Mr.P.Sivakumar, Mr.S.Karthikeyan, Dr.D.Prabhakaran, Dr.T.Kannadasan / International Journal of Engineering Research and Applications (IJERA) ISSN: 2248-9622 www.ijera.com
Vol. 3, Issue 1, January -February 2013, pp.343-348

# Experimental studies on Electrochemical and Biosorption treatment of effluent containing Nitrobenzene and Optimization using RSM.

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## Abstract

**A novel process combining Electrochemical Oxidation and Biosorption treatment was presented for Nitrobenzene abatement. The electrochemical oxidation was investigated batch-wise in the presence of NaCl (2g $L^{-1}$) electrolyte with lead as anode and copper as cathode electrodes. The conditions were optimized using response surface methodology (RSM), which result in 76.4% reduction of COD was found to be maximum and the optimum conditions were satisfied at current density 3.56 A dm-2, time 3 hours, flow rate 40 L hr -1, volume 9 L occur at minimum power consumption of 30.3 kWhr / kg COD. It is followed by biosorption treatment in the presence of biosorbents such as maize and rice stems at 15 g L-1. From this study it was observed that the maximum % of COD reduction was 97.7 % for the optimized time 4 days and volume 6 L for pretreated effluent containing nitrobenzene.**

**Keywords** - Biosorption, COD reduction, Electrochemical, Maize & Rice stem.

## 1. INTRODUCTION

In the last few decades, nitro aromatic compounds have been produced industrially on a massive scale. Most are highly recalcitrant to degradation. Nitrobenzene has been 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. As a toxic and suspected carcinogenic compound, nitrobenzene released to environment poses a great threat to human health. Even at low concentrations, it may present high risks to environment. Therefore, nitrobenzene is listed as one of prior pollutants by many countries [1].

## 2. EXPERIMENTAL SETUP

### 2.1 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 a cathode and an anode electrodes 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 was Lead plate as anode in the (of dimension 8.0cm×8.0cm×1.0 cm) was employed and a Copper plate (of dimension 8.0cm×8.0cm×1.0 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 electrochemical oxidation system was done with Centrifugal pump and the flow rate was measured by rotameter. The electrolyte taken was synthetic effluent containing Nitrobenzene in water.

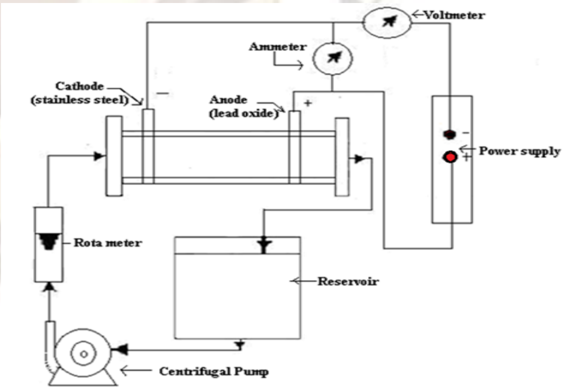


Fig.1: Schematic representation of Electrochemical Oxidation System

### 2.2 Biosorption Treatment

The biosorbents used were Maize stem and Rice stem, both collected from local farm land had been sorted out, 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 is grinded

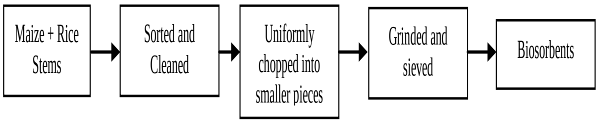


Fig.2. Preparation of Biosorbents

down to granules which are then sieved in a sieve shaker. In the same way the rise stem also been grinded down to granules. The finest granules obtained are stored orderly. 85 mesh no(0.177 mm) size granules are used.

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

| Source | DOF | Sum of squares | Mean square | F-value | P |
|---|---|---|---|---|---|
| Regression | 14 | 641.48 | 45.82 | 5.73 | < 0.0001 |
| 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 | | | |

## 4. 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: ACTUAL DESIGN OF EXPERIMENTS AND RESPONSE FOR THE % OF COD REMOVAL AND POWER CONSUMPTION

| Factors | Unit | Range and levels | | |
|---|---|---|---|---|
| | | -1 | 0 | +1 |
| Flow rate | L/hr | 20 | 40 | 60 |
| Current density | $A/dm^2$ | 1 | 3 | 5 |
| Volume | L | 3 | 6 | 9 |
| Time of reaction | hr | 1 | 2 | 3 |

The 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 - % reduction of COD and Response 2 - Power consumption (KWhr/ kg COD) is represented as factor A, B, C, D, R1 and R2 respectively.

### 4.1Response 1 - % reduction of COD

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

% of COD Removal,

$$R1 = +67.30 - 0.058*A + 3.73*B + 3.24*C + 4.62*D - 1.40*A*B - 0.075*A*C - 1.00*A*D + 1.47*B*C + 0.88*B*D + 2.43*C*D + 1.79*A^2 + 0.43*B^2 - 0.34*C^2 - 1.48*D^2 \quad (1)$$

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

| 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 |
| 17 | 60 | 3 | 6 | 3 | 71.6 | 46.58 |
| 18 | 40 | 1 | 3 | 2 | 63.6 | 16.94 |
| 19 | 40 | 1 | 9 | 2 | 68.8 | 6.19 |
| 20 | 20 | 1 | 6 | 2 | 60.1 | 7.37 |
| 21 | 40 | 1 | 6 | 3 | 66.5 | 13.16 |
| 22 | 40 | 5 | 6 | 1 | 64.1 | 20.47 |
| 23 | 40 | 3 | 6 | 2 | 67.3 | 26.97 |
| 24 | 40 | 3 | 9 | 1 | 60.6 | 7.36 |
| 25 | 60 | 3 | 6 | 1 | 66.1 | 13 |
| 26 | 40 | 1 | 6 | 1 | 59 | 3.58 |
| 27 | 20 | 3 | 3 | 2 | 68.8 | 59.29 |
| 28 | 40 | 3 | 3 | 3 | 65.5 | 51.66 |
| 29 | 20 | 3 | 9 | 2 | 74.2 | 33.72 |

The combined effects of the individual parameters on the % of COD reduction was analyzed using 3D surface plot and results are as follows

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

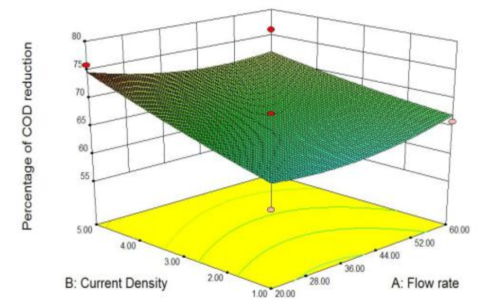


Fig 3: Flow Rate and Current Density on Percentage of COD Removal

Figure 3 shows that the % of COD removal increased with increase in current density and also observed that % of COD removal decreased with increase in flow rate. Because the degradation rate of organic matter is increased with current density, which eventually increased the COD reduction. Maximum % COD removed was 75 for high current density (5 A/dm$^2$) and low flow rate (20 L/hr).

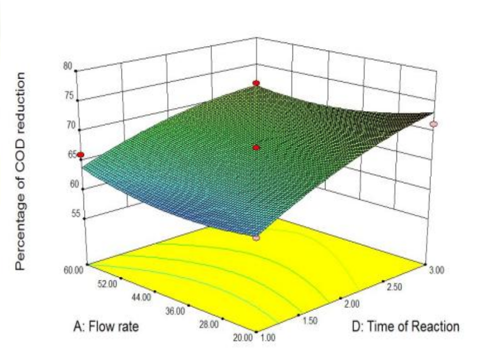


Fig 4: Flow Rate and Time on Percentage of COD Removal

Figure 4 shows that the Percentage of COD removal decreased with increase in flow rate at the same time Percentage of COD removal increased with increase in time of electrolysis. Maximum % COD removed was 71.3 for high Time of reaction (3 hr) and low flow rate (20 L/hr).

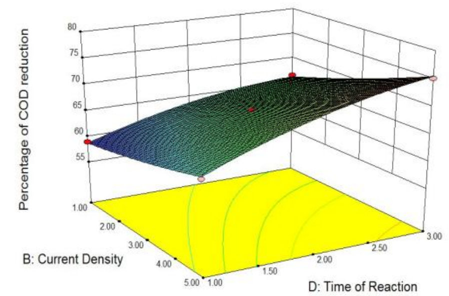


Fig 5: Current density and Time on Percentage of COD Removal

Figure 5 shows that the COD removal increases with increasing Current Density and increases with time of electrolysis. So the current density and time of electrolysis is very important operational parameter for COD removal in electrochemical oxidation process. Maximum % COD removed was 75.1 for high Time of reaction (3 hr) and high Current density (5 A/dm2).

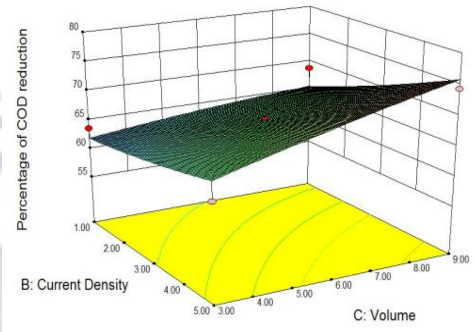


Fig 6: Current density and volume on Percentage of COD Removal

Figure 6 shows that the COD removal increases with increasing Current Density and decreases with increase in volume.

### 4.2 Response 2 - Power consumption

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

Power consumption,

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

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 |
| 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 are as follows

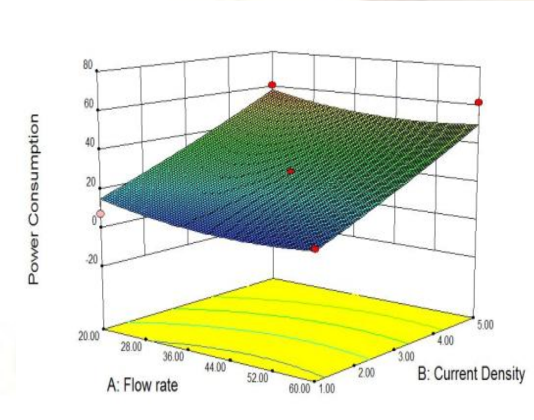


Fig 7: Flow rate and Current density on Power consumption

Figure 7 shows that Power Consumption increased with increase in current density, which is eventually, increased the COD reduction. But flow rate is doesn't alter effect the efficiency of Power Consumption compared to current density. Maximum power consumption was 61.05 KWhr/Kg COD for low flow rate (20 L/hr) and high current density (5 A/dm2).

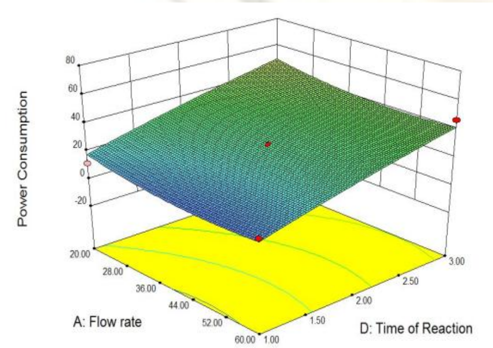


Fig 8: Flow rate and Time on Power consumption

Figure 8 shows that time for the concentration of mediator in the electrolyte decreases 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 flow rate have only small effect on power consumption. Maximum power consumption was 46.09 kWhr/kg COD for low flow rate (20 L/hr) and high time of electrolysis (3 hr)

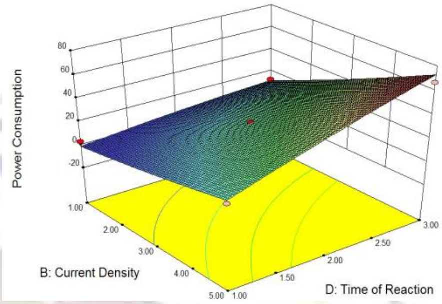


Fig 9: Current Density and Time on Power consumption

Figure 4.18 shows that the increase in Current density and in Time also increases power consumption. It shows the Maximum power consumption was 66.55 kWhr/kg COD occur at high current density (5 A/dm2) and high time of electrolysis (3 hr).

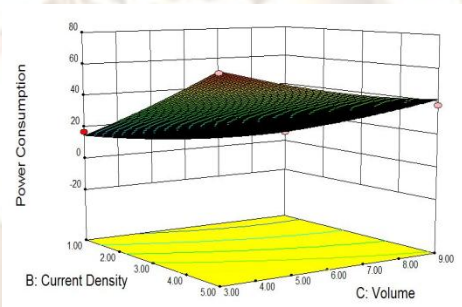


Fig 10: Current Density and Volume on Power consumption

Figure 10 shows the effect of Flow Rate and Volume on Power Consumption. It shows that maximum power consumption was 25.2 KWhr/Kg COD occur at high flow rate (60 L/hr) and low volume of electrolyte (3 L).The Maximum % of COD reduction was found to be 76.4 % at current density 3.56 A $dm^{-2}$, time 3 hours, flow rate 40 L $hr^{-1}$, volume 9L occur at minimum power consumption of 30.3 KWhr/Kg COD.

**4.3 Biosorption treatment**

Biosorption treatment is done and the Percentage removal of COD is calculated and the maximum Percentage COD removal was 97.7 %. The results obtained by Biosorption process is given below.

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

| Time (days) | COD (mg/l) | Percentage reduction of COD |
|---|---|---|
| 0 | 497.3 | - |
| 1 | 303.85 | 38.9 |
| 2 | 193.45 | 61.1 |
| 3 | 68.62 | 86.2 |
| 4 | 11.44 | 97.7 |

FOR 6 L

| Time (days) | COD (mg/l) | Percentage reduction of COD |
|---|---|---|
| 0 | 338.7 | - |
| 1 | 195.1 | 42.4 |
| 2 | 88.74 | 73.8 |
| 3 | 36.92 | 89.1 |
| 4 | 12.53 | 96.3 |

FOR 9 L

| Time (days) | COD (mg/l) | Percentage reduction of COD |
|---|---|---|
| 0 | 340 | - |
| 1 | 211.48 | 37.8 |
| 2 | 108.46 | 68.1 |
| 3 | 55.08 | 83.8 |
| 4 | 19.38 | 94.3 |

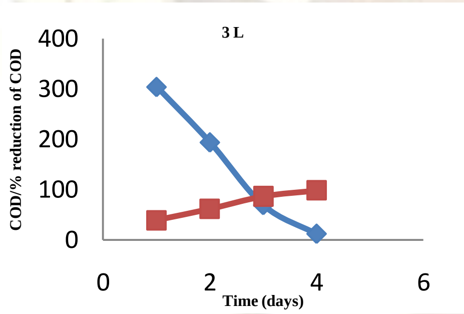


Fig 11: COD % reduction of COD on Time for 3 L volume electrolyte

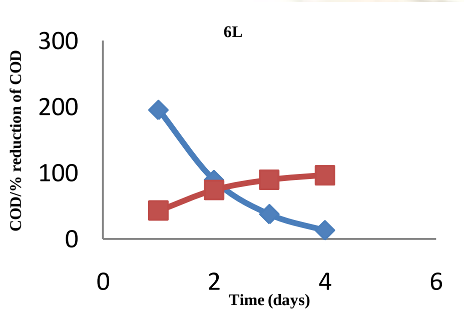


Fig 12: COD % reduction of COD on Time for 6 L volume electrolyte

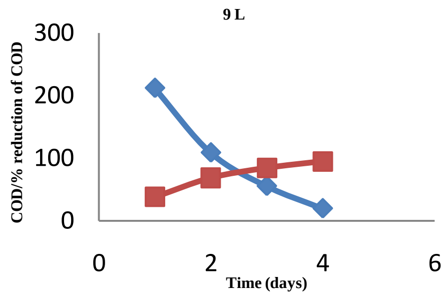


Fig 13: COD % reduction of COD on Time for 9 L volume electrolyte

From figure 11 to 13 implies that as time of Biosorption treatment increases the COD decreases and thus increase in Percentage reduction of COD. The maximum reduction of COD was found to be 97.7 % for 3 L volume of electrolyte.

## 5. CONCLUSION

The Experimental studies of Electrochemical treatment followed by the Biosorption treatment was 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.

## ACKNOWLEDGEMENT

No significant achievement can be a solo performance especially when starting a research work from ground up, the success of this project depends largely on the encouragement and guidelines of many others. I take this opportunity to express my gratitude to the people who have been instrumental in the successful completion of this project.

First and foremost I offer my sincerest gratitude to my Guide, Dr. D Prabhakaran who has supported me throughout my work with his patience and knowledge whilst allowing me the room to work in my own way.

I am obliged to thank my respected Principal Dr. V.Selladurai, My Head of the Chemical Engineering Department Dr.T.Kannadasan for supporting and sponsoring my work.

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