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

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ABSTRACT

In order to degrade the synthetic effluent containing ethyl benzene, comparative studies were carried out on electrochemical and photo oxidation processes. The galvanostatic mode of electrochemical oxidation was carried out with lead oxide as anode and stainless steel plate as cathode in the presence of 2 g/L of NaCl as a supporting electrolyte. The technique of Response Surface Methodology (RSM) was used to optimize the process which results in 73.42% COD removal. The optimum conditions were satisfied at current density 1.82 A/dm^2, time 2 hrs, flow rate 10 L/hr, and volume 3.63 L occurring with a minimum power consumption of 15 Kw.hr/kg COD. It was followed by the photo oxidation process carried out in the presence of Ultra Violet radiation emitted from Ultra Violet source. From this study, the percentage of COD reduction and Biodegradability Index was found to be a maximum of 98.42 % and 0.712 respectively. The optimized irradiation time was 45 minutes for pretreated effluent. This combined method appears to be a promising technology and has budding application for ecological remediation.

Keywords: COD reduction, Electrochemical, Photo oxidation, Response Surface Methodology, Ultra Violet.

1. INTRODUCTION

Water is a heritage which must be protected, defended and treated as such [1]. The wastewater are generated from almost all the process industries; the contaminants depending upon the process. Mainly pharmaceutical, textile, acrylic Fibre, pesticides and other organic chemicals manufacturing industries generate waste water [2]. Degradation of these non-biodegradable organic compounds is impossible in conventional biological treatment processes [3, 4]. So it is necessary to find a substitute for the treatment of wastewater which has become indispensible.

Ethyl benzene is a toxic organic compound. This aromatic hydrocarbon is important in the petrochemical industry as an intermediate in the production of styrene, which in turn is used for making polystyrene, a common plastic material. Often ethyl benzene enters the environment in the form of industrial discharges from petroleum refining, plastic, resins and pharmaceutical industrial effluents or oil spills. It is also present in automobile and aviation fuels. The US Environmental Protection Agency's has found that short-term exposure of ethyl benzene at levels above 0.7 ppm causes drowsiness, fatigue, headache and mild eye and respiratory irritation [5]. 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 prior pollutants.

Electrochemistry can play many roles in clean technology and pollution-control [6]. The advantage of this technique over traditional methods is that it employs electrons rather than chemicals and microorganisms which offer better environmental compatibility. It is an environmentally friendly technology because it uses only electricity, with its energy consumption depending on COD, herby making this process highly cost effective.

Photo degradation oxidizes harmful environment pollutants and converts it into harmless innocuous substances by the loss of one or more electrons from a chemical species as a result of photo excitation of that species and the reaction of a substance with oxygen under the influence of light [7].

2. EXPERIMENTAL

2.1. Experimental Setup

2.1.1. Electrochemical Treatment

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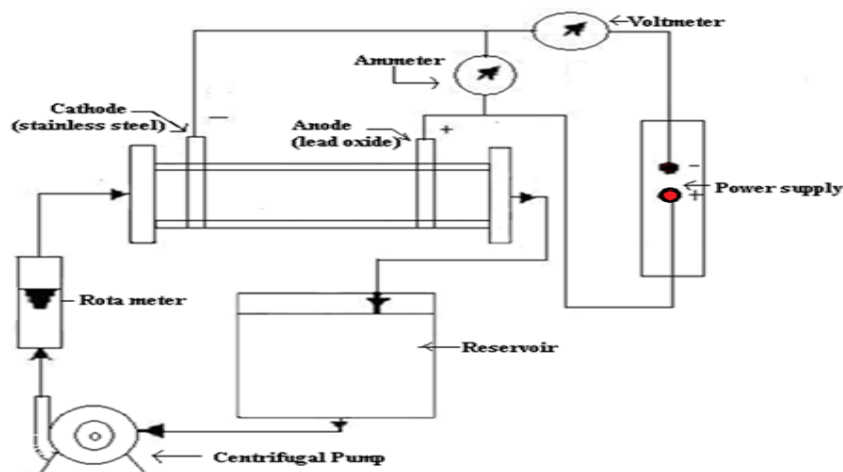

Fig.1. Schematic representation of Electrochemical Oxidation System

2.1.2. Photo oxidation method

Photo oxidation is a process in which pre-treated effluent is passed through UV reactor for degradation. The pre-treated effluent contains ethyl benzene. This procedure was carried out in the absence of supporting catalyst. The pre-treated effluent was allowed to flow through the walls of the reactor as a thin film. Ultraviolet lamp was provided inside the reactor for ultraviolet irradiation in order to initiate the reaction. In order to achieve further degradation, the effluent was re-circulated. COD was determined periodically to know the extent of degradation of the effluent in the reservoir. The schematic representation of the setup is shown in Fig. 2.
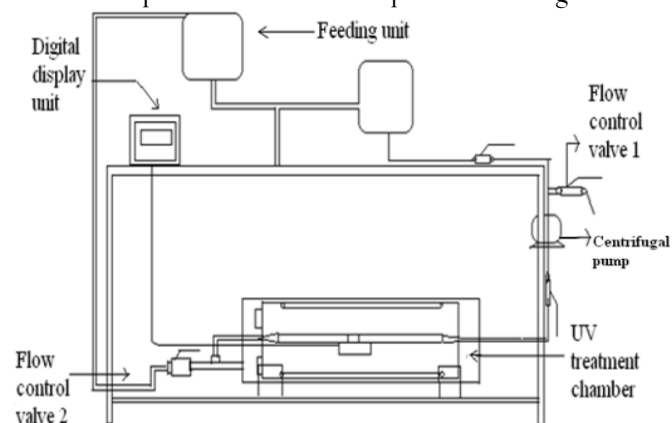

Fig.2: Schematic representation of Ultraviolet Radiation Reactor

2.2. Experimental Procedure

Electrochemical oxidation process was carried out in room temperature using a colourless synthetic effluent containing ethyl benzene with a COD range of 610 to 680 mg/L. A known quantity (2 to 6 L) of effluent was taken in electro-oxidation reactor and subjected to electric charge (current density of 1 to 5 A/dm^2). As per the demand of Box-Behnken method, the flow rate was maintained at 10 to 65 L/hr in the first step of operation to improve biodegradability. The volume of the reactor cell was 0.098 dm^3. The effluent treated in the reactor cell was re-circulated to the reservoir. In electrolysis, NaCl of concentration 2g/L was added to the effluent prior to electrolysis as a supporting electrolyte. The concentration of the reactant (COD) and the products in the batch reactor are functions of time. The electrolysis can be carried out in any of the two modes galvanostatic and potentiostatic; however the galvanostatic mode was selected in this study. After electrolysis, to subside all the chemical reactions, the content of the reactor was kept idle for 12 hrs. The experimental range and levels of independent process variables for batch recirculation reactor is shown in Table 1.

In the second step, photo oxidation process was carried out in an UV Reactor by subjecting the pre-treated effluent containing Ethyl benzene to ultraviolet radiation. The reactor

was charged with water solution (1L). The water was circulated through the reactor and was exposed to Ultra Violet radiation for 15 min (time needed for Pen Ray Ultra Violet radiation lamp to reach steady energy output). The effluent was re-circulated by the centrifugal pump at a rate of 180L/hr. Samples were withdrawn at different time intervals. On the completion of the process the reactor was cleaned with water in order to prevent corrosion of the equipment. The samples were later used for COD, BOD and pH test analysis.

Table 1: Experimental range and levels of independent process variables for batch recirculation reactor

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

3. RESULTS

The analysis is done to understand the influence of independent variables, i.e., electrolyte volume, current density, electrolyte flow rate, time, COD reduction, and power consumption. The dependent output variable is found to be maximum.

3.1. Response 1 - % reduction of COD

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

% of COD Removal,
$$Y_1 = +66.91 - (2.07*A) + (3.280833*B) - (2.53*C) + (4.589167*D) - (1.515*A*B) + (0.2425*A*C) - (1.4875*A*D) - (0.945*B*C) - (0.725*B*D) - (1.9625*C*D) - (0.95917*A^2) - (1.06042*B^2) - (1.55667*C^2) - (1.5804*D^2) \quad (1)$$
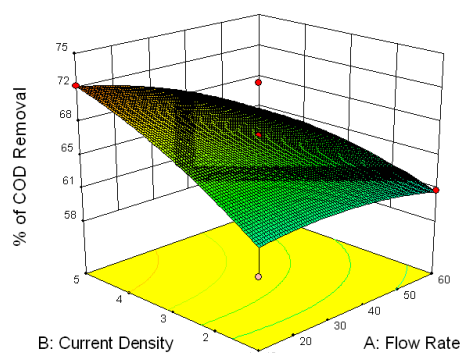

Fig.3: Flow Rate and Current Density on Percentage COD Removal

Fig. 3 shows that the percentage of COD removal increases with an increase in current density but decreases with an increase in flow rate. The degradation rate of organic matter is increased with current density, which eventually increases the COD reduction. Flow rate is slightly affecting the efficiency of COD removal compared to current density since maximum percentage of COD removal is 72% for high-current density (5 A/dm^2) and low flow rate (10 L/hr).
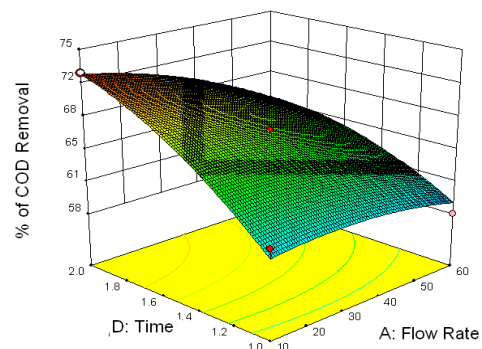

Fig. 4: Flow Rate and Time on Percentage COD Removal

Fig. 4 shows that the percentage of COD removal decreases with an increase in flow rate, whereas it increases with an increase in time of electrolysis. It is also observed that maximum percentage of COD removed is 73% which occurs at the maximum time of electrolysis (2 hr) and low flow rate (10 L/hr).
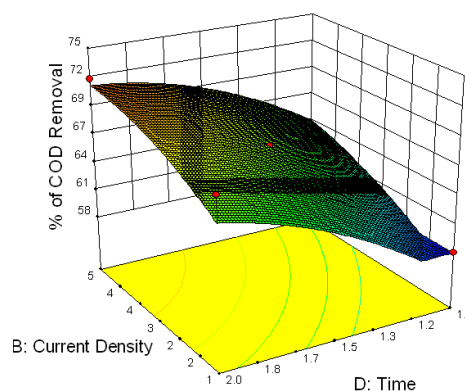

Fig. 5: Time and Current Density on Percentage COD Removal

The surface plot in Fig. 5 shows that the COD removal increases with increasing current density and time of electrolysis. So the current density and time of electrolysis are very important operational parameters for COD removal in the electrochemical oxidation process. Also it shows that 72% of COD is removed at high time of electrolysis (2 hr) and high-current density (5 A·dm^{-2}).
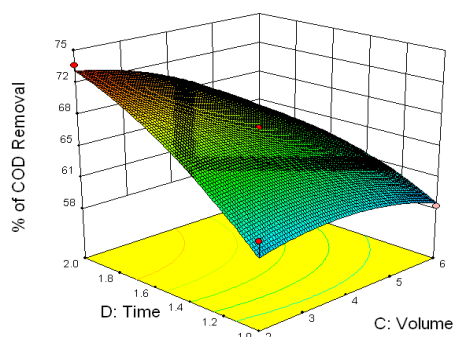
Fig. 6: Volume and Time on Percentage COD Removal

Fig. 6 shows that the maximum percentage of COD removed is 58% for high volume of electrolyte (6L) and low time of electrolysis (1hr). The maximum percentage of COD removal is 73% which is obtained from (2L) low electrolyte volume and lower time taken for electrolysis 2 hrs; therefore, percentage of COD removal decreases with decrease in time of electrolysis and the volume of electrolyte.

3.2. Response 2 – Power consumption

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

Power consumption,

$$Y_2 = +18.0849 + (0.770835 * A) + (12.76261 * B) - (11.3251 * C) + (5.431 * D) + (0.494953 * A * B) - (0.42678 * A * C) + (0.6418 * A * D) - (7.39679 * B * C) + (3.19274 * B * D) - (2.41927 * C * D) + (0.158383 * A^2) + (0.19244 * B^2) + (6.180598 * C^2) - (0.127675 * D^2) \quad (2)$$
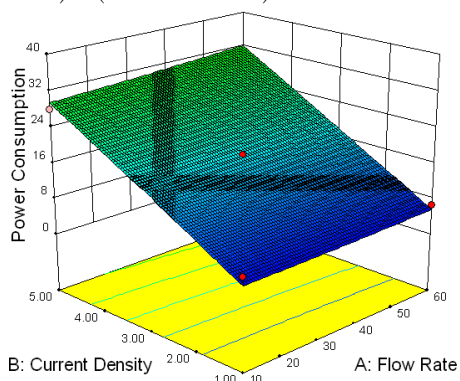

Fig. 7: Flow Rate and Current Density on Power Consumption

Fig.7 shows that the power consumption increases with an increase in current density that eventually increases the COD reduction. Flow rate does not alter the efficiency of power consumption when compared with current density. Maximum power consumption is 25 kW·hr/Kg COD for lower flow rate (10 L/hr) and higher current density (5 A/dm^2). It also shows that the maximum power consumption is 7 kW·hr/Kg COD which occurs at higher flow rate (60 L/hr) and lower current density (1 A/dm^2).
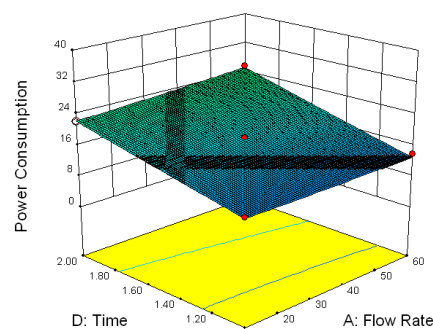

Fig. 8: Flow Rate and Time on Power Consumption

Fig. 8 shows that the time for the concentration of the mediator in the electrolyte decreases and therefore, the conductivity of the effluent decreases. We also observe that there is a temperature rise of effluent due to the inferior conductivity of the electrolyte and hence the power required to destruct the organic matter increases. Also from fig. 9, we observe that the flow rate has only a small effect on power consumption. Maximum power consumption is 14 kW·hr/kg COD occurring at the high flow rate (60 L/hr) and lower time of electrolysis (1 hr). On the other hand, maximum power consumption is 22 kW·hr/kg COD for lower flow rate (10 L/hr) and for the time of electrolysis of 2 hrs.
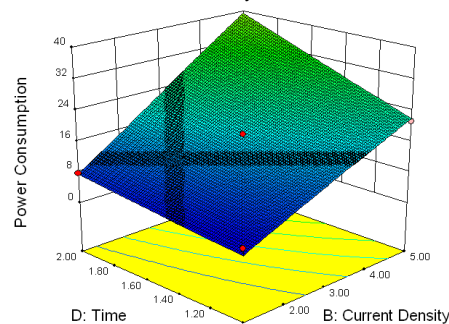

Fig. 9: Current density and Time on Power Consumption

Fig. 9 shows that the increase in current density and time increases the power consumption. It shows that the maximum power consumption is 22 Kw.hr/kg COD and it occurs at a high current density (5 A/dm^2) and low time of electrolysis (1 hr). We also observe that maximum power consumption is 8 Kw·hr/kg COD for low current density (1 A/dm^2) and less time of electrolysis (1 hr).
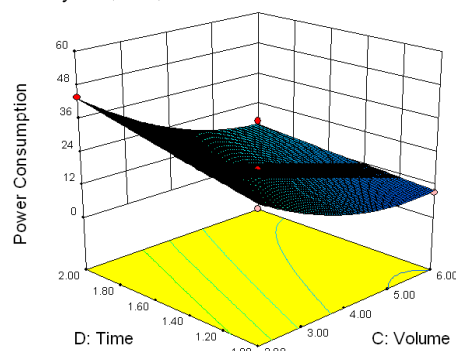

Fig. 10: Volume and Time on Power Consumption

Fig. 10 shows that the maximum power consumption of 9 kW·hr/kg COD occurs at high volume of electrolyte (6L) and low time of electrolysis (1hr). It is clear that the maximum power consumption is 44 kW·hr/kg COD which occurs at low volume of electrolyte (2L) and high time of electrolysis (2 hr).
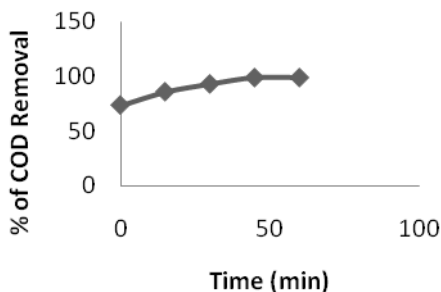
3.3. Photo oxidation method

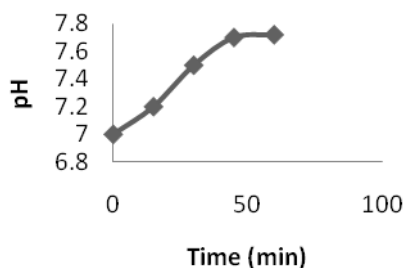**Fig. 11: *Time Vs Percentage COD removal for pre treated effluent***

Fig.12: Time Vs pH for pre treated effluent

From the figures 11 and 12 the maximum percentage of COD removal occurs when time increases which results in an increase in pH. From fig. 11, we observe that the photo degradation efficiency increases in terms of percentage COD removal with an increase in the residence time. It shows the degradation rate as a function of irradiation time on illumination of wastewater under Ultra Violet light source. The rate of degradation is found to be more in for Ultra Violet light. From fig.12, we observe that the rate of degradation increases in neutral on an alkaline range, as compared to the acidic pH conditions.

4. CONCLUSION

The combined electrochemical and photo oxidation experiments were carried out for prepared effluent containing ethyl benzene. Initially, electrochemical degradation experiment was conducted for simulated effluent containing ethyl benzene in the presence of 2 g/L of Sodium chloride as supporting electrolyte in the presence of lead oxide as anode and stainless steel as cathode electrodes. The operational parameters were analyzed by using response surface methodology and the individual and combined effects of the parameter on Chemical Oxygen Demand reduction and power consumption were investigated. Three-level four-factor Box-Behnken experimental design was applied. The optimized parameter for COD removal was found to be 73.42% satisfying the optimum conditions at 100% effluent concentration, current density 1.82 A/dm^2, time 2hrs, flow rate 10 L/hr, volume 3.63 L at minimum power consumption of 15 Kw·hr/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. From this study, it was found that synthetic effluent containing ethyl benzene compounds could be treated by a combination of electrochemical and photo oxidation method.

5. ACKNOWLEDGEMENT

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