JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

REMOVAL OF METHYLENE BLUE DYE USING ZINC OXIDE NANOPARTICLES AS ADSORBENT: RSM APPROACH

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Abstract: This study was undertaken to investigate response surface methodology (RSM) for the removal of methylene blue (MB) from aqueous solution using zinc oxide as adsorbent. The effect of various process parameters namely initial concentration (10–100 mg L^{-1}), adsorbent dose (0.05–0.40 g), time (60–240), pH (7) and stirring rate (150 rpm) was taken as parameter. A total of 15 adsorption experimental runs were carried out using the detailed conditions designed by RSM based on the Box–Behnken design (BBD). The regression co-efficient (R^2) of the models developed and the results of validation experiments conducted at optimal conditions strongly suggests that the predicted values are in good agreement with experimental results Regression analysis showed good fit of the experimental data to the second-order polynomial model with coefficient of determination (R^2) value of 0.9760 and model F value of 40.68. The predicted R^2 value is 0.7979.

***Index Terms* - Nanoparticles, Zinc oxide adsorbent, Methylene blue, Adsorption, RSM, ANOVA, Box behnken design.**

I. INTRODUCTION

Now a days the various industrial activities causes a significance of environment challenge. The fast growth of industrialization and Urbanization cause environmental contamination and a lack of water. Dyes are used to colouring purpose in the textile, food, cosmetics, paper, plastics, and leather sectors. A large quantity of water, dye and chemicals are used in textile industry. These industries releases huge quantity of coloured waste water which pollute the water bodies in respect of aesthetic value [1]. Certain Dyes are poisonous, and they may cause cancer and mutations. During decomposition, many dyes release chemicals as by products which are poisonous and have a negative impact on the environment. The contamination of dye in water bodies causes the low sunlight penetration and poor photosynthetic activities [2]. Adsorption procedure is attractive compared to other methods because of its high effectiveness, cost, availability, and simple of design. Adsorption can be either physisorption (which involves fairly weak intermolecular forces), or chemisorption (which involves basically the formation of a chemical bond between the sorbent molecule and the surface of the adsorbent) [3].

Zinc oxide nanoparticles is the preferred adsorbent for dye removal because of extended high adsorption capability, microporous structure, and surface area [3].The experiments using batch adsorption are performed to assess the capacity of the zinc oxide adsorbent for removal of methylene blue dye from aqueous solution. The batch operations are designed to examine dye adsorption using the adsorbent [4]. The parameters of the batch experiments were pH of the solution, adsorbent dosage, stirring rate, initial dye concentration, Contact duration. Different adsorption model equations were used to find out the best model that fitted well to the experimental data. The statistical model, response surface methodology (RSM) via Box-Behnken design (BBD) were applied to batch experimental data set for optimization and to confirm the validity of the zinc oxide adsorbent for dye removal [5]. All together a batch study for the economic, easy and eco–friendly solution of dye pollution in aqueous solution has been done.

II. OBJECTIVES OF THE STUDY

- Evaluate the zinc oxide nanoparticles adsorbent ability to remove methylene blue from a synthetic sample by considering the various parameters namely Time, Dosage, Concentration, pH.
- To analyse zinc oxide nanoparticles as adsorbent characterization.
- To assess the adsorption performance of zinc oxide nanoparticles adsorbent using Response Surface Methodology and ANOVA model

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III. METHODOLOGY

3.1 Preparation of Methylene Blue Synthetic Sample

Methylene Blue stock was primed by dissolving exactly weighed (1.0 gm) in distilled water to its intensity of 1000mg/L. The trial will be prepared by mixing the dye stock solution in precise magnitude to required value for adsorption of colour before using in the batch studies [5].

3.2 Adsorption Studies

Batch experiments were carried out in a magnetic stirrer setup with stirrer equipment, with 1000 ml of distilled water placed in a beaker. A dye solution of known concentration and a known amount of ZnO particles were added to this at a specified pH. The run was completed at a preset rpm, and the results were satisfactory. Zinc oxide nanoparticles in varying concentrations of 0.05 to 0.4 grams were added to a beaker and stirred at a rate of 150 rpm for 60 to 240 minutes. After each run, the percent MB removal was calculated by using below equation 1 [6].

$$\text{Removal efficiency (\%)} = \frac{c_i - c_f}{c_i} \times 10 \qquad (1)$$

C_i = initial MB concentration, C_f = final MB concentration.

3.3 EXPERIMENTAL DESIGNS

The Box-Behnken design (BBD) is used to plan the experimental studies for the adsorption of MB on zinc oxide nanoparticles in Minitab 19. A total of 15 adsorption experimental runs were carried out using the detailed conditions of variables via. Time, intial concentration of Methylene blue dye and adsorbent dosage are designed by RSM based on the Box–Behnken design (BBD). The proposed quadratic model for Box-Behnken design fits well to the experimental data since it may be used to route design space allowing to ANOVA results. The experimental data which gives the levels of variables are shown in table-1.

Table 1: Variables and levels considered for the adsorption of MB onto Zinc Oxide

Variables	**Levels**		
	Units	**Low**	**High**
Adsorbent Dosage	grams	0.05	0.4
Initial Concentration	mg/l	10	100
Agitation Time	minutes	60	240

IV. RESULTS AND DISCUSSION

4.1 Characterization of Zinc Oxide Nanoparticles

SEM is used to investigate the surface morphology of zinc oxide nanoparticles. Figure 1 and 2 show SEM images of ZnO nanoparticles before and after adsorption. In the SEM picture of ZnO nanoparticles powder, the presence of pores and internal surface are evident prior to adsorption. The microscope analysis reveals that methylene blue adsorption has completely blurred the porous structure observed in Figure 1.

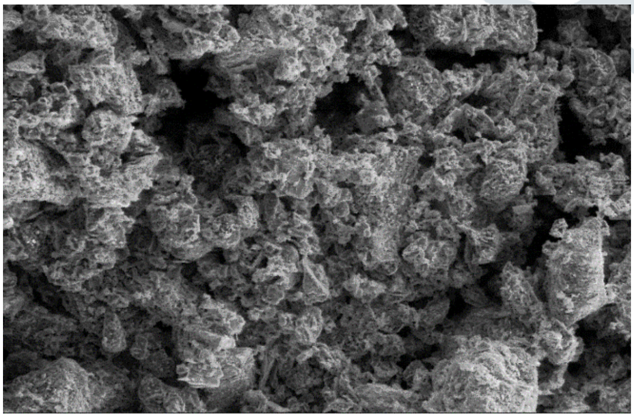

Figure 1. SEM of ZnO Nanoparticles before Adsorption

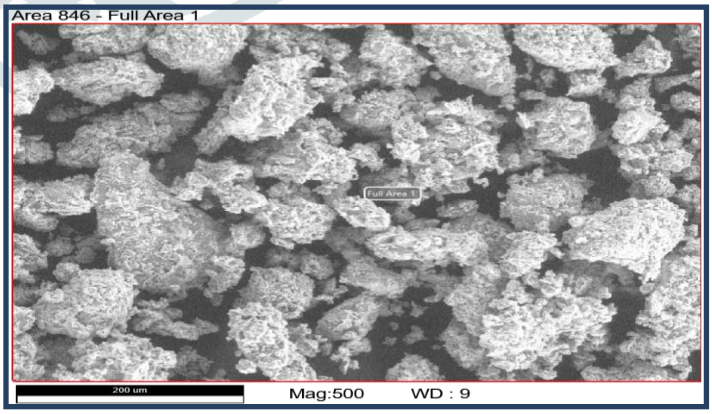

Figure 2. SEM of Zno Nano Particles after Adsorption

4.2 EDX Analysis

Energy dispersive X-ray analysis (EDX), as seen in figure 3 and 4 was used to Pre and post evaluation of the Methylene blue adsorption on ZnO nanoparticles. The pattern of EDX shown in Figure 4 the adsorption of Methylene blue on ZnO nanoparticles was increases in the strength of the Zn and other new metal are found in the adsorption from the Zn solution.

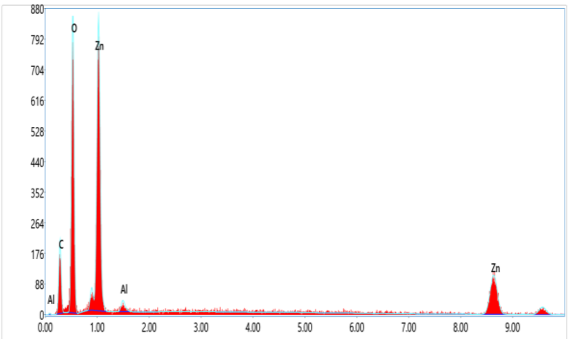

Figure 3. EDX Analysis of before Adsorption

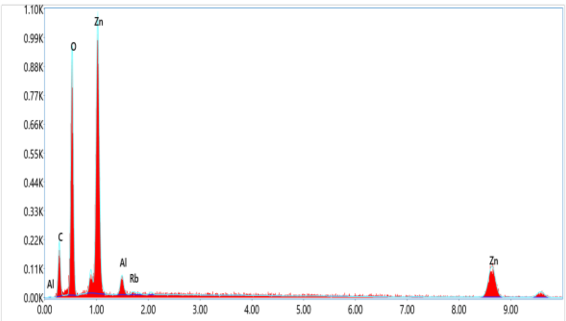

Figure 4. EDX Analysis of after Adsorption

4.3 RSM Modelling

The collected data were evaluated with Minitab software, as shown in Table 2, and the expected values were rather near to the actual response values for the particular run in experiment.

The output of the created response surface model is shown in Table 3 that is ANOVA model. The suggested response surface model's statistical suitability for describing the methylene blue adsorption process on ZnO nanoparticles in the investigated range is determined by the ANOVA test. The model is significant, as indicated by the F-value of 93.98% and model terms are significant if their values are less than 0.05. C, A^2, and C^2 are the three most essential model terms here. Terms of model are not considered significant if their p-values are larger than 0.1. The model is more fitting and the individual coefficients are more significant as the Fisher f-value is higher.

The terms that influence the model using the f value are as follows: $AC>BC>CA>A^2>B^2>C^2$ the most affected model is shown for the initial concentration and agitation time. The R^2 represent degree of fitness, or coefficient of determination of 98.7% illustrate the excellent connection between expected and actual results which is done by the experiment. The model is valid since these numbers are near to unity (Chattoraj et al 2013).

R^2 is the % of response variation explained by the model, it should range from 0 to 100%. As a result, it is 96.04 % here in the Table 4. R^2-(adj) permits model comparison with predictors, which aids in model selection. Equation 2 is the relation between the response and the independent process variables in a quadratic model:

$$R\% = 97.64 - 0.0839\ A - 0.3696\ B - 14.3\ C + 0.00040\ A * A + 0.000067\ B * B + 39.4\ C * C + 0.000244\ A * B - 0.0324\ A * C - 0.059\ C * B. \quad (2)$$

Table 2: RSM Method, Methylene Blue Adsorption on Zno Nanoparticles Box-Behnken Design Matrix with Actual and Predicted Values was created.

Runs	**Time (sec) A**	**Initial concentration of dye (mg/l) B**	**Adsorbent dosage (gms) C**	**Actual values (% removal)**	**Predicted values (% removal)**
1	150	100	0.4	58.00	57.83
2	150	10	0.4	88.75	89.25
3	240	10	0.225	93.20	94.64
4	60	55	0.4	71.64	73.25
5	150	55	0.225	73.02	73.02
6	150	55	0.225	73.02	73.02
7	60	55	0.050	71.92	73.87
8	60	10	0.225	90.85m	88.78
9	240	55	0.050	84.40	82.78
10	150	100	0.050	60.90	60.39
11	150	55	0.225	73.02	73.02
12	240	100	0.225	64.00	66.12
13	240	55	0.40	82.08	80.12
14	60	100	0.225	57.70	56.25
15	150	10	0.050	89.80	89.96

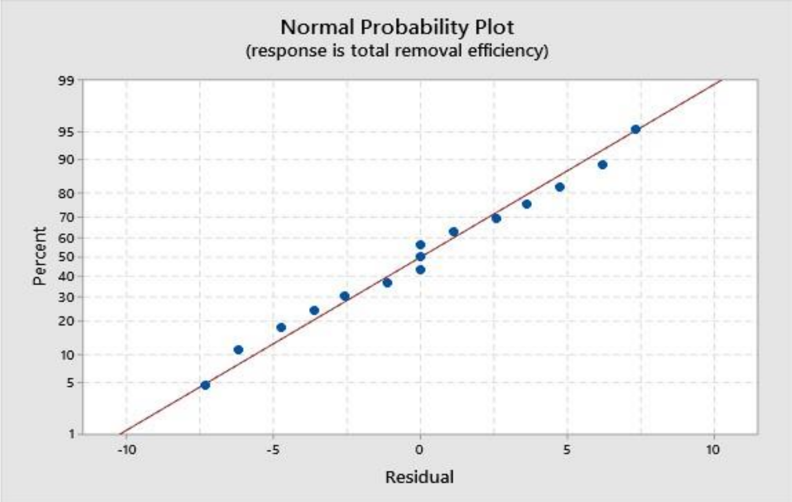

Figure 5: Normal Probability Plot of Residuals

Table 3: Analysis of Varience (ANOVA) for Percentage Removal of MB on Zno nanoparticles.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	2039.5	226.62	42.61	0.000
Linear	3	1990.4	663.48	124.75	0.000
Time	1	124.58	124.58	23.42	0.005
Concentration	1	1860.5	1860.50	349.81	0.000
Dosage	1	5.36	5.36	1.01	0.361
Square	3	43.30	14.43	2.71	0.155
Time*Time	1	39.78	39.78	7.48	0.041
Concentration*Concentration	1	0.07	0.07	0.01	0.915
Dosage*Dosage	1	5.38	5.38	1.01	0.361
2-Way Interaction	3	5.80	1.93	0.36	0.783
Time*Concentration	1	3.90	3.90	0.73	0.431
Time*Dosage	1	1.04	1.04	0.20	0.677
Concentration*Dosage	1	0.86	0.86	0.16	0.705
Error	5	26.59	5.32		
Lack-Of-Fit	3	26.59	8.86	*	*
Pure Error	2	0.00	0.00		
Total	14	2066.1			

Table 4: Model Summary of Zinc Oxide Nanoparticles

S	R-sq	R-sq(adj)	R-sq(pred)
2.30622	98.71%	96.04%	79.41%

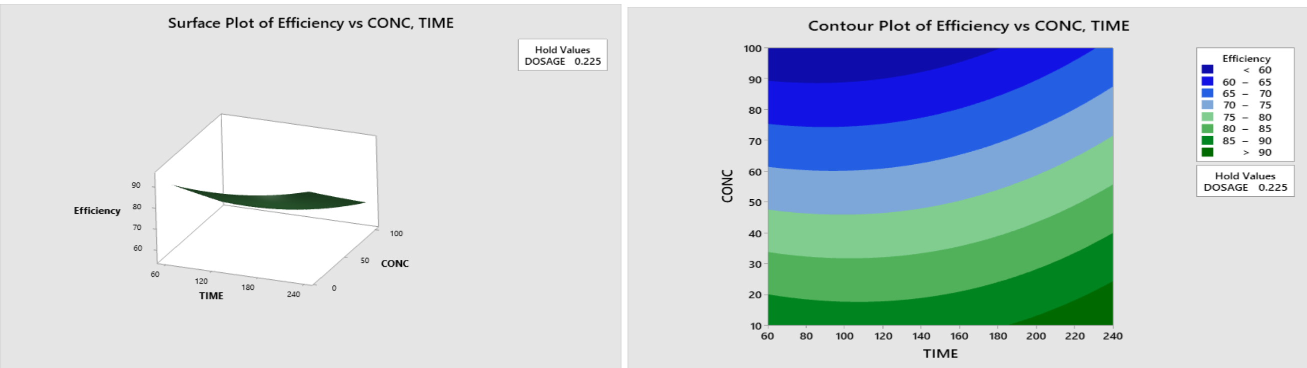

Figure 6: 3D Surface Plot and 2D contour plot of the Concentration and Time Effect on Removal Efficiency

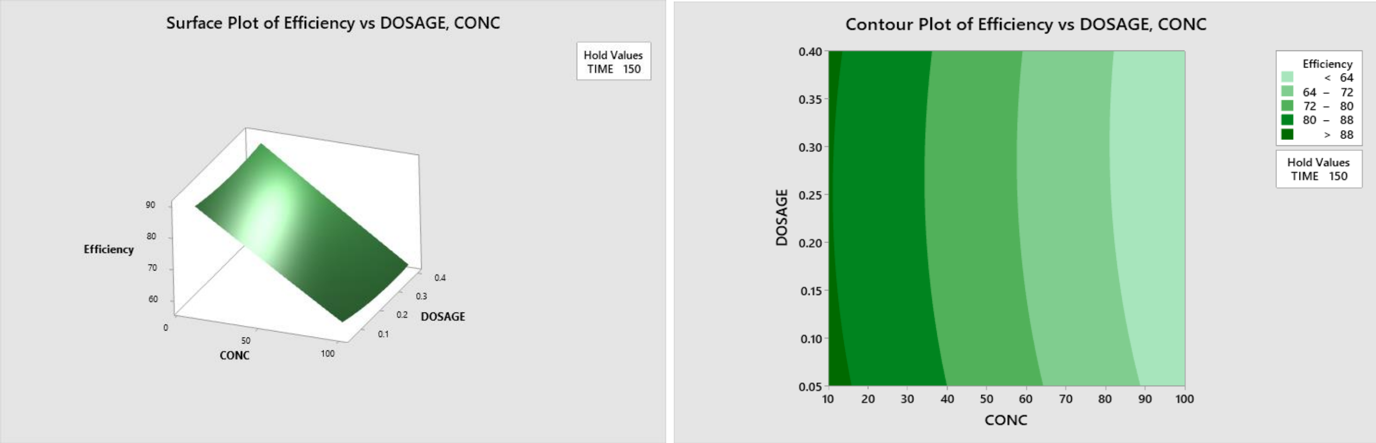

Figure 7: 3D Surface Plot and 2D Contour plot of the Dosage and Concentration Effect on Removal Efficiency

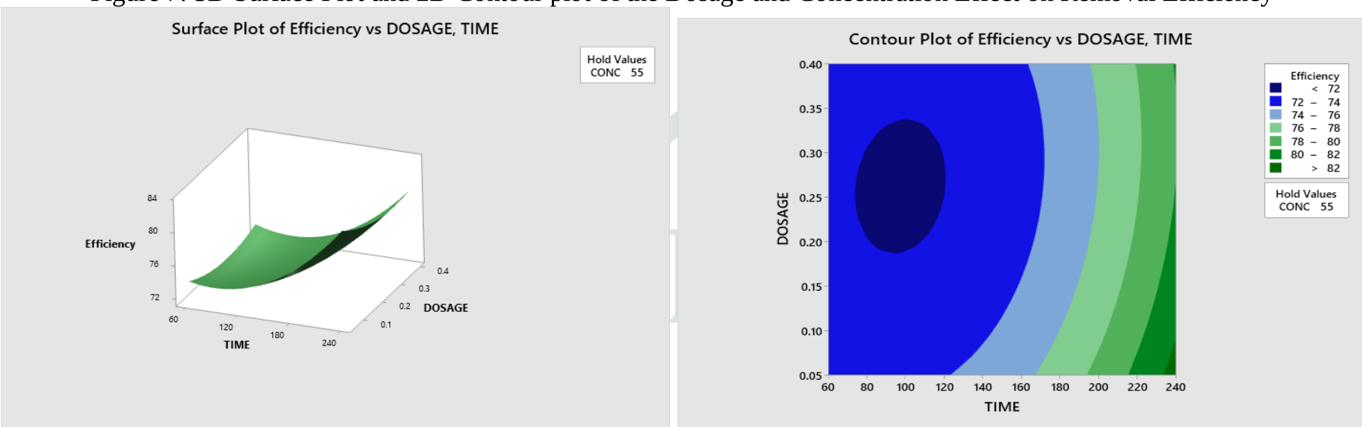

Figure 8: 3D Surface Plot and 2D Contour plot of the Time and Adsorbent Dosage Effect on Removal Efficiency

4.4 Response Plots

RSM is a statistical approach used to investigate the combined impact of independent process factors on responses (Cao et al.2014). The interactions between the process variables and their corresponding output responses are depicted in 2D contour and 3D surface plots in figure (6-8). Fig 6, 7 and 8 shows that with increasing adsorbent dose, methylene blue adsorption on ZnO nanoparticles increased. Because the adsorbents have a larger surface area, they have the highest removal efficiency and the agitation time is a critical parameter. The adsorption of the adsorbate methylene blue was enhanced with increasing agitation duration and dosage of ZnO nanoparticles, and this is attributed to the availability of more active adsorption sites. For the existence of ample time for the processes and the presence of methylene blue dye respectively. The interaction between nano dosage and methylene blue dye adsorption on ZnO nanoparticles has a detrimental influence on the adsorption process.

4.5 Conclusion

The capabilities of RSM in the interaction impacts of the process variables and their optimal conditions were investigated to anticipate the output response. Optimal condition for methylene blue removal of 94.64% is obtained at pH of 7, time 240 minutes, the adsorbent dosage of 0.225 grams, and initial concentration of 10 mg/l, so it may be inferred from the current work that the zinc oxide nanoparticles can be utilized to remove methylene blue from its aqueous solution. It is concluded that regression co-efficient (R^2) of the models developed and the results of validation experiments conducted at optimal conditions strongly suggests that the predicted values are in good agreement with experimental results Regression analysis showed good fit of the experimental data to the second-order polynomial model with coefficient of determination (R^2) value of 0.9760 and model F value of 40.68. The predicted R^2 value is 0.7979.

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