Efficient Removal of Coralene Red 3G Dye in Ec Process with Zn/TiO₂ using Statistical Algorithm

Parameswari Kalivel, Jegathambal Palanichamy, M.Vijila

Abstract — This work describes the statistical approach for the efficiency of electrodes Zn/TiO₂ prepared by spray pyrolysis and thermal decomposition of TiCl₃ in treating Coralene Red 3G dye for its color removal in electrocoagulation process with the optimization of operational parameters. Using Design Experts software, ANOVA design model was carried out and the efficiency of color removal for the parameters such as pH, concentration of dye, electrolyte, applied current and time were derived. Replicates were maintained for all experiments, and the results were statistically analyzed by performing ANOVA at 5% level of significance using SPSS software. A better efficiency was observed for the electrodes Zn/TiO₂ obtained from spray pyrolysis.

Keywords: Electrocoagulation, Coralene Red 3G dye, Zn/TiO₂, Analysis of Variance

I. INTRODUCTION

Advances in technology have resulted in increased demand for water from the various types of industries. The amount of water generated and discharged from these industries as waste has been growing rapidly, containing a wide variety of pollutants [1]. The effluent from various units in such textile hub have high levels of COD, color and salt. In treating the wastewater from these industries, simple methods like chemical coagulation causes more amounts of sludge and biological methods take much time and cannot degrade complicated dyes. Advanced oxidation methods are costly and uneconomical [2-4].

The electrochemical method is a better treatment method with high efficiency for treating textile wastewaters containing a high concentration of dye since these processes are mostly quite expensive and not effective [5]. Research related to wastewater treatment has focused on electrocoagulation (EC) over the past few years since it is simple in operation with less production of sludge [7]. EC has been successfully used for decades in order to treat the wastewaters of textile [8] food and protein [9] phosphate [10] tannery wastewater [11] restaurant wastewater and defluoridation [12]. Although standard electrode materials (Al and Fe) in EC process may have been excellent in color removal of the dye but likely to get dissolved and consumed more energy. The EC method's accounts for novel electrode tools in the literature remain highly inadequate.

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The conventional electrode materials like Al and Fe are more active in reducing color and can be dissolved [13]. Therefore, a modern, economically viable EC electrode or electrode / hybrid system, with less current and time is highly desirable. On continuation of our research works in this area, modified electrodes Zn/TiO₂ prepared from two different methods were compared for the color removal efficiency of Coralene Red 3G dye in EC [14].

II. EXPERIMENTAL METHODS

Preparation of Electrode

The electrodes Zn/TiO₂ were prepared by thermal decomposition and spray pyrolysis methods at 250°C using the same precursor. [15]

B. Synthetic Dye Solution

From one of the small textile dyeing industry in Coimbatore, Tamil Nadu, the disperse dye used in this work has been acquired (Commercial name; Coralene Red 3G). Synthetic wastewater was prepared at concentrations of 150mg/L in distilled water.

Electrocoagulation (EC) Process

The electrocoagulation unit is set up as an electrochemical reactor with glass beaker along with magnetic stirrer and DC energy. Two sets of EC process were run Zn/TiO₂ – Zn/TiO₂ from spray pyrolysis (SP) and Zn/TiO₂ – Zn/TiO₂ from thermal decomposition (TD) (Hereafter these electrodes will be represented ‘A’ Spray pyrolysis (SP) Zn/TiO₂ – Zn/TiO₂ and ‘B’ Thermal Decomposition Zn/TiO₂ – Zn/TiO₂) The electrode region of 28.16 cm² and a distance of 10mm between the two electrodes was used.

A sample solution of 250 ml was drawn in a 500 ml capacity beaker and a magnetic stirrer was used to stir the solution. Before each test, electrodes were washed with water and placed in 15% hydrochloric acid to remove dirt from the electrode plate. After each test, the electrodes were washed with water, dried and weighed. The subsequent processed sample was filtered and the filtrate was used for analysis. Individual impacts of electrolysis moment and applied current on the percentage of efficiency of extraction of color (EEC %) have been quantified in this research. All experiments at 25°C were performed.
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Two sets of EC processes were conducted with 'A' and 'B' electrodes with operating parameters such as pH, EC time, NaCl electrolyte and applied current were adopted for optimization to obtain greater color elimination.

D. Efficiency of Extraction of Color (EEC %)

The spectrophotometer JascoV-670 was used to determine the dye solution's wavelength (542 nm). Upon electrocoagulation, the following formula was used to measure EEC percent.

$$\text{EEC} \% = 100 \times \frac{(A_b - A_t)}{A_b}$$

(1)

Where Ab and At respectively where the dye's absorption in solution before electrocoagulation and at the moment t and to measure the pH of the solution pH meter is used (Eutech).

E. Structural Investigation and Surface Morphology

Micro structure of the particles present in the electrode was studied by X-Ray diffractometer [SHIMADZU-6000]. Scanning Electron Microscope (SEM) [JEOL 6390], was used to analyze the surface morphology. Elemental analysis was done by Energy Dispersive X-Ray Spectroscopy (EDS).

F. Statistical Analysis

The 2 Level ANOVA studies were carried out using the Design Expert software. The following table illustrates the results obtained after carrying out each experiment. Operational parameters like varying pH, concentration of dye, NaCl, current and time were analyzed for finding its efficiency of the each parameter for optimization. Imitates were maintained for all experiments, and the results were statistically analyzed by performing regression analysis at 5% level of significance using SPSS software [6].

III. RESULTS AND DISCUSSION

A. XRD Analysis of the Zn/TiO$_2$

The X-ray diffractogram of Zn/TiO$_2$ obtained from both the methods and zinc are shown in Fig 1. The diffraction peaks of TiO$_2$, and zinc are present in the investigated electrode. The electrode from spray pyrolysis method has more numbers of TiO$_2$ peaks than compared to the one obtained by thermal decomposition method. The planes corresponding to (002), (100), (101), (102), (103) are the peaks for zinc substrate. From the XRD results, deposition of TiO$_2$ is confirmed with 2theta values (30,32,35,47,56,63,68) and deposition of Zn with 2 theta values (36,43,54,70,78). Peaks (104), (110), (024) and (018) are the peaks of TiO$_2$ present in the electrode from thermal decomposition method, besides these peaks, four more peaks of TiO$_2$ are present in the electrode from spray pyrolysis method, and since with more TiO$_2$ peaks in this electrode showed better results in the percentage color removal of the dye under electrocoagulation study.

B. SEM and EDX Analysis

Fig 2 represents the SEM micrograph of zinc, Zn/TiO$_2$ from TD and SP methods. From the SEM micrographs, the TiO$_2$ particles are irregular in shape and appeared in an agglomerated state. The electrode by TD has been found with cracks, but from SP method crystalline particles are irregular in shape and appeared in an agglomerated state. The electrode by TD has been found with cracks, but from SP method crystalline particles are seen on zinc.

![Fig 1. XRD Pattern for Zn and TiO$_2$/Zn by TD, and SP](image1)

![Fig 2 SEM Monograph (a) Zn, (b) Zn/TiO$_2$ (TD) (c) Zn/TiO$_2$ (SP)](image2)
The coating of TiO$_2$ on zinc substrate has increased the surface roughness which in turn resulted in more contact area. And the increase in more contact area resulted in increasing the efficiency of dye removal in the case of Zn/TiO$_2$ by SP method in EC process. The percentage of elements in the uncoated and coated zinc substrate are done through EDS analysis and the percentage composition of elements in both the electrodes are given in Table 1 [16].

Table 1: Percentage composition of elements in the electrodes

| Element | Zn Substrate Weight (%) | ZnTiO$_2$ (TD) Weight (%) | Zn/TiO$_2$ (SP) Weight (%) |
|---------|-------------------------|---------------------------|---------------------------|
| O       | 7.27                    | 0.70                      | 59.81                     |
| Zn      | 92.25                   | 11.14                     | 15.58                     |
| Zn      | 42.71                   |                           | 20.37                     |

The results obtained were analyzed using ANOVA (Analysis of Variance) and the following results were obtained for adsorption capacity:

The $r^2$ value comparing pH to Dye was 0.689 (significant at $P < 0.05$). In the present study, this method was used to develop the effectiveness of absorption of the dye in solution for all the parameters like varying pH, concentration of dye, NaCl, current and time. The "Pred R-Squared" of 0.689 agrees with the "Adj RSquared" of 0.658. This model can be used to find the efficiency of adsorption of the dye with the flocs the metal hydroxides formed from both the anode and cathode during EC process. The result shows slight deviation from the fitted non-linear equation of Langmuir model as indicated by the high value of $R^2$ ranging from 0.658 to 0.689. The highest $R^2$ value was obtained at 25°C [18]. The values of (1/n) obtained were in the range 0 and 1 thus indicating the favorable nature of the process and heterogeneous nature of the adsorbent surface. Therefore, the linear regression model is also well fitted using the data. Hence, it can be concluded that TiO$_2$/Zn is indeed releases more of Ti(OH)$_3$ which adsorb the dye molecules, using design of experiment in two factor model [19].

From the table 2, the electrodes Zn/TiO$_2$ (SP) has more consistency than Zn/TiO$_2$ (TD) in treating the Coralene Red 3G dye for its color removal in electrocoagulation process.

Table 2: Effect of varying parameter on EEC%
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Table 3: ANOVA Analysis Table for Electrodes.

| Source       | Sum of Squares | df  | Square of Mean | F Value | P Value | P Value Prob. > F | Significant @ 5% |
|--------------|----------------|-----|----------------|---------|---------|------------------|------------------|
| For All      | 6426.3         | 4   | 1606.59        | 3.652   | 0.01040 | < 0.05           |                  |
| A-pH         | 5032.7         | 1   | 5032.755       | 22.20   | 0.00082 | < 0.05           |                  |
| B-Dye        | 2007.2         | 1   | 2007.253       | 3.145   | 0.10652 |                  |                  |
| C-NaCl       | 2206.4         | 1   | 2206.483       | 5.506   | 0.04088 | < 0.05           |                  |
| D-Current    | 15.962         | 1   | 15.96213       | 0.594   | 0.45855 |                  |                  |
| E-Time       | 674.70         | 1   | 674.7000       | 5.067   | 0.04809 | < 0.05           |                  |
| AB           | 1242.57        | 1   | 1242.57        | 1.742   | 0.20038 |                  |                  |
| AC           | 17.18          | 1   | 17.18          | 0.0279  | 0.86879 |                  |                  |
| AD           | 956.97         | 1   | 956.97         | 2.7761  | 0.10985 |                  |                  |
| AE           | 1242.57        | 1   | 1242.57        | 2.9377  | 0.010589|                  |                  |

The F-value of 22.20 obtained from the model implies it’s significant [20]. There is a 0.05% chance that a “Model F-Value” this large could happen due to the presence of more of Ti$_2$O$_3$.

IV. CONCLUSION

In conclusion, the percentage of dye removal has a linear relationship with pH, amount of adsorbent and concentration of dye with current and time and there is also a significant interaction between amount of adsorbent and concentration of dye. The electrodes Zn/TiO$_2$ from spray pyrolysis has more efficiency than the one from thermal decomposition in treating the Coralene Red 3G dye for its color removal in electrocoagulation process because of more number of TiO$_2$ peaks which in turn formed more Ti(OH)$_3$ and adsorption of dye with these flocs resulted in increasing the coagulation of dye molecules, so better removal of disperse dye.

REFERENCES

1. COIN qDS, Comprehensive Industry Documents Series on Textile Industry, Central Pollution Control Board, India, 59 (2000)
2. Verma A.K., Dash R.R. and Bhunia P., A review on chemical coagulation /flocculation technologies for removal of colour from textile wastewaters, Journal of Environmental Management, 93, 154 – 168 (2012)
3. Zodi S., Merzouk B., Potier O., Lapicque F. and Leclerc J.P., Direct red 81 dye removal by a continuous flow electrocoagulation/flocculation reactor, Separation and Purification Technology, 108, 215-222 (2013)
4. Alinsafi A., Khemis M., Pons M., Leclerc J., Yacoubei A.,Benhammou A. and Nejmeddine A., Electro-coagulation of reactive textile dyes and textile wastewater, Chemical Engineering and Processing, Process Intensification, 44, 461 – 470 (2005)
5. Kobya M., Demirbas E., Can O. and Bayramoglu M., Treatment of levafix orange textile dye solution by electrocoagulation, Journal of Hazardous Materials, 132, 183–188 (2006)
6. M.Srinivas Kini*, K.Balakrishna Prabhu, Ankit Gundecha and Devika U “Statistical Analysis of Congo Red Dye Removal Using Sawdust Activated Carbon”, International Journal of Applied Engineering Research ISSN 0973-4562 Volume 12, Number 19 (2017) pp. 8788-8804
7. Hooshmandfar A., Ayatii B. and Darban A.K., Optimization of material and energy consumption for removal of Acid Red 14 by simultaneous electrocoagulation and electrof flotation, Water Science and Technology, 73(1), 192–202 (2006)
8. Can O., Kobya M., Demirbas E. and Bayramoglu M., Treatment of the textile wastewater by combined electrocoagulation, Chemosphere, 62, 181–187 (2006)
9. Yildiz Y.Ş., Optimization of Bomaplex Red CR-L dye removal from aqueous solution by electrocoagulation using aluminum electrodes, Journal of Hazardous Materials, 153, 194–200 (2008)
10. Lin S.H. and Peng C.F., Treatment of textile wastewaters by electrochemical method, Water Res, 28, 277-867 (1994)
11. Ogutveren U.B. and Koparal A.S., Colour removal from textile effluents by electrochemical destruction, J Environ Sci Health., A29, 1-16 (1994)
12. Iravimi S., Demircioglu N. and Yildiz Y.S., The effects of pH on phosphate removal from wastewater by electrocoagulation with iron plate electrodes, J Hazard Mater, B137, 231-1235 (2006)
13. Nawczyle J. et al, Electrochemical treatment of tannery wastewater containing high strength pollutants, Trans Inst Chem Eng., 74B, 59-68 (1996)
14. Chen X., Chen G. and Yuc P.L., Separation of pollutants from restaurant wastewater by electrocoagulation, J Environ Eng., 126, 858-863 (2000)
15. Parameswari Kalivel, Jegathambal Palanichamy and Mano Magdalene Rubella Potential of Ti2O3/Zn Electrodes versus Zn by Electrocoagulation Process for Disperse Dye Removal Asian Journal of Chemistry, Vol. 31, No. 8 (2019), 1835-1841
16. Ali, G., et al. A comparison of similarity indices for catchment classification using a cross-regional dataset Advances in Water Resources, 40, 11–22 (2012)
17. Mohamed Chaker Ncibi Applicability of some statistical tools to predict optimum adsorption iso thermals linear and non-linear regression analysis, Journal of Hazardous Materials 153 (1-2), 207-212, (2008)
18. Helset, D.R.and Hirsch, R.M., Statistical methods in water resources, book 4, hydrologic analysis and Interpretation. Virginia: US Geological Survey. (2002)
19. Ahmet Gürses, MehmetYaначен and Cetin Dogar Electrocoagulation of some reactive dyes: a statistical investigation of some electrochemical variables* Waste Management, Volume 22, Issue 5, P. 499 2002)
20. Mohd Rafatullah, Abbas F.M. Alkarkhi, T.T TengRemoval of Terasil Red R dye by using Fenton oxidation: A statistical analysis, Desalination and water treatment 52(22-24) (2014)
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