PEROXI-COAGULATION TREATMENT OF SIMULATED PETROCHEMICAL WASTEWATER: PROCESS OPTIMIZATION BY RESPONSE SURFACE METHODOLOGY

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Abstract : In the recent years, petrochemicals are being extensively used in various chemical industries. Among various petrochemicals, purified terephthalic acid (PTA) is a widely applicable petrochemical product. Large amount of wastewater containing various toxic compounds is generated during PTA production. para-Toluic acid (p-TA) is one of the major pollutants of PTA wastewater. The present study emphasizes on the treatment of synthetic petrochemical wastewater containing p-TA (400 mg/L) by peroxi-coagulation (PC) process. Optimization of operating parameters viz. pH, current density, electrode distance, and electrolysis time during PC treatment was performed by Response Surface Methodology. Maximum removal of p-TA- 77.40% and COD- 71.50% was obtained with minimum electrical energy consumption (kWh/kg CODremoved)- 22.32 at optimum operating conditions.

Index Terms - para-Toluic acid; Box Behnken Design; Peroxi-coagulation; Optimization; Petrochemical

I. INTRODUCTION

Purified terephthalic acid (PTA) is a petrochemical product manufactured by oxidation of p-xylene [1]. PTA is extensively applicable as a raw material during the production of fibres, textile, dyes, plastic bottles, pesticides etc. [1-2]. Large amount of wastewater (3000-4000 litres) having high COD value (4-10 $kgCODm^{-3}$) is generated during per ton of PTA production [3]. Various toxic aromatic compounds viz. para-toluic acid, benzoic acid, terephthalic acid, phthalic acid, and 4-carboxybenzaldehyde etc. are present in high concentration in PTA wastewater [4-6]. Toxic compounds present in PTA wastewater exhibit carcinogenic effects and also other harmful effects on human liver, bladder, kidneys etc [6-10]. Therefore, it is essential to treat the aqueous solution containing these toxic compounds before its use or surface discharge. Several treatment techniques such as extraction, adsorption, oxidation, and electrochemical methods etc. have been applied to treat PTA wastewater. But having properties like high efficiency, economic and environmental friendly, electrochemical techniques are being effectively used for wastewater treatment having toxic contaminants. PC is an electrochemical advance oxidation process. During PC treatment, ferrous ions (Fe^{2+}) and hydrogen peroxide (H_2O_2) are electrochemically produced and due to simultaneous production of both Fenton's reagents (i.e. H_2O_2 with Fe^{2+}), probability of reaction between H_2O_2 with Fe^{2+} is high [11-13].
Major reactions during PC treatment are;

At anode
$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^- \qquad (1)$$
At cathode
$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (2)$$
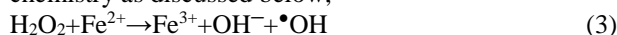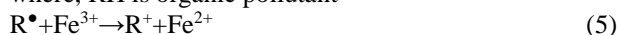After production of Fenton's reagents during treatment, formation of hydroxyl radicals ($^\bullet$OH) takes place via Fenton's reaction chemistry as discussed below;
$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + {}^\bullet OH \qquad (3)$$
$$RH + {}^\bullet OH \rightarrow R^\bullet + H_2O \qquad (4)$$
where, RH is organic pollutant
$$R^\bullet + Fe^{3+} \rightarrow R^+ + Fe^{2+} \qquad (5)$$
$$Fe^{2+} + {}^\bullet OH \rightarrow Fe^{3+} + OH^- \qquad (6)$$

In the present study, treatment of p-TA from aqueous medium was performed by PC method. This process was optimized through Box Behnken Design (BBD) under Response Surface Methodology (RSM). RSM is an important and efficient tool for the optimization of process. Effect of process variables such as pH, current density (CD), electrode distance and electrolysis time was studied and optimized to obtain maximum removals and minimum electrical energy consumption (EEC). Analytical grade chemicals were used during entire study. para-Toluic acid (99% purity) was procured from Loba Chemie Pvt. Ltd., Mumbai (India). All other chemicals like sodium chloride (NaCl), sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), potassium dichromate ($K_2Cr_2O_7$), isopropyl alcohol (C_3H_8O), silver sulphate (Ag_2SO_4) etc. were supplied from RCFL, New Delhi (India).

II. PREPARATION OF SYNTHETIC WASTEWATER AND ANALYSIS OF SAMPLE

Aqueous solution of p-TA (400 mg/L) was prepared with distilled water at laboratory scale. Concentration of p-TA was taken according to previous studies [14] and measured through HPLC (Waters, USA). All the samples and reagents are kept at 4 ºC to prevent biodegradation. Initial COD of the solution was found 836 mg/L by COD analyzer (Aqualytic, Germany). In this study, removal efficiency and energy consumption was estimated by following equations [15-16].

$\%\text{Removal} = \dfrac{c_i - c_f}{c_i} \times 100$ (7)

where, C_i- initial concentration, C_f- final concentration

$\text{Electrical energy consumption (kWh/kgCODremoved)} = \dfrac{VIT \times 100}{(\% \text{ Removal of COD})C_{CODi} \times V_S} \times 1000$ (8)

where V- voltage, I-current (amp), T- time (hour), C_{CODi} – initial COD (mg/L) and V_S- volume of aqueous solution (liter)

III.   EXPERIMENTAL PROCEDURE

Peroxi-coagulation treatment of simulated petrochemical wastewater (p-TA= 400 mg/L) was conducted in an open batch cell having volume of 1.7 liter. Iron and graphite are used as anode and cathode respectively during treatment. The effective electrode area was 131.2 cm^2. NaCl (0.5g/L) was used as a supporting electrolyte during PC treatment. Prior to electrolysis, air was bubbled (2.5 L/min) through a fish aerator to saturate the solution with oxygen until the completion of each run favouring in situ generation of H$_2$O$_2$ at cathode surface. The schematic diagram of experimental setup is shown in Fig.1.
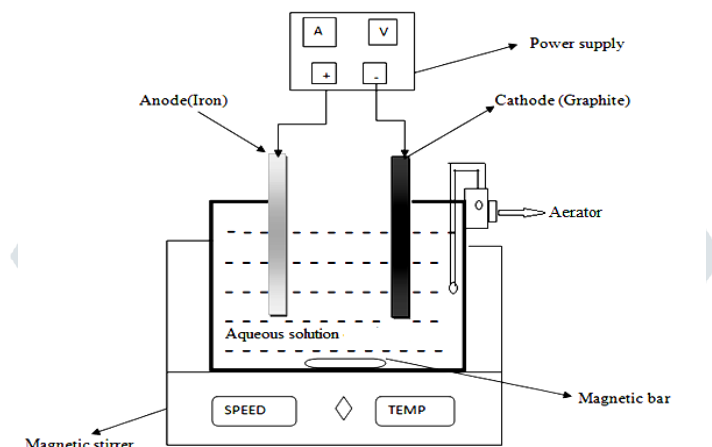

Fig.1. Schematic diagram of experimental set up for PC treatment

Range of operating parameters was estimated by some random test runs for PC treatment as shown in Table 1. Entire PC experiments were carried out at operating conditions given by RSM under CCD design

Table 1: Process Variables and Their Ranges Obtained By CCD For PC Process

Levels	Box Behnken Design characteristics			
	Parameter (Range)			
	X_1 pH (1-5)	X_2 CD (A/m^2) (45.72→76.20)	X_3 Electrode gap (cm) (1→3)	X_4 Time (min) (20→80)
-1(-α)	1	45.72	1	20
0	3	60.96	2	50
+1(α)	5	76.20	3	80

IV. RESULTS AND DİSCUSSİON

A. EFFECT OF OPERATING PARAMETERS ON REMOVAL EFFICIENCY AND ENERGY CONSUMPTION

Effect of operating parameters such as pH, current density (CD), electrode gap and time were studied on p-TA and COD removals and energy consumptiion during PC treatment as shown in Figs. 2(a-f). Removal was found more at acidic conditions. This is due to the generation of metal hydroxide flocs and hydroxyl radicals (•OH) at acidic pH [17-18]. At very low pH, formation of oxonium ion (H$_3$O$_2$+) occurs instead of •OH and at high pH, H$_2$O$_2$ decomposes into H$_2$O and O$_2$ resulting lower removal [19]. Higher CD favors more amount of charge generation as well as •OH production, resulting high removal. But beyond optimum

CD, removals decrease due to low charge generation. Simultaneously removal increases with time and beyond optimum value it starts decrease due to the consumption of charges. It is also found the optimum electrode distance during PC treatment where removal was higher. Beyond this value removal decreases due to more distance covered by charges and particles in the solution. (Electrical energy consumption) EEconsumptiion strongly depends on CD and time as shown in Eq [8]. Beyond the obtained optimum conditions, energy consumption increases with high CD and time as well as due to lower COD removal.
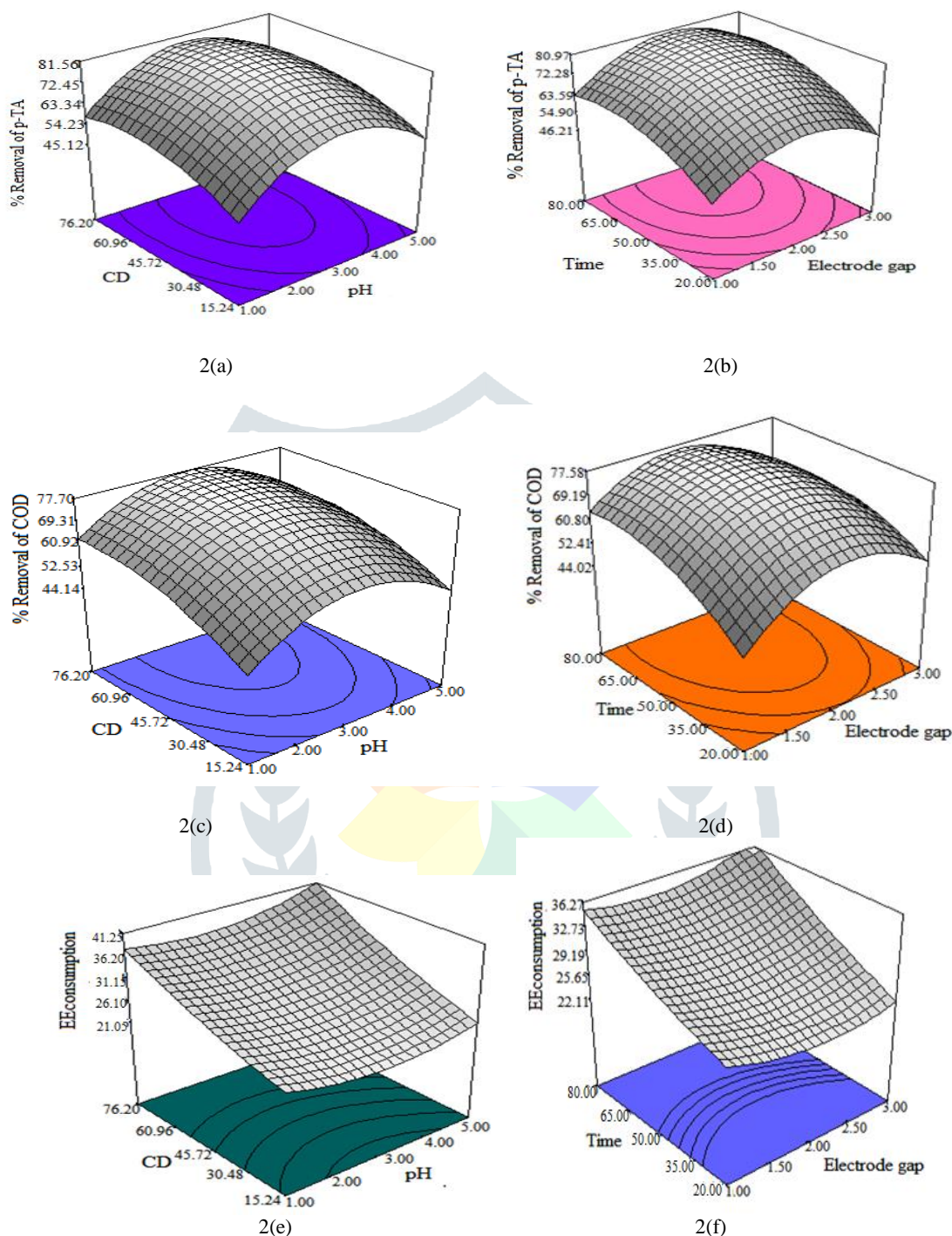

2(a)   2(b)

2(c)   2(d)

2(e)   2(f)

Fig. 3. Effects of pH, CD, electrode gap and time on removal efficiency and energy consumption

B. OPTİMİZATİON STUDY

PC process was optimized to get higest removal and lowest energy consumption. The optimum conditions and the optimized result are shown in Table 2. It can be observed that BBD model was found highly efficient due to the closeness of BBD predicted and experimental test results as shown below.

Table 2: Optimum Operating Conditions Predicted By BBD And Experimental Test Run By PC Process

pH	CD (A/m²)	Electrode gap (cm)	Time (min)	% Removal of p-TA		% Removal of COD		EEconsumption (kWh/kg COD removed)	
				BBD Pre.	Test Run	BBD Pre.	Test Run	BBD Pre.	Test Run
3	52.44	2	55.12	77.40	73.21	71.50	69.15	22.32	24.16

V. CONCLUSIONS

In the present work, peroxi-coagulation treatment of simulated petrochemical containing para-toluic acid was performed. Maximum removal of p-TA- 77.40% and COD- 71.50% with minimum energy consumption 22.32 kWh/kg COD$_{removed}$ was obtained at optimum pH- 3, CD- 52.44 A/m², electrode gap- 2 cm and time- 55.12 min. Closeness of model predicted and experimental results shows an efficient CCD developed model.

REFERENCES

[1] H.A. Wittcoff, B.G. Reuben and J.S. Plotkin, "Industrial Organic Chemicals", 2nd ed., Wiley-Interscience, 2004.

[2] R. Kleerebezem, L.W. Hulshoff Pol and G. Lettinga, "High rate treatment of terephthalic acid production wastewater in a two-stage anaerobic bioreactor", Biotechnol. Bioeng., vol. 91, pp. 169–179, 2005.

[3] H. Macarie and J.P. Guyot, "Inhibition of the methanogenic fermentation of p-toluic acid (4-methylbenzoic acid) by acetate", Appl. Microbiol. Biotechnol., vol. 38, pp. 398–402, 1992.

[4] R. Kleerebezem, L.W. Hulshoff Pol and G. Lettinga, "Anaerobic biodegradability of phthalic acid isomers and related compounds", Biodegradation, vol. 10, pp. 63–73, 1999.

[5] R. Kleerebezem, L.W. Hulshoff Pol and G. Lettinga, "The role of benzoate in anaerobic degradation of terephthalate". Appl. Environ. Microbiol., vol. 65, pp. 1161–1167, 1999.

[6] X.X. Zhang, S. Sun, Y. Zhang, B. Wu, Z.Y. Zhang, B. Liu, L.Y. Yang and S.P. Cheng, "Toxicity of purified terephthalic acid manufacturing wastewater on reproductive system of male mice (Mus musculus)", J. Hazard. Mater., vol. 176 pp. 300–5, 2010.

[7] R.B. Meyer, A. Fischbein, K. Rosenman, Y. Lerman, D.E. Drayer and M.M. Reidenberg, "Increased urinary enzyme excretion in workers exposed to nephrotoxic chemicals", Am. J. Med. vol. 76, pp. 989–98, 1984.

[8] L. Cui. Y. Shi, G. Dai, H. Pan, J. Chen, L. Song, S. Wang, H.C. Chang, H. Sheng and X. Wang, "Modification of n-methyln- nitrosourea initiated bladder carcinogenesis in wistar rats by terephthalic acid", Toxicol. Appl. Pharmcol., vol. 210, pp. 24–31, 2006.

[9] L. Cui, G. Dai, L. Xu, S. Wang, L. Song, R. Zhao, H. Xiao, J. Zhou and X. Wang, "Effect of oral administration of terephthalic acid on testicular functions of rats", Toxicology., vol. 201, pp. 59–66, 2004.

[10] J.C. Lamb, R.E. Chapin, J. Teague, A.D. Lawton and J.R. Reel, "Reproductive effects of four phthalic acid esters in the mouse", Toxicol. Appl. Pharmcol., vol. 88, pp. 255–69, 1987.

[11] E. Atmaca, "Treatment of landfill leachate by using electro-Fenton method", J. Hazard. Mater., vol. 163, pp. 109–114, 2009.

[12] A. Eslami, M. Moradi, F. Ghanbari and F. Mehdipour, "Decolorization and COD removal from real textile wastewater by chemical and electrochemical Fenton processes: a comparative study", J. Environ. Health Sci. Eng. vol. 11, pp. 31, 2013.

[13] E. Brillas, I. Sirés and M.A. Oturan, "Electro-Fenton process and related electrochemical technologies based on Fenton's reaction chemistry", Chem. Rev., vol. 109, pp. 6570–6631, 2009.

[14] S.K.F. Marashi, H.R. Kariminia and I.S.P. Savizi, "Bimodal electricity generation and aromatic compounds removal from purified terephthalic acid plant wastewater in a microbial fuel cell", Biotechnol. Lett., vol. 35, pp. 197–203, 2013.

[15] V.K. Sandhwar and B. Prasad, "A comparative study of electrochemical degradation of benzoic acid and terephthalic acid from aqueous solution of purified terephthalic acid (PTA) wastewater, Journal of water process engineering. doi: 10.1016/j.jwpe.2017.03.006.

[16] V.K. Sandhwar and B. Prasad, "Terephthalic acid removal from aqueous solution by electrocoagulation and electro-Fenton methods: process optimization through response surface methodology", Process Saf. Environ. Prot., vol. 107, pp. 269–280, 2017.

[17] M. Kallel, C. Belaid, R. Boussahel, M. Ksibi, A. Montiel and B. Elleuch, "Olive mill wastewater degradation by Fenton oxidation with zero—valent iron and hydrogen peroxide", J. Hazard. Mater., vol. 163, pp. 550–554, 2009.

[18] R.J. Watts, M.K. Foget, S.H. Kong and A.L. Teel, "Hydrogen peroxide decomposition in model subsurface systems", J. Hazard. Mater., vol. 69, pp. 229–243, 1999.

[19] M. Zhou, Q. Yu, L. Lei and G. Barton, "Electro-Fenton method for the removal of methyl red in an efficient electrochemical system", Sep. Purif. Technol., vol. 573, pp. 380–387, 2007