditions. First order kinetic model was found able to describe the degradation kinetics and provided best correlation for the removal rate within the acceptable error range.

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1. Introduction

A large number of aromatic compounds are formed during processing of petroleum and natural gas. Para (p-) xylene is one of such aromatic compound used for the production of purified terephthalic acid (PTA). PTA is extensively used as the raw material for the manufacture of polyethylene terephthalate bottles, polyester, polyester films, textile fibers and many other products (Macarie et al., 1992; Moraes et al., 2004; Joung et al., 2009). PTA manufacturing process is carried out by oxidation of para-xylene using manganese or cobalt salt catalyst. The PTA manufacturing process mainly consists following three steps: (a) Oxidation of p-Xylene into crude terephthalic acid (CTA) (b) Hydrogenation/Purification of CTA to PTA (c) Recovery and regeneration of catalyst. The main sources of wastewater generation during PTA production are cleaning and washing water, catalyst recovery section water, distillate acid water and PTA scrubbing water. PTA scrubbing unit generates maximum amount of

wastewater, followed by distillate acid water, catalyst recovery and cleaning water (Pophali et al., 2007). Block diagram representation of PTA manufacturing process is shown in Fig. 1. Approximately, 3—4 m^3 wastewaters with a COD load 5—20 g/L is generated for per ton of PTA (Karthik et al., 2008; Macarie and Guyot, 1992). The wastewater generated during PTA manufacturing process contains of toxic compounds like phthalic acid (PA), *para*-toluic acid (p-TA), terephthalic acid (TPA), benzoic acid (BA), and 4-carboxybenzaldehyde (4-CBA) (Kleerebezem et al., 1997, 1999a,b; Zhang et al., 2010). These aromatics contribute approximately 75% of the COD of PTA wastewater. Phthalic acid (PA) is the major pollutants of PTA wastewater present in high concentration. PA and its derivatives are important industrial materials used for the manufacture of products such as toys and bottles, plasticizers, polymers, films, adhesives etc. On the other side, phthalates have adverse impacts on humans and environments due to their toxic, carcinogenic, and endocrine disrupting effects (Chen and Sung, 2005; Parkerton and Konkel, 2000; Zhu et al., 2010). Within this context, United States Environmental Protection Agency (USEPA) was proposed phthalic acid and some of their phthalates as priority pollutants (USEPA, 1994). Therefore, it is very essential to find
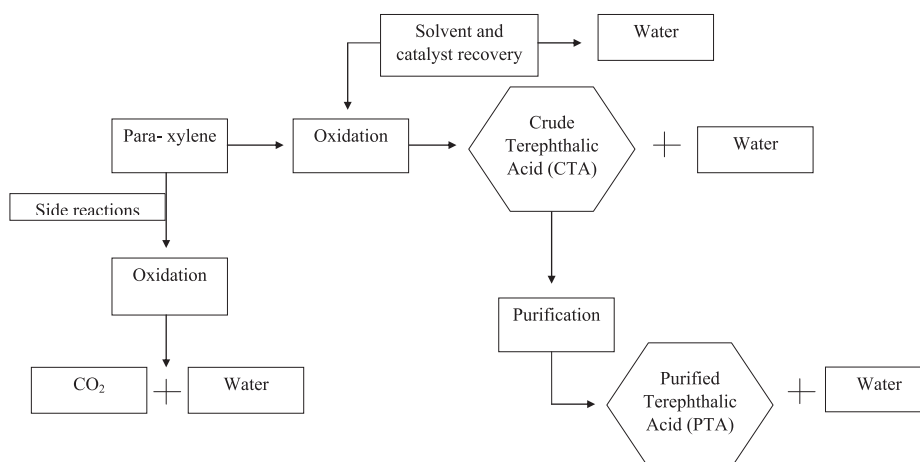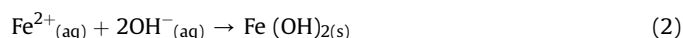
Fig. 1. Block diagram of PTA manufacturing process.

efficient techniques to treat wastewater containing these hazardous aromatics before its use or discharge. Recently, electrochemical techniques have attracted much attention for treatment of organic compounds from wastewater. Electrochemical processes are versatile in treatment of different wastewaters having various qualities such as automation, economic, high efficiency and low sludge formation features. During electrochemical treatments, iron anode can play both roles of coagulant and catalyst. However, reduction and oxidation reactions in electrochemical cell influence formation of iron species thereby determining the system function (Ghanbari and Moradi, 2015; Atmaca, 2009). Electrocoagulation (EC) is an effective technology to treat pollutants from wastewater where sacrificial anodes are used to produce active coagulant precursors. In EC, in situ generation of coagulants occurs by electrically dissolving metal ions at anode, while hydrogen gas (H_2) is evolved at the surface of cathode. Metal hydroxides flocs formed during coagulation are responsible for pollutants removal by charge neutralization, adsorption and sweep flocculation. Ultimately, these flocs are removed through sedimentation or flotation (Chen, 2004; Mollah et al., 2004; Holt et al., 2005). The main reactions of EC process are as follows (Sengil and Ozacar, 2006).
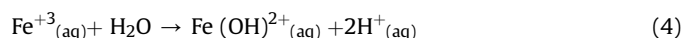
In EC process;

At anode:

$$2Fe_{(s)} \rightarrow 2Fe^{2+}_{(aq)} + 4e^- \tag{1}$$

$$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe\,(OH)_{2(s)} \tag{2}$$

At cathode:

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

Overall:

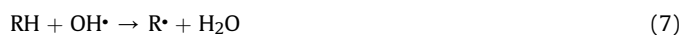$$Fe^{+3}_{(aq)} + H_2O \rightarrow Fe\,(OH)^{2+}_{(aq)} + 2H^+_{(aq)} \tag{4}$$

In peroxi-coagulation (PC) process, generation of both reagents of Fenton reaction i.e. hydrogen peroxide (H_2O_2) and Fe^{2+} ions takes place simultaneously. In this process, probability of reaction of Fe^{2+} with H_2O_2 is high due to simultaneous production of both reagents (Brillas et al., 2009; Sirés and Brillas, 2012). While in peroxi-electrocoagulation (PEC) process H_2O_2 is externally added into the electrocoagulation system and an iron anode acts as source of Fe^{2+} ions (Losito et al., 2008).

In PC treatment, H_2O_2 is generated at cathode as shown below.

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

During PC and PEC processes, H_2O_2 is catalyzed through Fe^{2+} ions to form hydroxyl radicals (•OH- a strong oxidant with high oxidation potential) as discussed below (Paterlini and Nogueira, 2005; Neyens and Baeyens, 2003; Ma et al., 2005; Sandhwar and Prasad, 2017a,b,c,d).

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

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

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

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

where, RH is an organic pollutant.

Proper investigations of previous studies reveal that it has not been studied related to comparison of three electrochemical processes (i.e. EC, PC and PEC) using iron and graphite as anode and cathode for phthalic acid treatment from aqueous solution. The main objective of this research work is to compare the efficiency of EC, PC and PEC processes for the better and optimized treatment of aqueous solution containing phthalic acid. Various effective optimization techniques were used previously in the different processes (Alwan, 2015). Response Surface methodology is one of the most efficient tools for the process optimization. In this study, entire electrochemical experiments were carried out based on central composite design under response surface methodology.

2. Materials and methods

2.1. Materials

Analytical grade chemicals were used in this study. Phthalic acid ($C_6H_4\,(COOH)_2$) was supplied by Sisco Research Laboratories Pvt. Ltd. Mumbai, India. Acetic acid (CH_3COOH), sodium sulphate (Na_2SO_4), sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2), methanol (CH_3OH), mercury (II) sulphate ($HgSO_4$), potassium dichromate ($K_2Cr_2O_7$), and silver sulphate (Ag_2SO_4) and 2-propanol (C_3H_8O) were purchased from Ranbaxy Fine Chemical Ltd, Delhi, India.