Removal of Indigo Blue Dye Using Iron Oxide Nanoparticles– Process Optimization Via Taguchi Method

SANGITA YADAV*, SUBHASH CHANDER*, NEHA*, SWETA KUMARI*, ANKUR* and ASHA GUPTA*

Department of Environmental Science and Engineering, GJUS&T, Hisar-125001, Haryana, India.
*Corresponding author E-mail: guptaaha.env@gmail.com, gupta06amit@gmail.com

ABSTRACT

In this study, the parameters for the adsorption of indigo blue dye onto iron oxide nanoparticles were optimized in a batch system (Fe_3O_4@ME nanoparticles nanomaterials synthesized using bacterial extracts and Fe_3O_4 nanomaterials synthesized using bacterial cell mass). The Taguchi optimization approach (an L9 array design) was utilized to estimate the significance and interaction impacts of many examined parameters (initial concentration of indigo blue dye, adsorbent dose, and contact time) on the adsorption process. It was observed that the ideal conditions were 0.125 g of adsorbent, 13 mg/lit of initial dye concentration, and 90 min of contact time at pH 7, room temperature. In this study, at optimized conditions, the percent dye removal for Fe_3O_4 and Fe_3O_4@ME nanoparticles was 86 and 76, respectively. The percentage contribution of each process parameter to the elimination of indigo blue dye was determined using the Analysis of Variance (ANOVA) method. It was found that Taguchi could accurately forecast the outcomes. In order to support the accuracy of the process parameter optimization under the specified experimental conditions, it was found that the percentage removal of the indigo blue dye obtained in the confirmatory experiments carried out under optimized conditions was higher than that optimized in each of the Taguchi design's test runs.

Keywords: Iron oxide nanomaterials, Indigo blue dye, Taguchi, Analysis of Variance (ANOVA), Optimization.

INTRODUCTION

For water and wastewater treatment procedures, the presence of micro and nanopollutants in water resources has recently emerged as a significant challenge. These pollutants are composed of waste products from both natural and manmade, such as pesticides, industrial chemicals, heavy metals, radioactive elements, personal care items, steroid hormones, industrial chemicals, and many other new emerging contaminants (Robledo-Padilla *et al.,* 2020). Industrialization has significantly impacted the world economy in recent decades but has also had various detrimental environmental effects (Patnaik, 2018). One of the primary sources of pollution is the discharge of harmful chemicals into the environment via industrial wastewater (Yadav *et al.,* 2022; Shindhal *et al.,* 2021). The discharge

of colored compounds is one of the main reasons for water contamination. These dyes are routinely dumped into natural streams that people use for everyday activities like drinking, bathing, and taking showers; therefore, this type of pollution may result in various significant issues for individuals. Most significantly, these wastewaters seriously endanger people's health because they are toxic and cancer-causing. Additionally, impeding the introduction of synthetic dyes into natural streams has a negative effect on the photochemical processes cesses that take place in aquatic ecosystems (Zolgharnein, and Rastgordani, 2018). Dyes must thus be eliminated from all discharges due to more excellent knowledge of their toxicity and strict environmental safety regulations to prevent contamination of the biological ecology (Pundir *et al.,* 2018). As a synthetic dye with an aromatic molecular structure that is more durable and more difficult to biodegrade, indigo dye wastewater treatment is one of the most challenging processes. By changing their chemical composition, new molecules called xenobiotics may develop that are potentially more dangerous than the original substances (Robledo-Padilla *et al.,* 2020). These carcinogens have several adverse effects on aquatic organisms and significantly affect the environment's natural food chain. Despite the development of numerous chemical, physical, and biological methods such as coagulation/flocculation, ozonation, electrochemical methods, biological treatment, photocatalyst, and adsorption for the treatment of wastewaters containing indigo blue dyes in the last decade, the design and development of new industrial techniques with high efficacy and reusability to treat these wastewaters before releasing them into the environment is a crucial requirement (Haghgir *et al.,* 2022).

One of these strategies, adsorption, has proven to be particularly successful in eliminating different pollutants from wastewater streams (Abbasi, 2020). In the simple, efficient, cost-effective adsorption approach, various synthetic and natural materials can be used as adsorbents (Mosoarca *et al.,* 2022b; Mosoarca *et al.,* 2022c). Examples of frequently used adsorbents include activated carbon, lignin, zeolite, metal-organic frameworks, biomass residue, nanomaterials, etc. As nanotechnology has developed quickly in recent years, the application of nanomaterials in the environmental sphere has increased

(Sultan *et al.,* 2022; Wang *et al.,* 2022). Nanosized materials are destructive sorbents with several benefits over their commercial analogs, including strong surface reactivity and ease of synthesis from readily available natural materials. They have also been shown to be superior adsorbent materials (Janani *et al.,* 2022; Mansour *et al.,* 2022). Time, initial dye concentration, pH, adsorbent dose, temperature, and ionic strength influence adsorption. In order to get the highest dye removal efficiency feasible, these parameters should be optimized. Optimizing experiment conditions is essential for adsorption. The Taguchi approach is one of the best methods for determining the best design configuration in multifactor situations (Babji *et al.,* 2022; Mosoarca *et al.,* 2022a). Numerous earlier experiments that use various optimization techniques to maximize dye removal are documented in the literature. The Taguchi method can maximize the response while minimizing the number of tests andconsidering how the various variables interact and affect each other.

However, some articles recommend Taguchi designs to enhance dye removal. Abbas *et al.,* (2022) and Mahapatra, and Kumar, (2022), also found the Taguchi method appropriate, for the optimization process. This study removed indigo blue dye from synthetic water by adsorbing using iron oxide nanoparticles as an adsorbent. One of the key objectives was to use the Taguchi technique to determine the optimum adsorption parameters after assessing the effects of various controllable factors on the efficiency of the process and the signal-to-noise ratio (S/N). The percentage contribution of each parameter to the dye removal process was calculated using the ANOVA analysis. Additionally, it was determined that Taguchi model forecasts were accurate.

Methodology
Determining dye in the solution

The initial and final concentrations of the indigo blue dye in the solutions were calculated using UV-Visible spectroscopy. On a UV-Vis Spectrophotometer, the wastewater's equilibrium time and maximum absorbance wavelength (λ_{max}) were measured. The standard solutions (10, 20, 40, 60, 80, and 100 mg/L), which cover the working ranges, were prepared using the reference standard stock solution for indigo blue dye, which has a concentration of 1000 mg/L. Using

the calibration curve produced by the standard solutions of indigo blue dye, the concentration of the sample was determined by measuring its absorbance. The percentage of indigo blue dye adsorption (%b) by iron oxide nanoadsorbents was expressed as follows:

$$\%b \text{ dye removal} = (c_0 - c_e)/c_0 \times 100 \tag{1}$$

Where C_o (mg/L) is the initial concentration and C_e (mg/L) is the final concentration in the solution (Ghosh and Sinha, 2015).

EXPERIMENTAL

The initial indigo blue dye concentration, contact time, and adsorbent dosage were used as independent (input) variables to investigate the effects of each on the removal of indigo blue dye from the aqueous matrix and there cumulative effects on dye adsorption. These parameters and their range were selected based on the literature (Palai *et al.,* 2021) and according to some preliminary experiments. The pH and temperature conditions were set at 7 and 280 Celsius to make the adsorption process more affordable and environmentally friendly, respectively.

In particular, batch systems (polycarbonate cylindrical cells with lids) with continuous agitation (150 rpm) were used for the adsorption test. Because most conventional technologies are unsuccessful in treating dye pollution at low concentrations due to high operating costs, the initial indigo blue dye solution range was chosen to be 6-20 mg/L (Ghosh and Sinha, 2015). Table 1 displays the range of the initial indigo blue dye concentration, contact time, and adsorbent dosage employed in the this study. All statistical examinations for optimizing experimental variables were performed using Minitab software version 21.

Table 1: Range of the investigated parameters

Parameters	Range	
	Low	High
Dose (g)	0.05	0.2
Conc. (mg/lit.)	6	20
Contact time (minutes)	60	120

The variance analysis (ANOVA) was used to assess the degree to which these models accurately matched the experimental data. The Fischer (F-test) test with a 95 percent confidence interval was used to assess the statistical significance of the models and the interaction effects of each factor on the responses. The decision was made assuming that a model is a suitable approach to the actual data, the error resulting from lack of fit is insignificant, and the variation brought on by the regression is substantial at a 95% confidence level. Additionally, the model's appropriateness was evaluated using the regression coefficient (R^2), corrected regression coefficient (ADJ-R^2), predicted multiple determination coefficient (Pre-R^2), and the sum of squares of predicted residual errors (PRESS).

Taguchi

The Taguchi technique, an orthogonal design array-based fractional factorial design, was developed by the statistician and engineer Genichi Taguchi. This design makes it easy to conduct a limited number of experiments to examine the effects of various components on reactions at various levels. The orthogonal array architecture facilitates the organization of the variables and the levels at which they should be modified. In addition, the factorial design evaluates all possible combinations, saving time, money, and resources, whereas the Taguchi technique only examines at pairs of possibilities. These arrays can be used to determine the crucial elements of an experiment and predict the interactions between variables and operational parameters (Sy Mohamad *et al.,* 2020). Analyzing the signal-to-noise ratio (S/N) is also essential for assessing the results of experiments. Generally speaking, three alternative signal-to-noise ratios (S/N) can be used: lower is better, nominal is best, and larger is better. The signal-to-noise ratio can be calculated by using the following equation:

$$S/N - 10\log_{10}[1/2\Sigma(1/PRE_i) \tag{2}$$

Where n is the number of experiments conducted under similar experimental conditions, and PRE denotes the outcomes of the measurements (Ghosh, and Mondal, 2019).

RESULT AND DISCUSSION

Taguchi and statistical analysis
The Taguchi method was used to identify the optimum conditions for indigo blue dye adsorption.

In the Taguchi method, the phrases "signal" and "noise" refer to the desired and undesirable values for the output characteristic, respectively. The Taguchi technique uses the signal-to-noise (S/N) ratio to assess quality traits that differ from the target value. The S/N ratios change depending on the type of characteristic. In an orthogonal array of Taguchi experimental designs with two levels, the initial dye concentration, contact time, and adsorbent dose were the three variables employed. The Taguchi technique states that analyzing experimental results requires an investigation of the signal-to-noise ratio because the current experiment focuses on the "larger the better" option. The optimal levels of the parameters for getting the maximal response variable (dye adsorption%) were identified and are displayed in Fig. 1 according to the S/N ratio as the primary effect graph for the SN ratio. The results of the regression analysis were displayed in the main effect graphs. Only the significant variables at a 95% confidence level are displayed.
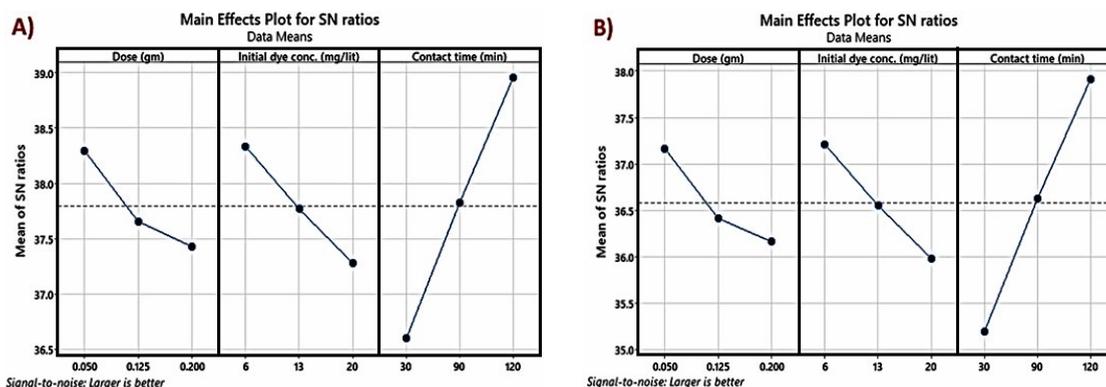

Fig.1. Main effects plot for SN ratio A) Fe_3O_4 and B) Fe_3O_4@ME nanoparticles

Regression analysis was used to determine the indigo blue dye's adsorption rate (Eqs. 3 and 4). Model graphs, including 3D graphs and predicted vs actual value plots, as well as analysis of variance (ANOVA) (Table 2) and model statistic summary (Table 3), are used to express the mathematical model fitting and statistical analysis of observed experimental data for both nanoparticles for indigo blue dye adsorption (%). The significance of the regression coefficients was evaluated using a Student's t-test with a 95% confidence level. Additionally, the model showed an adjusted correlation coefficient R^2 (adj) for Fe_3O_4 and Fe_3O_4@ME nanoparticles of 90.86%, and the predicted R^2 coefficient for Fe_3O_4 and Fe_3O_4@ME nanoparticles is 94.28 and 94.29%, respectively, which fit the statistical model rather well.

Dye adsorption Fe_3O_4=
74.73–48.9 Dose (g)- 0.619 Initial conc. (mg/lit)+ 0.2206 Contact time (min)   (3)

Dye adsorption Fe_3O_4@ME=
64.73–48.9 Dose (g)-0.619 Initial conc. (mg/lit)+ 0.2206 Contact time (min)   (4)

Table 2: Analysis of variance (ANOVA) for the adsorption of indigo blue dye using Fe_3O_4 and Fe_3O_4@ME nanoparticles

Source	DF	Fe_3O_4 Adj SS	Adj MS	F-Value	P-Value	Source	DF	Fe_3O_4@ME Adj SS	Adj MS	F-Value	P-Value
Regression	3	806.7	268.899	27.52	0.002	Regression	3	806.7	268.899	27.52	0.002
Dose (mg)	1	80.67	80.667	8.26	0.035	Dose(mg)	1	80.67	80.667	8.26	0.035
Conc. (mg/lit)	1	112.67	112.667	11.53	0.019	Conc.(mg/lit)	1	112.67	112.667	11.53	0.019
Contact time (min)	1	613.37	613.365	62.77	0.001	Contact time (min)	1	613.37	613.365	62.77	0.001
Error	5	48.86	9.771			Error	5	48.86	9.771		
Total	8	855.56				Total	8	855.56			

Figure 2 illustrates the accuracy of the predicted adsorption percent data using the Taguchi technique. The adsorption of indigo blue dye using Fe_3O_4 and Fe_3O_4@ME nanoparticles

may be demonstrated to be reasonably predicted using Taguchi experimental design, even though it is based on a limited number of experiments as all the points are scattered around the middle straight line in a normal probability plot. The "actual" impacts are determined using a normal probability plot.
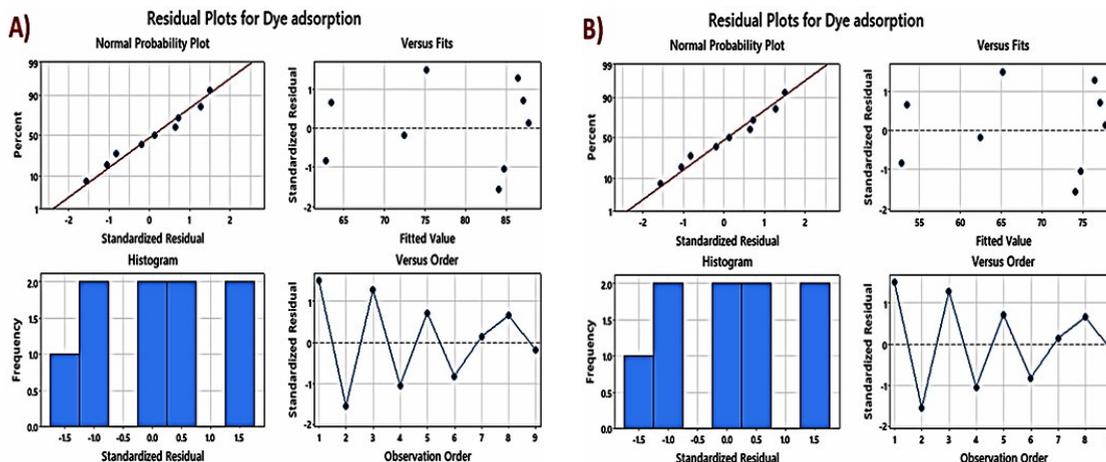

Fig. 2. Residual plots for PBD for A) Fe_3O_4 and B) Fe_3O_4@ME nanoparticles

The relative importance and interactions of the main effects were readily evident on the Pareto chart (Fig. 3). The horizontal columns in the Pareto chart display these values for each effect. The calculated effects were tested using a student's t-test to see if they differed statistically from zero. Values above a reference line or falling inside the 95 percent confidence interval are considered significant (Bingol *et al.,* 2010). According to Fig. 3, the three major components (A, B, and C) that were beyond the reference line were significant at the 0.05 level.
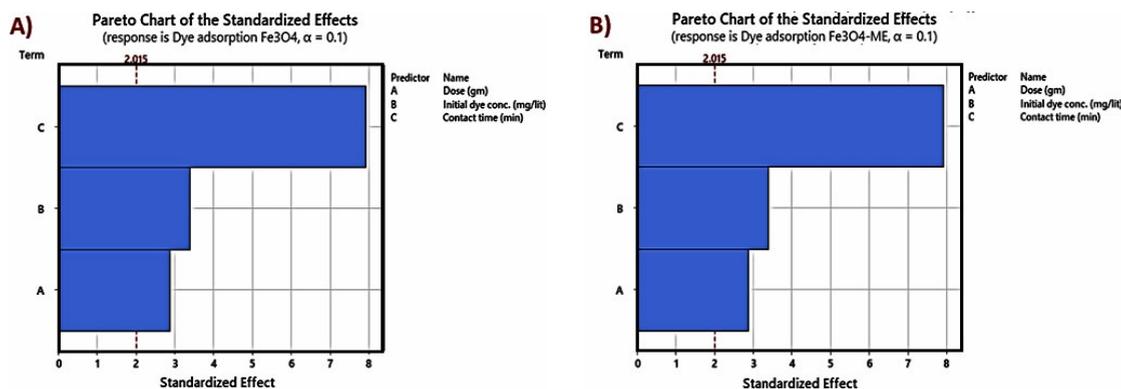

Fig. 3. Pareto plots of A) Fe_3O_4 and B) Fe_3O_4@ME nanoparticles

By examining surface plots of the adsorption percent vs different pairings of effective factors, one can better understand the simultaneous effects of the experimental variable on the dye adsorption process. The combined effects of the initial dye concentration, contact time, and adsorbent dosage are shown in Figures 4 and 5.

Table 3: Model summary statistics

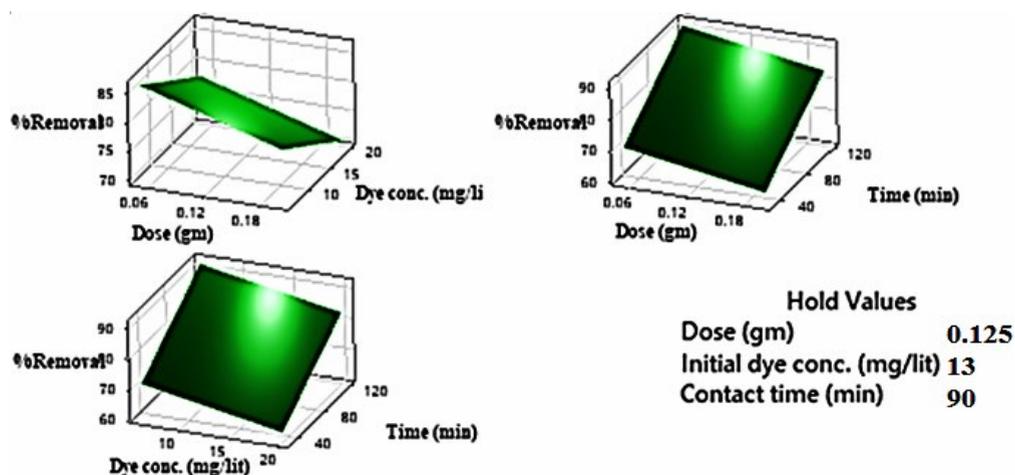| Model	R^2	Adjusted R^2	Predicted R^2	Std. Dev
Taguchi (Fe_3O_4)	0.9428	0.9086	0.7652	3.12593
Taguchi (Fe_3O_4@ME)	0.9429	0.9086	0.7952	3.12593

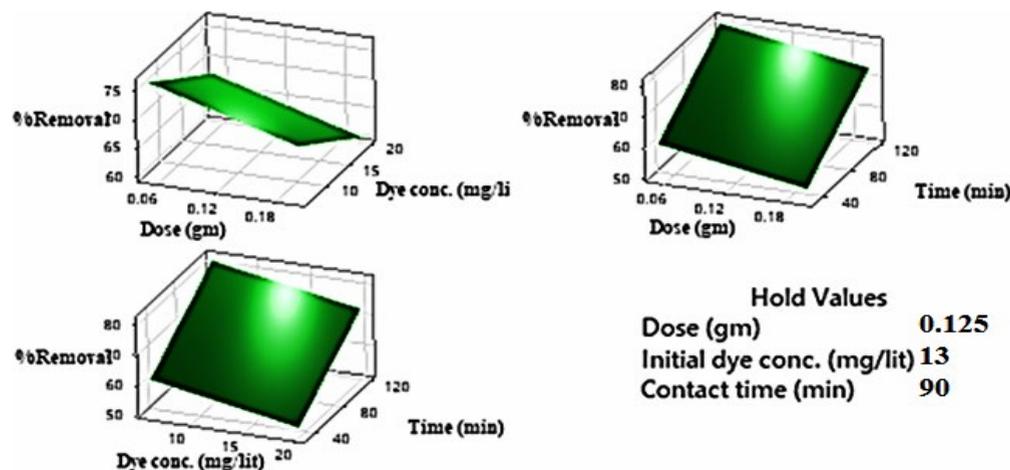**Fig. 4. Three-dimensional response surfaces for indigo blue dye adsorption using Fe₃O₄ nanoparticle**

Fig. 5. Three-dimensional response surfaces for indigo blue dye adsorption using Fe₃O₄@ME nanoparticles

CONCLUSION

Indigo blue dye removal from a synthetic aqueous solution was the main focus of the current investigation, which focused on using Fe_3O_4 and Fe_3O_4@ME nanoparticles as adsorbents. Using batch mode tests, the Taguchi method optimized the process variables for the indigo blue dye's adsorption. Using the Taguchi experimental design with an L9 orthogonal array, the process parameters were optimized for the highest percent elimination of indigo blue dye. The following is the order in which each parameter contributes to the percent removal of indigo blue dye: contact time>initial dye conc.> adsorbent dose for both Fe_3O_4 and Fe_3O_4@ME. The confirmation experiment's dye removal percentage was higher than all test runs.

Process parameters were carefully optimized to raise the indigo blue dye removal percentage. Additionally, the model demonstrated an adjusted square correlation coefficient R^2 (adj) of 90.86%, for Fe_3O_4 and Fe_3O_4@ME nanoparticles, which fit the statistical model well. In this study, at optimized conditions, the percent dye removal for Fe_3O_4 and Fe_3O_4@ME nanoparticles was 86 and 76, respectively. This may be associated with presence of cell biomass for Fe_3O_4 nanomaterials which increases the percentage adsorption of indigo blue dye. This suggests that Fe_3O_4 has a greater impact on dye adsorption than Fe_3O_4@ ME. These results suggest that indigo blue dye may be removed from synthetic aqueous solutions and that iron oxide nanoparticles can be utilized to treat industrial wastewater.

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