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Sequential Studies On Electrochemical and Biosorption Treatment on Effluent Containing Nitrobenzene and Optimization Using Rsm

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--Abstract--

Different processes were studied to abate the COD levels in nitrobenzene. The process electrochemical oxidation following Biosorption turned to be a novel one. Electrochemical oxidation was carried out in an electrolytic cell, with nitrobenzene in water as electrolyte and lead, copper as anode and cathode respectively. Response surface methodology (RSM) was used to optimize the conditions, in which a maximum (76.4%) of COD abated. Biosorption treatment in the presence of biosorbents such as maize and rice stems was followed. Finally 97.7% COD in nitrobenzene was abated after the biosorption treatment.

Keywords: *Biosorption, COD Abatement, Electrochemical Oxidation, Maize Rice Stem, RSM.*

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I. INTRODUCTION

Industrial production of nitro aromatic compounds has been increasing massively during last few decades. Since Nitrobenzene is widely used in the industries for the production of aniline, aniline dyes, explosives, pesticides and drugs, and also as a solvent in products like paints, shoes and floor metal polishes, the production of nitrobenzene has been increasing massively. But nitrobenzene is treated as one of prior pollutants by many countries. Since even at low concentrations it may cause high risks to environment, being a toxic and a carcinogenic compound. Here the problem arises with the COD levels in the nitrobenzene. Higher the COD levels, nitrobenzene becomes highly toxic. So nitrobenzene with low COD levels can be used in a better way to meet the commercial demand.

II.Experimental Setup

Electrochemical Treatment

The experimental setup consists of an undivided electrolytic cell of 300 ml working capacity, closed with a PVC lid having provisions to fix cathode and anode electrodes at a distance of 2.5 cm apart. A salt bridge with reference electrode was inserted through the holes provided in the lid. The electrode used was Lead plate (of dimension 8.0cm×8.0cm×1.0 cm) as anode and a Copper plate (of dimension 8.0cm×8.0cm×1.0 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 the help of a Centrifugal pump and the flow rate was measured by rotameter. The electrolyte taken was synthetic effluent containing Nitrobenzene in water.

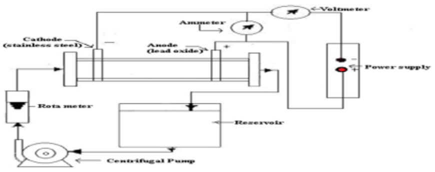

Fig.1: Schematic representation of Electrochemical Oxidation System

A. Biosorption Treatment

The biosorbents used were Maize stem and Rice stem. The Maize and Rice stem were collected from local farm land. It was then sorted and segregated. The maize stems were chopped down to small pieces and dried at a temperature of 80 - 100^o Celsius for two days [2]. Thus the dried stem was ground to granules which were then sieved in a sieve shaker. In the same way the rice stem was also ground to granules. The finest granules obtained were stored orderly. 85 mesh no(0.177 mm) size granules were used.

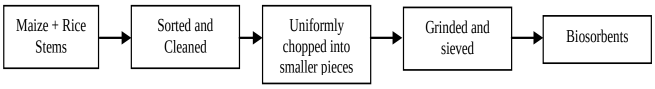

Fig.2: Preparation of Biosorbents

III. EXPERIMENTAL PROCEDURE

Electrochemical oxidation process was carried out in room temperature for colour less synthetic effluent containing Nitrobenzene having COD in the range of 1351.41 to1436.77 mg/L. Table 1 indicates the factors involved as per Box-Behnken method. The effluent treated in this reactor cell was re-circulated to the reservoir. In electrolysis, NaCl was 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 products in the batch reactor were function of time. The electrolysis can be carried out in any of the two modes- galvanostatic and potentiostatic. The present study on galvanostatic process is followed in industries using rectifiers. After electrolysis, to subside all the chemical reactions, the content of the reactor was kept idle for 12 hrs. The effluent from a well-mixed reservoir was rapidly re-circulated through the reactor. In the second step, biosorption experiment was done by collecting the water samples after the electrochemical treatment. Here water samples (3 to 9L) were mixed with the already prepared biosorbents (Maize and Rice stem granules mixed in equal proportion 15g/L). The samples were left idle. For every 24 hrs samples were collected for the analysis. This was repeated for 4 days (96 hrs). The samples were later used for COD test analysis.

TABLE I: EXPERIMENTAL RANGE AND LEVELS OF INDEPENDENT PROCESS VARIABLES FOR BATCH RECIRCULATION REACTOR

Factors		Flow Rate	Current Density	Volume	Time of Reaction
Range and Levels		L/hr	A/dm^2	L	Hr
	-1	20	1	3	1
	0	40	3	6	2
	+1	60	5	9	3

IV.RESULTS

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 is maximum.Table II indicates the actual design of experiments obtained from Response Surface Methodology (RSM) and their responses. The factors such as flow rate (L hr^{-1}), current density(A dm^{-2}), Volume (L), time (hr), Response 1 - percentage reduction of COD and Response 2 - Power consumption (kWhr/kg COD) is represented as factor A, B, C, D, R1 and R2 respectively.

A. Response 1 - % reduction of COD

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

% of COD Removal,

$$R1 = +67.30 - 0.058 * A + 3.73 * B + 3.24 * C + 4.62 * D - 1.40 * A * B - 0.075 * A * C - 1.00 * A * D + 1.47 * B * C + 0.88 * B * D + 2.43 * C * D + 1.79 * A^2 + 0.43 * B^2 - 0.34 * C^2 - 1.48 * D^2$$

(1)

Analysis of variance to determine the significant effects of process variables was conducted and the results are presented in Table III. It can be noticed from Table II for the COD output response, that the F-values for the regressions are higher. The large F-value indicates that most of the variation in the response can be explained by the regression model equation. The lower p-value (<0.0001) indicates that the model is considered to be statistically significant. The model adequacies were checked by R^2 and R adj^2. A higher value of R^2 (0.8515) shows that the model can explain the response successfully

TABLE II: ACTUAL DESIGNOF EXPERIMENTS AND RESPONSE FOR THE % OF COD REMOVAL AND POWER CONSUMPTION

B.Response 1 - % reduction of COD

Run order	A	B	C	D	R1	R2
1	20	5	6	2	75.9	61.05
2	40	3	6	2	67.3	26.97
3	40	5	6	3	75.1	66.55
4	20	3	6	3	71.3	46.09
5	60	3	9	2	68.4	18.35
6	60	1	6	2	65.9	8.62
7	40	5	3	2	63.2	63.78
8	20	3	6	1	61.8	11.54
9	60	5	6	2	76.1	61.51
10	40	3	9	3	76.4	41.44
11	40	5	9	2	74.3	37.61
12	40	3	6	2	67.3	26.97
13	40	3	3	1	59.4	22.78
14	40	3	6	2	67.3	26.97
15	60	3	3	2	63.3	25.2
16	40	3	6	2	67.3	26.97

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% of COD Removal,

$$R1 = +67.30 - 0.058 * A + 3.73 * B + 3.24 * C + 4.62 * D - 1.40 * A * B - 0.075 * A * C - 1.00 * A * D + 1.47 * B * C + 0.88 * B * D + 2.43 * C * D + 1.79 * A^2 + 0.43 * B^2 - 0.34 * C^2 - 1.48 * D^2$$

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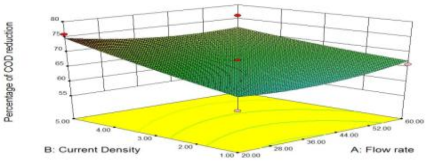
TABLE III: ANOVA RESULTS OF THE QUADRATIC MODELS FOR THE PERCENTAGE OF COD REMOVAL

Source	**DOF**	**Sum of squares**	**Mean square**	**F-value**	**P**
Regression	14	641.48	45.82	5.73	< 0.0001 (siginificant)
Residual error	14	111.89	7.99		
Lack of fit	10	111.89	11.19		
Pure error	4	0	0.00		
Total	28	753.37			

The combined effects of the individual parameters on the % of COD reduction are analyzed using 3D surface plot and results are as shown in figure 3.



R^2=0.8515, R_{adj}^2= 0.7030

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

Figure 3 shows that the percentage of COD removal increases with increase in current density and it is also observed that percentage of COD removal decreases with increase in flow rate. This is because the degradation rate of organic matter increases with current density, which eventually increases the COD reduction. Maximum percentage of COD removed is 75 for high current density (5 A/dm^2) and low flow rate (20 L/hr).

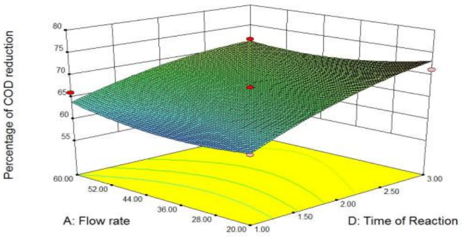


Fig 4: Flow Rate and Time on Percentage of COD Removal

Figure 4 shows that the percentage of COD removal decreases with increase in flow rate and at the same time percentage of COD removal increases with increase in time of electrolysis. Maximum percentage of COD removed was 71.3 for higher time of reaction (3 hr) and low flow rate (20 L/hr).

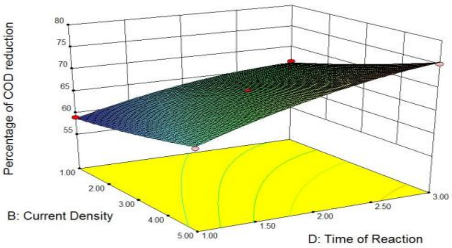


Fig 5: F Current density and Time on Percentage of COD Removal

Figure 5 shows that the COD removal increases with increase in both current density and time of electrolysis. So the current density and time of electrolysis are very important operational parameters for COD removal in electrochemical oxidation process. Maximum percentage of COD removed was 75.1 for higher time of reaction (3 hr) and higher current density (5 A/dm^2).

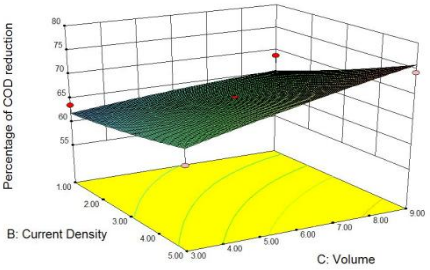


Fig 6: Current density and volume on Percentage of COD Removal

Figure 6 shows that the COD removal increases by increasing current density but decreases with increase in volume.

C. Response 2 - Power consumption

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

Power consumption,

$$R2 = +26.97 - 3.82 * A + 21.26 * B - 7.92 * C + 15.56 * D - 0.20 * A * B + 4.68 * A * C - 0.24 * A * D - 3.86 * B * C + 9.13 * B * D + 1.30 * C * D + 4.56 * A^2 + 1.38 * B^2 + 3.56 * C^2 - 1.45 * D^2$$

(2)

It can be noticed from Table IV for the power consumption output response, that the F-values for the regressions are higher. The large F-value indicates that most of the variation in the response can be explained by the regression model equation. The associated p-value is used to estimate whether the F-statistics are large enough to indicate statistical significance. The ANOVA indicates that the second-order polynomial model is significant and adequate to represent the actual relationship between the response (Power Consumption) and the variables, with a small p-value (<0.0001) and a high value of R2 (0.9352) for Power Consumption.

TABLE IV: ANOVA RESULTS OF THE QUADRATIC MODELS FOR THE POWER CONSUMPTION

Source	DOF	Sum of squares	Mean square	F-value	P
Regression	14	692.10	712.93	14.42	< 0.0001 (siginificant)
Residual error	14	692.10	49.44		
Lack of fit	10	58.69	69.21		
Pure error	4	0	0		
Total	28	10673.10			

The combined effects of the individual parameters on the power consumption was analyzed using 3D surface plot and results is as follows

R^2=0.9352, R_{adj}^2= 0.8703

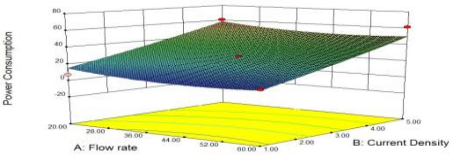


Fig 7: Flow rate and Current density on Power consumption

Figure 7 shows that power consumption increases with increase in current density, which eventually increases the COD reduction. Flow rate do not alter effect the efficiency of power consumption compared to current density. Maximum power consumption is 61.05 kWhr/Kg COD for low flow rate (20 L/hr) and high current density (5 A/dm2).

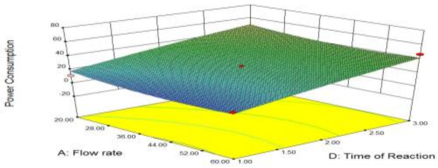


Fig 8: Flow rate and Time on Power consumption

Figure 8 shows that time for the concentration of mediator in the electrolyte decreases thereby decreasing the conductivity of the effluent. It is also observed that there is a temperature rise of effluent because of poor conductivity of the electrolyte and hence the power required to destruct the organic matter increases. Also the flow rate has small effect only on power consumption. Maximum power consumption is 46.09 kWhr/kg COD for low flow rate (20 L/hr) and high time of electrolysis (3 hr)

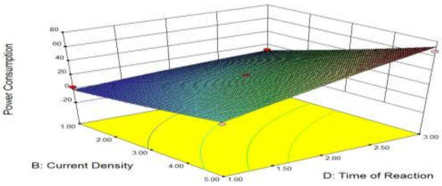


Fig 9: Current Density and Time on Power consumption

Figure 9 shows that the increase in current density and time also increases power consumption. It shows that the maximum power consumption is 66.55 kWhr/kg COD that occur at high current density (5 A/dm2) and high time of electrolysis (3 hr).

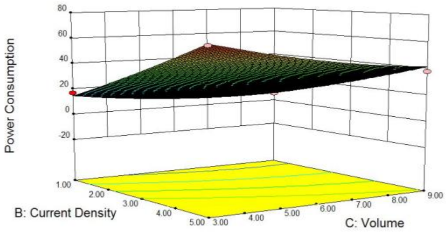


Fig 10: Current Density and Volume on Power consumption

Figure 10 shows the effect of flow rate and volume on power consumption. It shows that maximum power consumption is 25.2 kWhr/kg COD that occur at high flow rate (60 L/hr) and low volume of electrolyte (3 L).

The maximum percentage of COD reduction is found to be 76.4 % at current density 3.56 A dm^{-2}, time 3 hours, flow rate 40 L hr^{-1}, volume 9 L which occur at minimum power consumption of 30.3 kWhr / kg COD.

B. **Biosorption treatment**

Biosorption treatment is done and the percentage removal of COD is calculated and the maximum percentage COD removal is 97.7 %. The results obtained by Biosorption process is given below in Table V.

TABLE V: PERCENTAGE REDUCTION OF COD FOR 3 L, 6 L AND 9 L VOLUME OF ELECTROLYTE

Volume of electrolyte (L)	Time (days)	COD (mg/l)	Percentage reduction of COD(%)
3	0	497.3	-
	1	303.85	38.9
	2	193.45	61.1
	3	68.62	86.2
	4	11.44	97.7
6	0	338.7	-
	1	195.1	42.4
	2	88.74	73.8
	3	36.92	89.1
	4	12.53	96.3
9	0	340	-
	1	211.48	37.8
	2	108.46	68.1
	3	55.08	83.8
	4	19.38	94.3

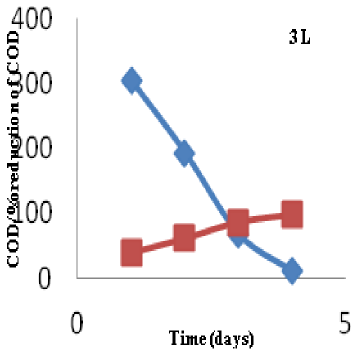


Fig 11: COD % reduction of COD on Time for 3 L volume electrolyte

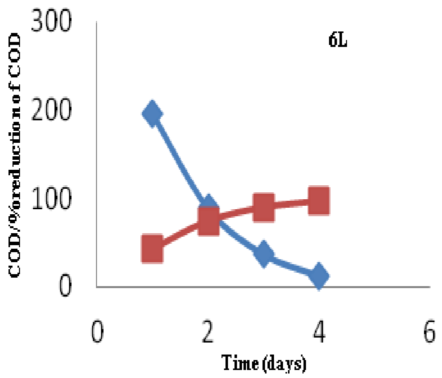


Fig 12: COD % reduction of COD on Time for 6 L volume electrolyte

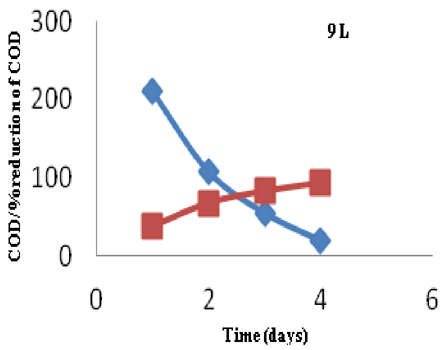


Fig 13: COD % reduction of COD on Time for 9 L volume electrolyte

Figures 11 to 13 imply that as time of Biosorption treatment increases, the COD decreases and thus percentage reduction of COD increases. The maximum reduction of COD is found to be 97.7 % for 3 L volume of electrolyte.

V. CONCLUSION

The experimental studies of electrochemical treatment followed by the Biosorption treatment were carried out for the synthetically prepared effluent containing Nitrobenzene. The initial step was the electrochemical Treatment experiments were conducted separately for the synthetic effluent containing Nitrobenzene and maximum % of COD reduction was found to be 76.4 % followed by Biosorption treatment were 97.7 % was the maximum % reduction of COD.

VI. ACKNOWLEDGEMENT

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