Designing design of expert (DOE) for treatment of sulfur black dye in textile effluent using zinc oxide nanobioadsorbents

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Abstract

This study uses biogenic fabricated ZnO and ZnO-ME nanomaterials (Nanomaterials fabricated from bacterial extracts - ZnO and bacterial cell mass - ZnO-ME) for the adsorption of sulfur black (SB) dye from textile effluent. This study used the Design of the Experimental method rather than the standard one-variable-at-a-time method to optimise batch absorption experiments. The optimum parameters for removing textile dye with desirability of 1 are 22 mg adsorbent dosages at room temperature (30^0 C) and 137 minutes of contact time. These results yield 67 and 76 percent of ZnO and ZnO-ME nanomaterials, respectively. Validation of the model shows that the calculated response is consistent with experimental results. The models demonstrated an excellent model fit for SB dye removal utilising ZnO and ZnO-ME nanomaterials, which had adjusted R^2 values of 0.9991 and 0.9952 and predicted R^2 values of 0.9961 and 0.9972, respectively.

Keywords: sulfur black dye, zinc oxide nanomaterials, response surface methodology-central composite design, real textile effluent, biogenic adsorbent

Introduction

The global freshwater crisis is escalating due to population growth, climate change, and industrial expansion, exacerbated by a growing number of consumers and polluters [1]. Among them, the utmost significant sources of industrial pollutants come from various industries, including the textile, cosmetic, leather, food, pharmaceutical, paint and varnish, and pulp and paper industries [2]. Textile industries use water, dyes, and pigments at various operational stages. According to a recent estimate, around 70 lakh tonnes of dyes are generated annually. The environment and human health are put at risk when these industrial waste dyes are dumped into water [3]. Despite its global economic importance, the textile industry contributes significantly to environmental contamination through dyes, which release hazardous wastewater effluents. This can harm aquatic life and human health, leading to conditions like headaches, gastritis, tissue necrosis, cancer, gene alterations, lung and renal illness, and headaches. Therefore, addressing dye exposure in the textile industry is crucial [4]. Sulfur dyes are inexpensive compared to other dyes and are used to create darker, more subdued hues, including green, dark blue, black, brown, and olive. Among all these sulfur dyes, sulfur black (SB) is the most widely and consistently used in textiles [5].

In recent years, various physical, chemical, and biological approaches have been developed to remove colours from dyeing effluent. However, because of their intricate chemical makeup, dyes are very resistant to degradation [6], making dye removal difficult. Dye removal from aqueous media can be achieved through various physicochemical or biological processes like chemical precipitation, ultrafiltration, microbial degradation, coagulation/flocculation, advanced oxidation, electrochemical treatments, reverse osmosis, and adsorption. However, traditional methods have limitations, such as ion exchange causing contamination, iron fouling, and organic matter adsorption. Reverse osmosis costs money and can cause membrane fouling during water treatment [7]. Advanced alternatives like nanoparticle-based adsorption techniques effectively remove dye from aqueous effluents, offering flexibility, efficiency, and energy efficiency [8]. Numerous adsorbents have been explored for removing dye and contaminants from dye-contaminated water, including zeolites, polymers, biogas waste slurry, activated carbon, clay materials, and nanomaterials. Recent research focuses on developing innovative, high-performance, and low-cost nanomaterials due to their unique physical, chemical, and biological properties [9]. Zinc oxide nanomaterials are among the most studied and synthesised metal oxide NPs [10]. Zinc oxide has the additional appealing quality of being sensitive to visible light and has the potential to be an effective adsorbent [11]. Adsorption is influenced by various factors, including time, initial dye concentration, pH, adsorbent dosage, temperature, and ionic strength, such as pH affects adsorption extent, substrate nature, ion concentration, ionic strength, and competing ions. Optimising these parameters can maximise dye removal efficiency [12]. The conventional one-parameter-at-a-time method is time-consuming and expensive due to its one-parameter change per time and lack of variable interaction investigation. Response surface methodology (RSM) can be used to maximise response, minimise test numbers, and consider interactions, as demonstrated in previous research for heavy metals, dyes, and pharmaceutical waste. [13,14].

This study fills a gap in zinc oxide nanoparticle adsorption studies, focusing on biogenic fabricated ZnO and ZnO-ME nanomaterials for the adsorption of SB dye from textile effluent. It uses the RSM-CCD statistical method to analyse the impact of independent factors on the response.

Materials and methods

Chemicals and sample collection

Wastewater samples, before treatment, were collected from the Rajasthan Spinning & Weaving Mills (RSWM) Limited textile industry in Banswara, Rajasthan, India. Zinc sulfate salts, SB dye, nutrient broth and agar were used to perform the experiments. Absolute ethanol, sodium hydroxide, nitric acid, and hydrochloric acid were also used in this study. Products and reagents were AR grade and purchased from Himedia Laboratory Pvt. Ltd. in Mumbai and S.D. fine chem. Ltd. in Mumbai. The working solution for experiments and the culture medium was prepared with double distilled water.

Physiochemical characterisation of real textile effluents

The pH and temperature of the collected raw textile effluent were measured on the spot using a handheld meter (pocket pcstestr 35 Eutech pH-temp meter). Furthermore, the APHA-recommended methods were used to evaluate BOD and COD before and after adsorption [15].

Adsorption experiment of textile effluents

The adsorption of SB dye on the ZnO and ZnO-ME nanomaterials was performed in batch mode. Distilled water was used to prepare stock solutions containing 1000 mg/L of SB dye. At a maximum wavelength of 600 nm for SB dye, dye concentrations were determined using a UV/VIS spectrophotometer. Equations (1) and (2) determined the SB dye removal efficiency and adsorption capacity using ZnO and ZnO-ME [16,17].

$$Removal\ Efficiency\ (\%) = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1)$$

$$Adsorption\ capacity\ (q_e) = \frac{(C_o - C_e) * V}{m} \tag{2}$$

where C_o (mg/L) is the initial concentration, C_e (mg/L) is the final concentration in the solution, m (gm) is the mass of the ZnO and ZnO-ME, V (L) is the working solution volume used in the experiments.

Experimental design - Batch study of textile effluents and Statistical analysis

The study used Design-Expert software version 13 (Stat Ease Inc.) to analyse the impact of contact time (60-180 min) and adsorbent dose (5-25 mg) on removing SB dye from textile effluent. It used a three-level full CCD (−1, 0, + 1) design to examine the impact of each variable on the efficacy of SB dye removal from the textile effluent. Sulfur black ($C_6\,H_3[OH]^-[NO_2]_2^+$) due to the presence of a negative charge on its surface, it precipitates out at a higher pH, which is why, in the current study, the solution's pH was held constant at 7.0. Lim et al. [18] showed the discolouration and precipitation of methyl blue and methyl orange dye at higher pH. Room temperature is used in this study to make the adsorption process more cost-effective and reliable.

Figure 1 depicts the visual representation of the CCD technology, where X stands for the operational parameters. According to the Figure, the CCD was characterised by three operations: 2n - factorial races, n - axial races, and n_c - central races [4]. Equation (3) was needed to compute the total number of experimental CCD tests, which came to 13 experiments in total. There would be no need for additional runs to be conducted as the experiment's error could be assessed after five repeats.

$$N = 2^n + 2\,n + n_c \quad \ldots (3)$$

Where N is the total number of experiments needed, n represents the number of factors, and n_c represents the number of central points. Below is the model's equation:

$$Y_{pred} = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \sum_{j=i+1}^{k} \beta_{ij} x_i\, x_j + \sum_{i=1}^{k} \beta_{i\,i}\ X_i^2 \quad \ldots (4)$$

where Xi and Xj are the coded values of the independent variables; β0 is the model constant; Y is the expected response (removal %); k is the number of the independent variables and βi, βii, and βij are the denoted regression coefficients for the linear, quadratic and interaction terms, respectively [14].

The software performed statistical analysis, reducing the number of experimental tests needed to evaluate each parameter's controlling influence and interaction [19]. The study used variance analysis (ANOVA) to compare models with experimental data and Fischer's test to evaluate the significance of each variable's interaction. The binary interactions were depicted in three-dimensional surface graphs. The model used optimisation to determine specific values for each independent variable and provide optimal adsorption conditions [20].

Result and discussion

Statistical analysis

13 experiments were designed and performed using different parameter combinations. Based on response to independent variables, a quadratic model for ZnO and a linear model for ZnO-ME were developed as robust models to predict the removal of SB dye. Statistical results obtained from the design expert software are presented in Table 1. Eqs. 5 and 6, represent the empirical correlation between the adsorption or removal efficiency in percentage (Y) of dye and the two process parameters, nanoadsorbent dose (A) in gm and contact time (B) in min., respectively.

Dye adsorption (ZnO)

$$Y = 61 + 4.5481 * A + 3.51777 * B + 2.33672e\text{-}14 * AB + -0.1875 * A^2 + 0.0625 * B^2 \quad \ldots (5)$$

Dye adsorption (ZnO-ME)

$$Y = 69.1538 + 4.97487 * A + 3.51777 * B \quad \ldots (6)$$

A single coefficient represents a single component's effect, while multiple factors indicate interaction. A plus sign indicates a synergistic impact, while a minus sign indicates an antagonistic effect. The lowest dye removal, 53 and 61 %, and the highest dye removal, 69 and 78 %, were obtained using ZnO and ZnO-ME nanomaterials, respectively.

To validate the quadratic model for ZnO and linear model for ZnO-ME, predicted and experimental values for the % adsorption of SB dye employing both types of nanomaterials were obtained and compared using RSM-CCD. Fig. 2 (A and B) (predicted vs actual graph) depicts the linear correlation between the predicted and experimental values. The figure represents a significant correlation between the experimental and predicted response values and the suitability of the analysis' underlying assumptions by showing that the data points on the plot were fairly distributed near the straight line [19]. Additionally, diagnostic plots were used to evaluate the model's suitability. Residuals are the differences between predicted and experimental values. Consequently, verifying the data's normality using the normal probability plot of the residuals is possible. The data points in Fig. 2 (C and D) are virtually evenly distributed around the middle straight line, indicating that the residuals in the model forecast are normally distributed. The plot of the studentised residuals against the predicted value can be seen in Fig. 2 (E and F). All residues are known to be randomly distributed within the standard deviation range (± 4.56 and 3.86 for ZnO and ZnO-ME nanomaterials, respectively), and none of them are out of range; thus, there is no need to do additional experiments [21].

Analysis of variance (ANOVA) analysis

Using ANOVA (Table 2), the importance of each factor in the model was assessed, such as model's significance and adequacy. At a significance level of 5%, the model's significance was assessed using ANOVA, as suggested by Ani et al. [22]. An important model is one with higher F-values and a lower p-value[23]. The p-values for both NMs in the model were less than 0.0001. The significant probability values for A, B, AB, and A^2, as well as A and B, for ZnO and ZnO-ME nanomaterials, respectively, indicate their importance in the process of colour removal during adsorption, with a p-value less than 0.05. The term "adequate precision" (AP) compares the predicted values' range and mean prediction error at the design points. The model is suitable for discriminating if this ratio is greater than 4 [26]. The ratio of 164.4 and 133.6 for ZnO and ZnO-ME nanomaterials, respectively, demonstrates an adequate signal [24]. A Student's t-test with a 95% confidence level was used to assess the regression coefficients' significance [25]. The models demonstrated an excellent model fit for SB dye removal utilising ZnO and ZnO-ME nanomaterials, which had predicted R^2 values of 0.9961 and 0.9972 and adjusted R^2 values of 0.9991 and 0.9952, respectively. The difference between the adjusted R^2 and predicted R^2 was less than 2. Therefore, these quadratic and linear models' predictions are accurate. Models are regarded as repeatable when their coefficient of variation (C.V.) is less than 10%. The remarkable repeatability of the model is demonstrated in this study by C.V. values of 0.23 and 0.38 percent for ZnO and ZnO-ME nanomaterials, respectively [21].

Table 1 Statistical results for the removal of SB dye on Zinc Oxide nanomaterials

Table 2 Analysis of variance (ANOVA) for the adsorption of SBdye using ZnO and ZnO-ME nanomaterials

3-D surface plots for adsorption

Three-dimensional response surface plots were made to examine the potential effects of various combinations of the independent variables on the adsorption efficiency. The relationship between adsorbent dosage, contact time, and adsorption efficiency is depicted in Fig. 3 (three-dimensional plot). As contact time and adsorbent dose were increased, adsorption efficiency quickly increased [4]. The effectiveness of the adsorption process was demonstrated to be dependent on these two interdependent parameters. This research demonstrates that interactions between ZnO and ZnO-ME nanomaterial dose and contact time are essential in explaining the efficiency of the nanomaterials in adsorbing SB dye from textile effluents. Extending the contact time will often enhance the amount of dye absorbed and removal efficiency. Initially, the amount of dye adsorbed onto the ZnO, and ZnO-ME nanomaterials surface rises quickly; eventually, the process slows down and attains equilibrium. During the adsorption process, this can be attributed to the presence of active sites on the surface of ZnO and ZnO-ME nanomaterials. As time elapsed, saturation of dye molecules occurs on the adsorbents (ZnO and ZnO-ME) and this results in electrostatic repulsion between the nanomaterials (adsorbents) and the dye molecules. This process inhibits the further adsorption of dye onto the surface of ZnO and ZnO-ME nanomaterials. The rapid solute adsorption, in this case, decreased due to the dearth of readily accessible open sites for dye adsorption (saturation) [16, 27]. The amount of dye desorbing at this time from ZnO and ZnO-ME nanomaterials and the amount of dye being adsorbed onto the ZnO and ZnO-ME nanomaterials are in a dynamic equilibrium period of time is known as the equilibrium time [12]. In the case of nanomaterial dosage, an increase in the dose of nanomaterials (ZnO and ZnO-ME), there is the enhancement of the amount of dye adsorbed onto the surface of nanomaterials, eventually enhancing the adsorption efficiency due to the availability of more active sites onto the surface of bionanoadsorbents. Enhancement in dye adsorption with increasing adsorbent dose is associated with more surface area and availability of more adsorption sites, ultimately leading to the adsorption equilibrium[17].

Optimisation of removal percentage

The process variables were optimised with Design-Expert software. RSM's ability to optimise multiresponse is one of its most important advantages. To improve the desirability function, the program looks for optimal conditions. To obtain the highest efficiency, the removal of SB dye was defined as maximal, whilst the dose of nanomaterials consumption and contact time was defined as a minimum from an economic standpoint. A total of 13 solutions were provided by the software, which also searched for the variables' optimum values to ensure the desirability of responses. The solutions were quite close to one another. The optimal contact time for maximum colour removal from textile effluent was 137 minutes, and the adsorbent dose was 22 mg for ZnO and ZnO-ME nanomaterials with desirability function one, which suggests a best-case response. The predicted response {65% and 74 % for ZnO and ZnO-ME} agrees with the experimental findings {67% and 76 % for ZnO and ZnO-ME}, enabling precise estimation of the performance of nanocomposites at predicted optimal conditions. The main contributing aspects to removing colour from wastewater are the pore formations and the increased surface area. The experiment, which was carried out under optimal conditions, revealed good agreement with the predicted value. It suggests that RSM's approach to improving textile wastewater treatment and dye removal is effective.

Physiochemical characteristics of textile effluents

Following analysis and optimisation of the impact of crucial operational parameters on the process efficiency of ZnO and ZnO-ME nanomaterials, the performance of the optimised process was evaluated for the treatment of effluent collected from RSWM Limited, Banswara, Rajasthan, India, a textile industry. Table 3 lists the important characteristics of wastewater samples before and after treatment. Before the wastewater entered the treatment facility, necessary samples were collected from the wastewater stream at the industrial plant's outlet. Temperature and pH were measured on-site right away and also after the application of nanomaterials for adsorption. BOD and COD experiments were also performed (before and after applying bionanoadsorbents) to check the overall efficiency of the nanomaterials. The chemical makeup of textile effluents varies over time, from factory to factory, and on a temporal basis at individual factories, depending on the materials employed in wet processing [28]. Without proper treatment, its discharge into the environment might seriously affect the flora, animals, and microbial biota [29]. The BOD/COD ratio is a suitable metric for assessing the biodegradability of wastewater. Therefore, wastewater with a BOD/COD ≥ 0.4 is regarded as biodegradable [30]. As shown in table 3, the biodegradability of textile samples after treatment with ZnO and ZnO-ME nanomaterials, was 0.29 and 0.43, respectively; this indicates an increase in its biodegradability. A comparison of various relevant prior publications is provided in Table 4. As a result, both nanomaterials hold potential as effective adsorbents for textile effluent treatment and can employed on commercial scale in industries. The slightly lower efficiency for dye removal of both the ZnO and ZnO-ME nanomaterials in this study is due to the presence of competitive species (anions or cations) other than dye molecules in the textile effluent. These species compete with the dye molecules for the adsorption on the active sites present on the surface of adsorbents [31]. Hence decreasing the efficiency of the nanomaterials for dye adsorption and enhancing the overall efficiency of nanomaterials to remove pollutants from industrial effluent.

Table 3 Characteristics of the raw textile wastewater and treated wastewater with ZnO and ZnO-ME nanomaterials

Table 4 Comparison of the current work with earlier ones

Conclusion

The study explores the adsorption of SB dye from textile industrial effluent using ZnO and ZnO-ME nanomaterials, addressing the toxic, resistant, and non-biodegradable dyes in textile effluent using RSM-CCD to analyse their individual and combined effects. Design Expert software developed a second-order quadratic model and linear equation for ZnO and ZnO-ME nanomaterials to forecast the responses to correlate the operational variables and SB dye adsorption efficiency. The regression models for SB dye removal using ZnO and ZnO-ME nanomaterials showed a high coefficient of determination, indicating good model fit and accurate predictions, with predicted R^2 values of 0.9961 and 0.9972 and adjusted R^2 values of 0.9991 and 0.9952, respectively. The models were also significant, as p values were less than 0.05 and F values were above 10. The optimal contact time for maximum colour removal from textile effluent was 137 minutes, and the adsorbent dose was 22 mg for ZnO and ZnO-ME nanomaterials with desirability function one, which suggests a best-case response. The predicted response {65% and 74 % for ZnO and ZnO-ME} agrees with the experimental findings {67% and 76 % for ZnO and ZnO-ME}, enabling precise estimation of the performance of nanocomposites at predicted optimal conditions. Thus response surface method is advantageous in large-scale adsorption-based water treatment technologies for its time and resource-saving benefits.

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Declaration of Competing Interest

The authors had no unreported conflicts of interest.

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Table 1 Statistical results for the removal of SB dye on Zinc Oxide nanomaterials

Adsorption ZnO					Adsorption ZnO-ME				
Source	**Sequential p-value**	**Adjusted R^2**	**Predicted R^2**	**Comments**	**Source**	**Sequential p-value**	**Adjusted R^2**	**Predicted R^2**	**Comments**
Linear	< 0.0001	0.9980	0.9964	Suggested	Linear	< 0.0001	0.9972	0.9952	Suggested
2FI	1.0000				2FI	1.0000			
Quadratic	0.0204	0.9991	0.9961	Suggested	Quadratic	0.3248	0.9971	0.9879	
Cubic	0.6779	0.9989	0.9698	Aliased	Cubic	0.9631	0.9960	0.8925	Aliased

2FI is the 2-factor interaction model.

Table 2 Analysis of variance (ANOVA) for the adsorption of SBdye using ZnO and ZnO-ME nanomaterials

ZnO							ZnO-ME						
Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**		**Source**	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	264.78	5	52.96	2538.40	< 0.0001	significant	**Model**	296.99	2	148.50	2121.73	< 0.0001	significant
A-Dose	165.48	1	165.48	7932.31	< 0.0001		*A-Dose*	197.99	1	197.99	2828.97	< 0.0001	
B-Contact time	99.00	1	99.00	4745.42	< 0.0001		*B-Contact time*	99.00	1	99.00	1414.48	< 0.0001	
AB	0.0000	1	0.0000	0.0000	1.0000		***Residual***	0.6999	10	0.0700			
A²	0.2446	1	0.2446	11.72	0.0111		*Lack of Fit*	0.6999	6	0.1166			
B²	0.0272	1	0.0272	1.30	0.2913		*Pure Error*	0.0000	4	0.0000			
Residual	0.1460	7	0.0209				***Cor Total***	297.69	12				
Lack of Fit	0.1460	3	0.0487										
Pure Error	0.0000	4	0.0000										
Cor Total	264.92	12											

Where, A is nanomaterial dosage (gm), B is Contact time (min).

Table 3 Characteristics of the raw textile wastewater and treated wastewater with ZnO and ZnO-ME nanomaterials

Parameter	Untreated Textile industry effluent	Treated textile industry effluent	
		ZnO	ZnO-ME
pH	10	8.2	8
Temperature (^{0}C)	28	28	28
SB dye (mg/l)	1315	408	290
COD (mg/l)	2540	695	400
BOD_5 (mg/l)	830	202	175
BOD/COD	0.32	0.29	0.43

Table 4 Comparison of the current work with earlier ones

Wastewater	Adsorbent	Color Removal (%)	Study type	References
Reactive Blue 19 **Acid Black 210**	ZnO	79 76	Simulation study	Khoshhesab, & Souhani, [32]
Direct Blue 78 **Acid Black 26**	Chitosan–zinc oxide	~91.74	Simulation study	Maroufi et al. [27]
Reactive Black HN and Reactive Magenta HB	Chitosan Zinc Oxide	95-99	Real textile effluent	Abul et al. [12]
SB	ZnO	69	Real textile effluent	Present study
SB	ZnO-ME	78	Real textile effluent	Present study

Fig. 1 Pictorial view of the RSM-CCD design

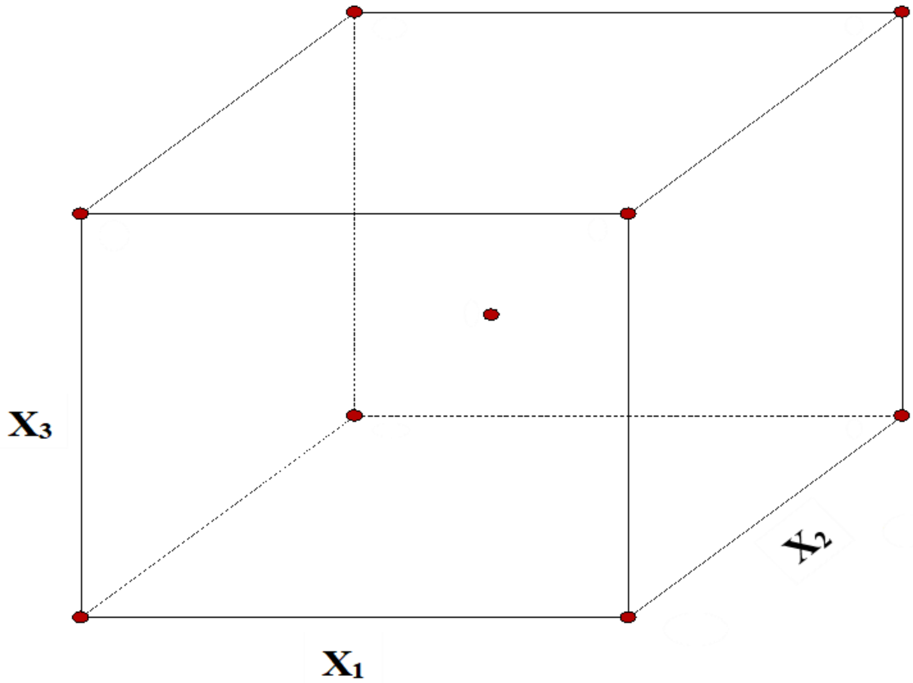

Fig. 2. Scatter plot of predicted vs. experimental (actual) for the percentage dye adsorption (A) ZnO and (B) ZnO-ME; Normal probability plot of studentized residual for the percent dye removal (C) ZnO and (D) ZnO-ME; and studentized residuals plots against predicted values (E) ZnO and (F) ZnO-ME

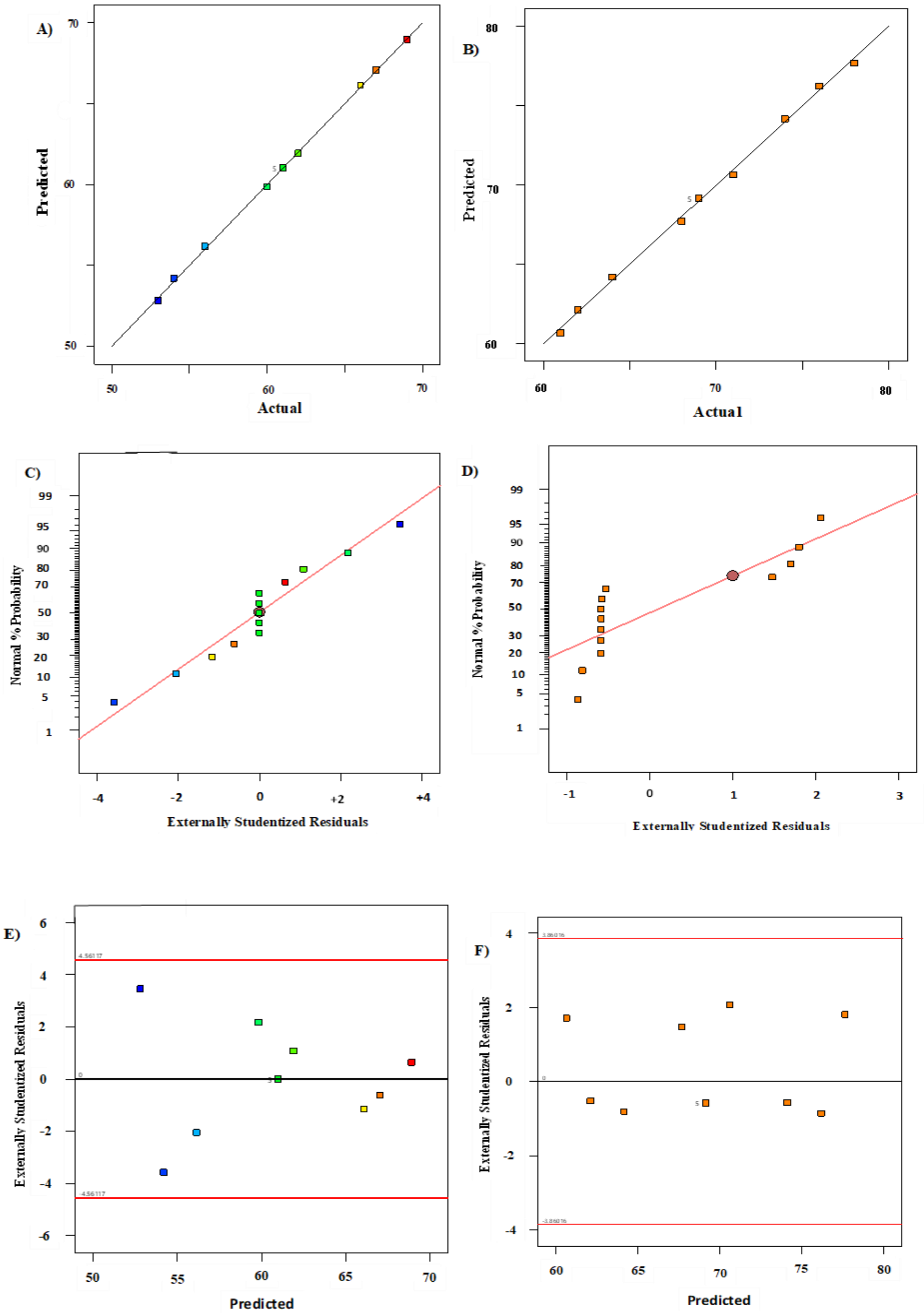

Fig. 3. 3D interactive surface plot for dye adsorption percent from textile effluent by (A) ZnO and (B) ZnO-ME