Experimental Studies on Electrochemical and Photo Oxidation of Effluent Containing Ethyl Benzene and Optimization Using RSM

D. Prabhakaran, T. Kannadasan, M. Thirumarimurugan, and C. Chellamboli

***Abstract*—In this paper, comparative studies were carried out on electrochemical and photo oxidation processes to degrade the synthetic effluent containing ethyl benzene. The electrochemical oxidation was carried out in galvanostatic mode with lead oxide as anode and a stainless steel plate as the cathode in the presence of 2 g/L of NaCl has been added as a supporting electrolyte. The electrochemical treatment was optimized by response surface methodology (RSM), which results in 73.42 % was the highest percentage of COD removal, and the optimum conditions were satisfied at current density 1.82 A/dm^2, time 2 h, flow rate 10 l/h, volume 3.63 L occurs at minimum power consumption 15 kWh/kg COD. It was followed by the photo oxidation process was carried out in the presence of Ultra Violet radiation emitted from Ultra Violet source was investigated. From the study, it was observed that percentage of COD reduction, and Biodegradability Index was found to be the maximum of 98.42 % and 0.712 respectively, the optimized irradiation time was 45 minutes for pretreated effluent has been investigated. This combined method appears to be a promising technology and has potential application for environmental remediation.**

***Index Terms*—COD reduction, electrochemical, photo oxidation, RSM.**

I. Introduction

Water is not a commercial product but, rather, a heritage which must be protected, defended and treated as such. The wastewater are generated from different processes contains various contaminants it depends upon process, mainly pharmaceutical, textile, acrylic Fiber, pesticides and other organic chemicals manufacturing industries generate waste water [1], [2], [3]. Degradation of these non-biodegradable organic compounds is impossible in conventional biological treatment processes [8], [4].

Ethyl benzene is a toxic aromatic compound found as a component of petroleum hydrocarbons. Often ethyl benzene enters the environment in the form of industrial discharges from petroleum refining, plastic, resins and pharmaceutical industrial effluents or oil spills. Ethyl benzene also finds wide application as starting material in the preparation of styrene that is used as a solvent for coatings, and in making rubber and plastic wrap. The US Environmental Protection Agency's has found that short-term exposure of ethyl benzene at levels above 0.7 ppm cause's drowsiness, fatigue, headache and mild eye and respiratory irritation. The long-term exposures to ethyl benzene can potentially damage the liver, kidneys, central nervous system and eyes. Hence, ethyl benzene is considered as one of the priority pollutants [5], [7]. Electrochemistry can play many roles in clean technology and pollution-control [1]. Photo degradation oxidizes harmful environment pollutants and converts it into harmless innocuous substances [6].

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D. Prabhakaran, T. Kannadasanwas, and M. Thirumarimuruganis are with the Coimbatore Institute of Technology, Coimbatore, Tamil Nadu, India (e-mail: dprabhakaran68@gmail.com, kannadasan@cit.edu.in, thirumarimurugan@cit.edu.in).

C. Chellamboli is with the National Institute of Technology, Coimbatore, Tamil Nadu, India (e-mail: c.chilambu@gmail.com).

II. Experimental Setup

A. Electrochemical Treatment

Electrochemical Oxidation experiment was conducted in batch electrolytic cell with recirculation (Fig. 1) was used. The experimental setup consists of an undivided electrolytic cell of 300 ml working capacity, closed with a PVC lid having provisioned to fix a cathode and an anode electrode keeping at a distance of 2.5 cm. A salt bridge with reference electrode was inserted through the holes provided in the lid. The electrode used lead oxide as an anode in the form of expanded mesh (of area 39.2 cm^2) was employed, and a stainless steel plate (of dimension 8.0 cm × 8.0 cm × 0.2 cm) was used as the cathode. A multi-output 2A and 30V (DC regulated) power source (with ammeter and voltmeter) was connected to the cell. Recirculation through an electrochemical oxidation system was done with Centrifugal pump, and the flow rate was measured by a rotameter. The electrolyte taken was synthetic effluent containing Ethyl benzene in water.

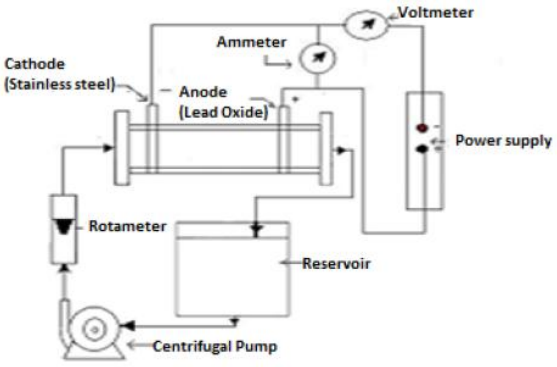

Fig. 1. Schematic representation of electrochemical oxidation system.

B. Photo Oxidation Method

Photo oxidation is a process in which pretreated effluent is passed through a UV reactor for degradation. The pretreated

effluent contains ethyl benzene and this process is carried out in the absence of supporting catalyst. The pretreated effluent is allowed to flow through the walls of the reactor as thin film. Ultraviolet lamp is provided inside the reactor for Ultraviolet irradiation to initiate the reaction. Here the effluent is recirculated for further degradation process. COD was determined periodically to know the extent of degradation of the effluent in the reservoir. The schematic representation of the set up is shown in Fig. 2.

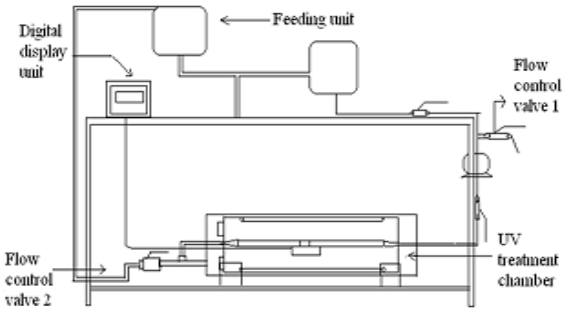

Fig. 2. Schematic representation of ultraviolet radiation reactor.

III. Experimental Procedure

Electrochemical oxidation process was carried out in a room temperature using a colourless synthetic effluent containing ethyl benzene having COD in the range of 610 to 680 mg/L. A known quantity (2 L to 6 L) of effluent has been taken in electro-oxidation reactor and subjected to input of electricity (current density 1 to 5 A/dm^2), and the flow rate of 10 to 65 L/h as demanded by Box-Behnken method in the first step of operation to improve biodegradability. The volume of the reactor cell is 0.098 dm^3. The effluent treated in this reactor cell is re-circulated to the reservoir. In electrolysis, NaCl has been added to the effluent prior to electrolysis as a supporting electrolyte with the concentration of 2 g/L. The concentration of the reactant (COD) and the products in the batch reactor are a function of time. The electrolysis can be carried out in any of the two modes galvanostatic and potentiostatic. The present study was galvanostatic. After electrolysis, to subside all the chemical reactions, the content of the reactor was kept idle for 12 h.

TABLE I: Experimental Range and Levels of Independent Process Variables for Batch Recirculation Reactor

Factors	Unit	Range and levels		
		-1	0	+1
Flow rate	L/h	10	35	60
Current density	A/dm^2	1	3	5
Volume	L	2	4	6
Time of reaction	h	1	1.5	2

In the second step, photo oxidation was carried out by subjecting ultraviolet radiation in pre-treated effluent containing Ethyl benzene and this process was done in an UV Reactor. Charge the reactor with the water solution (1 l), circulate water through the reactor and switch on the Ultra Violet radiation lamp for 15 min (time needed for Pen Ray Ultra Violet radiation lamp to reach steady energy output). Effluent was circulated by the centrifugal pump at a recirculation rate 180 L/h. Samples were withdrawn at different time intervals and after completing the process clean the reactor with water otherwise it corrodes the equipment. The Samples were used later for COD, BOD and pH test analysis.

IV. Results

By using a first-degree polynomial model an approximation was done. Compared to other simulation model this RSM model is easy to estimate and apply, even when little is known about the process. The analysis is done which is focused on how the COD reduction and power consumption are influenced by independent variables, i.e., electrolyte volume, current density, electrolyte flow rate and time. The dependent output variable was maximum.

A. Response 1 - % Reduction of COD

The final quadratic equation obtained for Percentage COD reduction is given below in equation (1).

% of COD Removal,

$$Y1 = +66.01 - 2.07A + 3.280833B - 2.53C + 4.589167D - 1.515AB + 0.2425AC - 1.4875AD - 0.945BC - 0.725BD - 1.9625CD - 0.95917A^2 - 1.06042B^2 - 1.55667C^2 - 1.5804D^2 \quad (1)$$

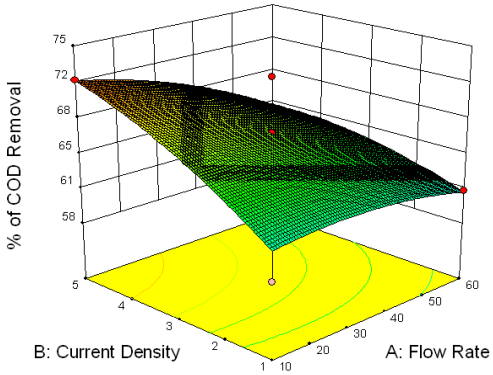

Fig. 3. Flow rate and current density on % of COD removal.

Fig. 3 shows that the percentage of COD removal increased with an increase in current density and observed that percentage of COD removal decreased with an increase in flow rate. Because the degradation rate of organic matter is increased with current density, which eventually increased the COD reduction. Flow rate slightly affect the efficiency of COD removal compared to current density because maximum percentage of COD removed were 72 for high-current density (5 A/dm^2) and low flow rate (10 L/hr).

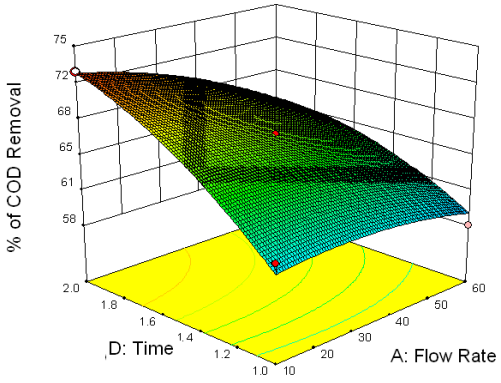

Fig. 4. Flow rate and time on % of COD removal.

Fig. 4 shows that the % of COD removal decreased with an increase in flow rate at the same % of COD removal increased with an increase in time of electrolysis. And also it was observed that maximum percentage of COD removed was 73%, occur at the maximum time of electrolysis (2 h) and low flow rate (10 L/h).

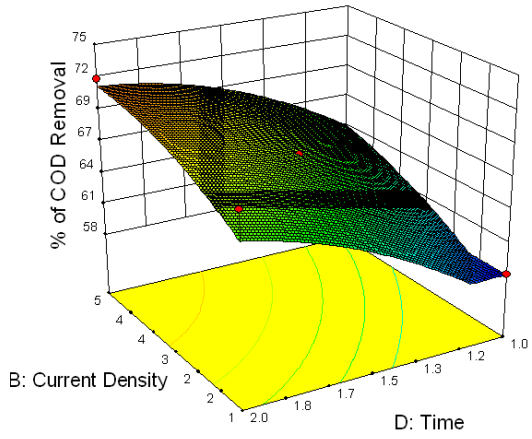

Fig. 5. Time and current density on % of COD removal.

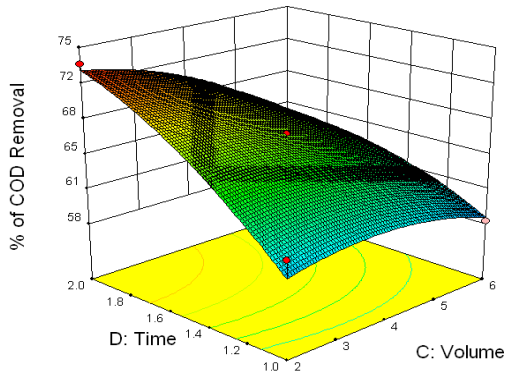

Fig. 6. Volume and time on % of COD removal.

Fig. 5 shows that the surface plot that the COD removal increases with increasing current density and increases with time of electrolysis. So the current density and time of electrolysis are a very important operational parameter for COD removal in the electrochemical oxidation process. And also it shows that 72 % of COD was removed at high time of electrolysis (2 h) and high-current density (5 A dm^{-2}).

Fig. 6 shows that the Maximum percentage of COD removed was 58% for high volume of electrolyte (6 L) and low time of electrolysis (1 h). The maximum % of COD removal is 73 % was obtained from (2 L) low volume electrolyte and the time taken for electrolysis is 2 h; therefore, % of COD removal decreased with decrease in time of electrolysis and increase in volume of electrolyte.

B. Response 2 - Power Consumption

The final quadratic equation obtained for Power consumption is given below in equation (2).

Power consumption,

$$Y2 = +18.0849 + 0.770835A + 12.76261B - 11.3251C + 5.431D + 0.494953AB - 0.42678AC + 0.6418AD - 7.39679BC + 3.19274BD - 2.41927CD + 0.158383A^2 + 0.19244B^2 + 6.180598C^2 \quad (2)$$

Fig. 7 shows that the power consumption increase with an increase in current density that is eventually increased the COD reduction and flow rate doesn't alter the efficiency of Power Consumption when compared with current density. Maximum power consumption was 25 kWhr/Kg COD for low flow rate (10 L/h) and high-current density (5 A/dm^2). And also it shows the Maximum power consumption was 7 kWh/Kg COD occur at high-flow rate (60 L/h) and low current density (1 A/dm^2).

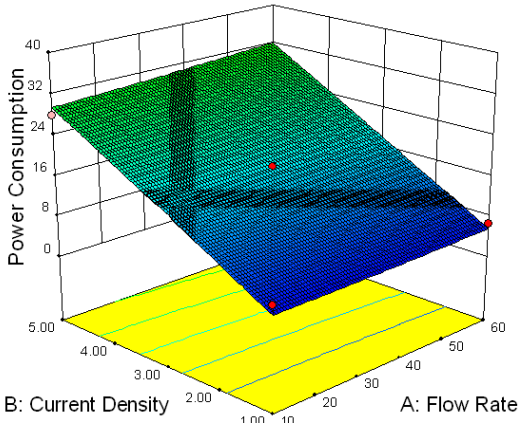

Fig. 7. Flow rate and current density on power consumption.

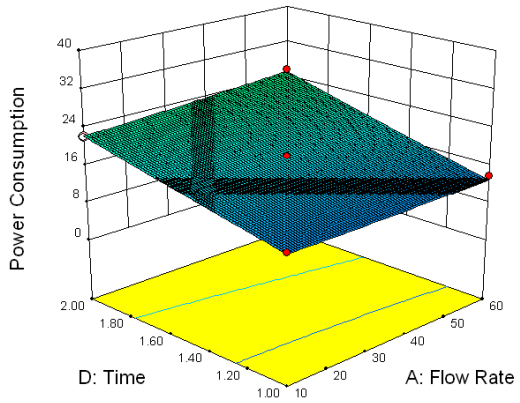

Fig. 8. Flow rate and time on power consumption.

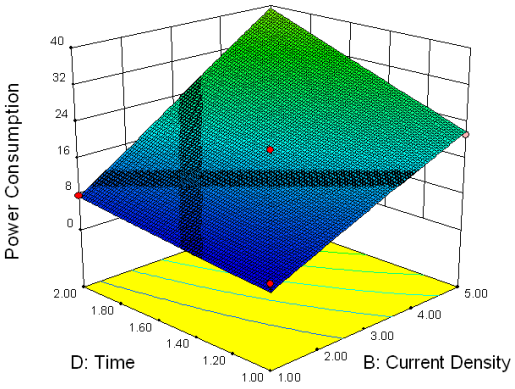

Fig. 9. Current density and time on power consumption

Fig. 8 shows that the Time for the concentration of the mediator in the electrolyte decreases and therefore, the conductivity of the effluent decreases and it is also observed that there is a temperature rise of effluent because of poorer conductivity of the electrolyte and hence the power required to destruct the organic matter increases. And also from Fig. 19, flow rate have only small effect on power consumption. Maximum power consumption was 14 kWh/kg COD occur at

the high-flow rate (60 L/h) and low time of electrolysis (1 h). On the other hand, Maximum power consumption was 22 kWh/kg COD for low flow rate (10 L/h) and time of electrolysis at 2 h.

Fig. 9 shows that the increase in Current density and in Time also increases power consumption. It shows the Maximum power consumption was 22 kWh/kg COD occur at the high-current density (5 A/dm^2) and low time of electrolysis (1 h). And also it was observed that maximum power consumption was 8 kWh/kg COD for low current density (1 A/dm^2) and low time of electrolysis (1 h).

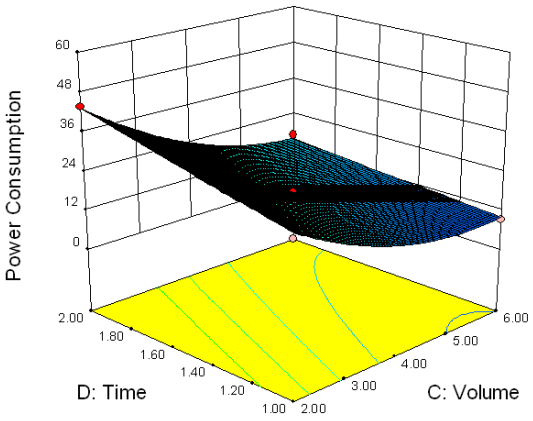

Fig. 10. Volume and time on power consumption

Fig. 10 shows that the maximum power consumption was 9 kWh/kg COD occur at high volume of electrolyte (6 L) and low time of electrolysis (1 h). And also it shows that maximum power consumption was 44 kWh/kg COD occur at low volume of electrolyte (2 L) and high time of electrolysis (2 h).

C. Photo Oxidation Method

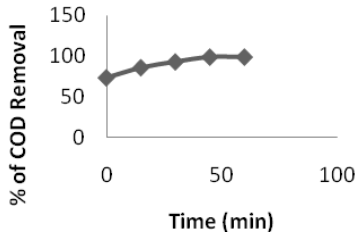

Fig. 11. Time Vs % of COD removal for pre treated effluent.

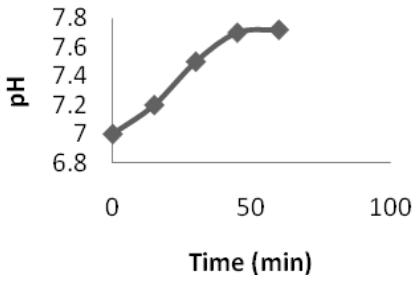

Fig. 12. Time Vs pH for pre treated effluent.

From the Fig. 11 and Fig. 12 the maximum % of COD removal occurs in increases in time and which results in an increase in pH. From the graph, it was observed that the photodegradation efficiency was increases in terms of % COD removal with an increase in the residence time. And also it shows the degradation rate as a function of irradiation time on illumination of wastewater under Ultra Violet light source, respectively. The rate of degradation was found to be more in the Ultra Violet light. From the graph 26, it was observed that the rate of degradation increases in the neutral on an alkaline range, as compared to the acidic pH conditions.

V. Conclusion

The combined electrochemical and photo oxidation experiments were carried out for prepared simulated effluent containing ethyl benzene. Initially, electrochemical degradation experiments were conducted separately for simulated effluent containing ethyl benzene in the presence of 2 g/L Sodium chloride electrolyte with lead oxide as anode and stainless steel as cathode electrodes was used. The operational parameters were analyzed by using response surface methodology and the individual and combined parameter effects on Chemical Oxygen Demand reduction and power consumption were investigated. Three-level four-factor Box-Behnken experimental design was applied. The optimized parameter was found to be 73.42 % was the highest amount of Chemical Oxygen Demand removal and the optimum conditions were satisfied at 100 % effluent concentration, current density 1.82 A/dm2, time 2 hrs, flow rate 10 L/hr, volume 3.63 L occurs at minimum power consumption 15 kWh/kg COD. Photo-degradation of effluent containing ethyl benzene was investigated for synthetic and pre treated effluent in the presence of the Ultra Violet light radiation. From this experiment percentage of Chemical Oxygen Demand reduction and Biodegradability Index was found to be a maximum of 98.42 % and 0.712 respectively, and the optimized irradiation time was 45 minutes respectively. From this study, it is possible that synthetic effluent containing ethyl benzene compounds could be treated by combined electrochemical and photo oxidation method.

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D. Prabhakaran was born on March 07, 1968, and completed B-Tech (1990) & M-Tech (2000) from Bharathiar University, Coimbatore, Tamil Nadu, India and M.B.A. (2001) from Madurai Kamraj University, Madurai, Tamil Nadu, India, Ph D. (2011) in Environmental Engineering from Anna University. He is an associate professor, in the department of Chemical Engineering, Coimbatore Institute of Technology, Coimbatore, Tamil Nadu, India. He has teaching experience over 20 years and his area of specialization at Undergraduate course is Environmental Engineering and Management, Process Engineering Economics, Process Dynamics Instrumentation and Control and for Post graduate course is Advanced Process Dynamics and Control, Fluidization Engineering. He has presented more than 20 national and international conferences and guided a number of projects for M.Tech and B.Tech and also published more than 10 papers in national and international journals such as International Journal of ChemTech, India, October 2009; Journal of Environmental Science and Health, Part A, UK, Taylor & Francis Group publications, March 2010; International Journal of Environmental Science and Technology, New York, Springer publications, 2009, etc., Dr. D. Prabhakaran is a life member in Indian Institute of Chemical Engineers & Indian society for Technical Education and also a member of Asia-Pacific Chemical, Biological & Environmental Engineering Society (APCBEES).

T. Kannadasan is the professor and head of the department of Chemical Engineering, Coimbatore Institute of Technology, Coimbatore, Tamil Nadu. He has 35 years teaching and Research experience. He is life member of Indian Institute of Chemical Engineers and Indian society of Technical Education, fellow member of the Institution of Engineers (India) and a senior member of Asia Pacific Chemical, Biological and Environmental Engineering Society (APCBEES). Guided 9 Ph.D and more than 20 Post graduation thesis. He served as The Director Center for Research, as well as the director in charge For Academic Courses at Anna University, Coimbatore, Tamil Nadu. He published more than 40 papers in international and national journals.

M. Thirumarimurugan is the associate professor of Department of Chemical Engineering, Coimbatore Institute of Technology, Coimbatore, Tamil Nadu. He has 15 years teaching and Research experience. Is a Life member of Indian Institute of Chemical Engineers and Indian society of Technical Education, Fellow Member of The Institution of Engineers (India) and a Senior Member of Asia Pacific Chemical, Biological and Environmental Engineering Society (APCBEES) Guiding 5 PhD students. He published more than 60 Journals in international and national journals.

C. Chellamboli was born on 19th December, 1988. She graduated from Tamil Nadu Agricultural University, India with bachelor's degree in Food Process Engineering (2009) and Post graduated from Coimbatore Institute of Technology, India with Master's degree in Chemical Engineering (2011). She worked as a Plant Incharge (Syrup Division) in Lion Dates Syrup, Tiruchirappalli, Tamil Nadu, India for few months. She is currently pursuing her Ph.D degree in Chemical Engineering from National Institute of Technology, Tiruchirappalli,Tamil Nadu, India. Area of specialization is Electrochemical Engineering, Bioengineering Technology and Food Process Engineering.