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Bismark brown dye adsorption on to silver nanoparticles synthesised using microwave green method: Modelling and desorption studies

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ABSTRACT

In this study an attempt was made to prepare the silver nano particle (AgNP) using microwave green method and also investigated the adsorption efficiency of bismark brown dye on to AgNP particle. Different adsorption conditions such as initial condcentration, temperature and contact time were investigated on the treatment efficiency. Central composite response surface design (CCD) was used to model the adsorption process. Results shows the best fit of Langmuir isotherm model to the experimental data. Pseudo-first-order rate equation clearly explain the kinetic of adsorption of bismark brown dye on to AgNP particle. Thermodynamic studies illustrate the spontaneous nature of the process.

KEYWORDS

Bismark brown;
Microwave irradiation;
Silver nanoparticle;
Green synthesis;
Central composite design;
Adsorption;
Desorption.

INTRODUCTION

Nowadays,water is the most important requirement in daily life that has been contaminated by the disposal of domestic, municipal, and industrial wastes. So, there is a need to utilize the available water resources effectively without polluting the water. Textile industries have shown a significant increase in the use of natural water resources with synthetic complex organic dyes as coloring materials[1]. Moreover, the dyes are to be necessarily removed from water and wastewater from the txtile industries. Bismark brown is an cationic azo dye widely used in textiles, paper, rubber, and plastic industries. Discharge of wastewater containing these dyes are harmful to the receiving ecological system[2]. So, there is a critical need to develop a technically and economically viable technique to remove the bismark brown dye from wastewaters. Last few decdes, various processes are used for bismark brown dye removal typically include physical, chemical, and biological methods[3]. Some processes such as electrochemical techniques and ion-pair extractions are also used for dye wastewater treatment, while others have been used in the industry for a long time[4].

Adsorption has been found to be superior to other techniques for water quality in terms of initial cost, simplicity of design, use of operation, and insensitivity to toxic substances[5]. The removal of dye from industrial wastewater is measured as an important application of adsorption processes. One of the most used and successful method for the removal of organic pollutants (dye) is their adsorption on activated carbon (AC). Even though, AC has high adsorption capacity, the use of AC on a large scale is

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limited by process engineering difficulties such as the dispersion of the AC powder and the cost of its regeneration[6]. So that, research interst have been shift to use the metal nanoparticles (NPs) with controlled size in adsorption process due to their morphology dependent properties. The mostly used metal NPs in adsorption process is noble silver nanoparticle (AgNP) due to its close lying conduction and valence bands in which electrons move freely[7]. A number of attempts have been made using different experimental conditions to prepare AgNPs of different sizes and shapes to use a adsorbent. Microwave irradiation is one of the novel green techniques developed during the last years for the synthesis of solid materials[8]. However, from the extensive literature survay, it was found that there is no research reports are available for the adsorption studies of bismark brown dye on to microwave green synthesized AgNP. Hence, in this work, an attempt has been made to remove dye using Ag-NPs beads particles. The effects of factors such as initial concentration, temperature and contact time were investigated. In addition, the equilibrium isotherms, adsorption kinetics, thermodynamic and desorption studies of dye onto the alginate-stabilized AgNPs beads were also investigated.

MATERIALS AND METHODS

Raw materilas

Bismark brown (a cationic dye) was obtained from the Sigma chemicals Chennai (India). Structure of the Bismark brown dye is shown in Figure 1. Silver nitrate ($AgNO_3$) was purchased from Merck chemicals, Mumbai (India). Sodium alginate was obtained from LOBA (India). Calcium chloride ($CaCl_2$) was purchased from local suppliers, Erode (India). Double distilled water was used throughout the experiments. All the chemicals (HCl and NaOH) used in this study were anlaytical grade and purchased from local suppliers from Erode, TamilNadu.

Preparation of AgNPs beads

50-mL conical flask was used to prepare the homogenous reaction solution by dissolving 0.2 mol/L sodium alginate and 0.0001 mol/L $AgNO_3$ using double distilled water. Then, the flask was placed on the microwave oven and the mixture was irradiated at a power of 250 W for the period of 5 min. Then, the colloidal solution having pale yellow color was cooled to room temperature and stored. Then, the above prepared AgNPs in solution was added drop wise into a 0.1 M $CaCl_2$ solution under constant stirring to produce beads of AgNPs. These AgNPs beads were stored in air tight bottle at room temperature.

Analytical measurements

A Samsung CE2877 domestic microwave oven (850W), Samsung Electronics Ltd, New Delhi, India, was employed for irradiating solutions. The surface morphology of the AgNP was examined by a JEOL-JSI, model No-5600, scanning electron microscopy (SEM). Absorption spectra were recorded in a Varian Carry 50 UV–visible spectrophotometer equipped with a peltier temperature controller unit. FTIR spectra of the AgNP were recorded on IR Affinity-1, Shimadzu spectrophotometer in the wavelength range of 400-4000 cm^{-1}.

Adsorption experiments

A standard solution of dye containing 105-450 mg/L concentrations were used for batch studies. Batch experiments were conducted in 250-mL conical flask in which 100 ml of dye solution containing 1.1 g/L of AgNPs beads were poured. The suspension was shaken in a rotary shaker with various temperature (25-45°C) and contact time (40-160 min). After shaking, the suspension was centrifuged and

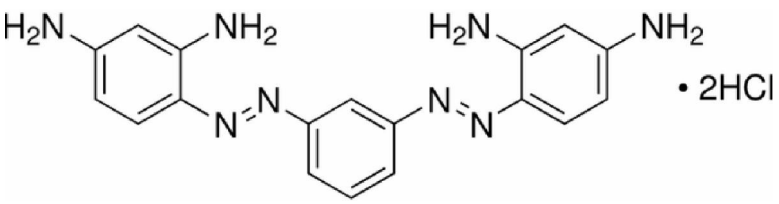

Figure 1 : Structure of the Bismark brown dye

the amount of dye in supernatant was examined using UV–visible spectrophotometer at a wavelength of 440 nm. The percentage removal of dye was calculated by the following equation[9]

$$RE = \left(\frac{c_0 - c_e}{c_0}\right) \times 100 \quad (1)$$

where, c_0 and c_e is the initial and final concentrations of dye. The value of q_e (amount of dye adsorbed at equilibrium) was calculated by the following equation[10]

$$q_e = \left(\frac{c_0 - c_e}{w}\right) v \quad (2)$$

The value of q_t (amount of dye adsorbed at time T) was calculated using by the following equation,

$$q_t = \left(\frac{c_0 - c_t}{w}\right) v \quad (3)$$

where, c_0 and c_t are the initial and concentrations of dye at time T, respectively (mg/L), V is the volume of the dyesolution (L), and W is the weight of the AgNP used (g/L).

Desorption studies

In order to desorb the dye, the AgNPs beads loaded with dye were exposed to 0.05 N HNO_3, centrifuged and washed with double distilled water. The AgNPs beads were then again exposed to 0.05 N HNO_3 to strip any remaining dye and then reused. In order to show the reusability of adsorbent beads an adsorption–desorption cycle of dye was repeated 30 times by the same process. The percentage desorption of dye (DD) was calculated from the following equation[11]

$$DD = \left(\frac{A}{B}\right) \times 100 \quad (4)$$

where, A and B are the amount of dye liberated by acid and amount of dye adsorbed on adsorbent, respectively.

CCD response surface design

In this present study, three factors three level central composite response surface experimental design (CCD) was employed to investigate the individual and interactive effects of process variables such as initial concentration (A), temperature (B) and contact time (C) on the percentage removal of dye from synthetic solutions. Design- Expert 8.0.7.1 (State-Ease Inc., Minneapolis, MN, USA) statistical package was used for the statistical calculations. The relationship between the response and three independent variables were evaluated by developing the second order polynomial mathematical models and the generalized form of equation was given below.

$$Y = \beta_0 + \sum_{j=1}^{k} \beta_j X_j + \sum_{j=1}^{k} \beta_{jj} X_j^2 + \sum_{i} \sum_{<j=2}^{k} \beta_{ij} X_i X_j + e_i \quad (5)$$

Adequcy of developed mathematical model was investigated by the pareto analysis of variance (ANOVA) and developed model was used to plot the response surface contour graphes in order to study the interactive effect of independent variables on the response. Finally, optimization of adsorption condtions was carried out using Derringers desired function methodology[12].

RESULTS AND DISCUSSIONS

Silver nano particle characterization

The FTIR spectra of bare and dye-adsorbed AgNPs beads are shown in Figure 2a. The spectra clearly shows the peaks at 1,368 and 1,485 cm^{-1} and it corresponds to the symmetric and antisymmetric stretching vibrations of $–COO^-$, respectively. The (COO^-) band of silver calcium alginate was found at 1,325 cm^{-1}. Meanwhile, a new peak appeared in the region at 416 cm^{-1} indicating the presence of C–C bending vibration. The particle morphologies of AgNP was analysed using SEM studies and the results are shown in Figure 2b. The UV–visible spectrum of AgNPs is shown in Figure 2c which exhibits a strong absorption at 400 nm. Thus, the pale yellow color of the colloidal silver sample provides clear evidence for the formation of AgNPs. The results indicates that the prepared AgNP have the ability to act as a adsorbent for dye removal[13].

Mathematical modeling

Adsorption of dye on to AgNP is investigated according to RSM coupled CCD design and the results are shown in TABLE 1. The CCD experimental data are investigated by two different analysis namely sequential model sum of squares and model

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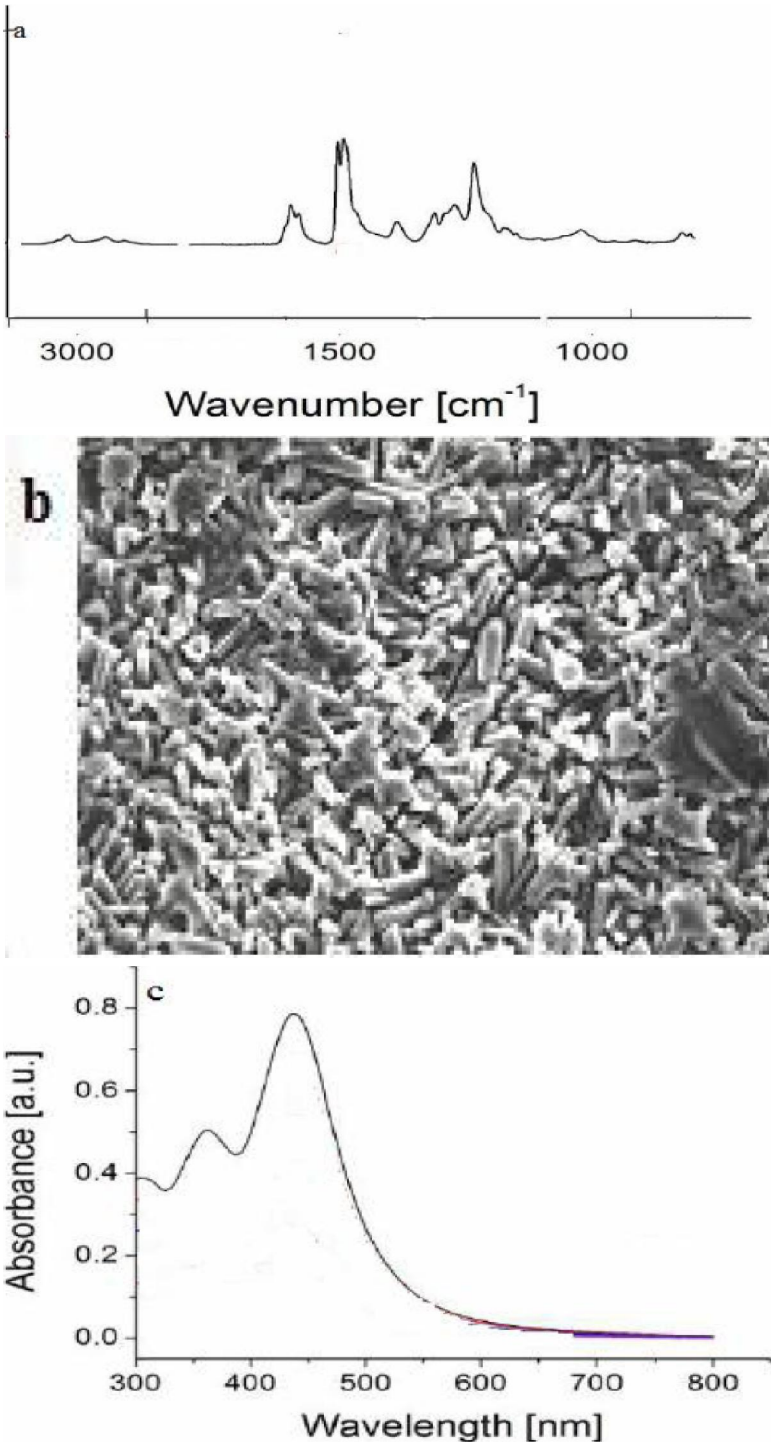

Figure 2 : Silver nano particle characterization

summary statistics in order to select effective mathematical model to describe the adsorption process and the results are shown in TABLE 2. From the results, it is observed that, quadratic model shows high R^2, adjusted-R^2, predicted-R^2, F-value and low p-value, when compared with other models. Therefore the quadratic model is selected to represent the effects of process variables on the dye adsorption process. To understand the interactive relationship between the response and adsorption conditions, mathematical model was developed from the CCD experimental data and final developed mathematical model obtained in terms of coded factors is given below

TABLE 1 : Actual values of the independent variables in CCD and experimental results

Run No	A	B	C	Y
1	300	35	100	75
2	450	45	40	40
3	300	35	100	75
4	300	35	100	75
5	300	35	100	75
6	450	25	40	26
7	300	52	100	79
8	300	35	200	85
9	150	25	160	70
10	300	18	100	32
11	150	45	40	42
12	300	35	-0.9	0
13	150	25	40	35
14	150	45	160	95
15	300	35	100	75
16	48	35	100	82
17	552	35	100	41
18	450	25	160	55
19	300	35	100	75
20	450	45	160	79

TABLE 2 : Adequacy of the model tested using model summary statistics

Model summary statistics for dye adsorption (%)						
Model	**Std.Dev.**	**R^2**	**Adjusted R^2**	**Predicted R^2**	**PRESS**	**Remarks**
Linear	19.6251	0.0406	-0.1808	-0.6655	8691.8	
2FI	18.4584	0.3471	-0.0446	-0.9293	10068.7	
Quadratic	2.0125	0.9946	0.9876	0.9131	453.6080	Suggested
Cubic	0.0000	1.0000	1.0000		+	Aliased
Source	**Sum of Squares**	**Df**	**Mean Square**	**F Value**	**Prob > F**	**Remarks**
Sequential model sum of squares for dye adsorption (%)						
Mean	77913.22	1.00	77913.22			
Linear	211.88	3.00	70.63	0.18	0.9058	
2FI	1599.76	3.00	533.25	1.57	0.2584	
Quadratic	3378.76	3.00	1126.25	278.08	< 0.0001	Suggested
Cubic	28.35	3.00	9.45	63660000.00	< 0.0001	Alised
Residual	0.00	4.00	0.00			
Total	83131.97	17.00	4890.12			

Dye removal (%) =

$$74.89-8.12A+10.91B+21.89C+0.75AB-2.50AC+3.50BC-4.05A^2-6.18B^2-10.77C^2 \quad (6)$$

Then the adequacy of developed mathematical models to represent the adsorption process is done by constructing diagnostic plots such as predicted versus actual plot (Figure 3a) and Normal % probability graphs (Figure 3b). The data points lies very close to the diagonal line for both the graphs and it depicts a good relationship between experimental and predicted data. Moreover, Pareto analysis of variance (ANOVA) was used to analyze the experimental data (TABLE 3). The higher model F-val-

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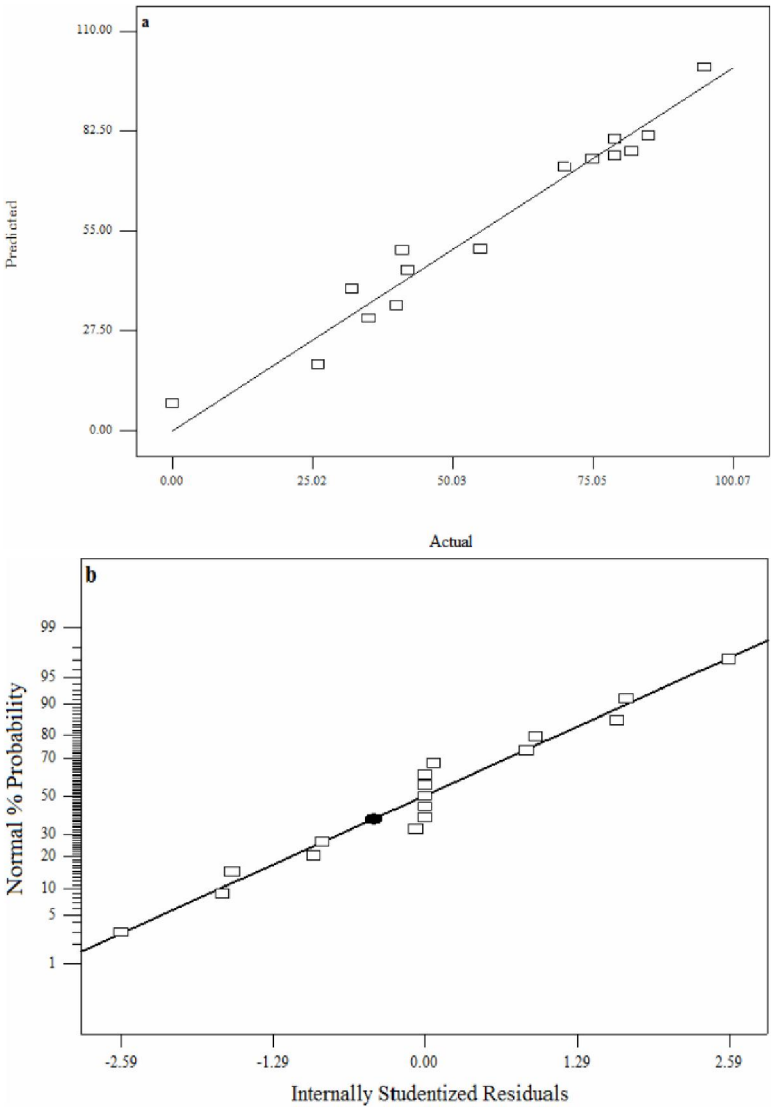

Figure 3 : Model adequacy plots

TABLE 3 : ANOVA analysis and statistical parameters of the model

Parameters	Sum of Square	df	Mean Square	F value	P-value	Remarks
Model	11369.5	9	1263.28	31.1606	< 0.0001	significant
A	901.429	1	901.429	22.235	0.0008	
B	1626.6	1	1626.6	40.1222	< 0.0001	
C	6544.15	1	6544.15	161.42	< 0.0001	
AB	4.5	1	4.5	0.111	0.7459	
AC	50	1	50	1.23332	0.2928	
BC	98	1	98	2.4173	0.1511	
A^2	236.831	1	236.831	5.84176	0.0362	
B^2	549.543	1	549.543	13.5552	0.0042	
C^2	1672.03	1	1672.03	41.2429	< 0.0001	
CV			9.98			
AP			21.58			
PRESS			3090			

ues, lower p-value of coefficiencts and adequate precision value (AP) and CV% values of the response demonstrated that the developed model is highly significant[14].

Effect of initial concentration

The initial concentration is one of the important parameter, which influences the performance of the adsorption process significantly. To examine its effect, the experiments were carried out at different initial dye concentration and the results are exhibited in Figure 3a-c. From the results, it is found that, removal of dye increased with decreasing dye concentration. This can explained by the fact that, initial dye concentration leading to faster and more strongly binding sites compared to higher concentrations of dye at the same dose of adsorbent[15].

Effect of temperature

The adsorption process of dye on to AgNP is highly affected by temperature. In order to investigate the effect of temperature in adsorption process, experiments were performed at different temperature and the results are depicted in Figure 3a-b. From the results, it is observed that the percentage of dye removal increased with increasing temperature upto 40°C. This effect may be attributed to the increase in the number of adsorption sites generated due to bond rapture. Beyond that, there is no significant effect on the removal of dye in adsorption process[16].

Effect of contact time

The contact time between the dyes and adsorbent is of great importance for the adsorption process. Effect of the contact time on the adsorption rate of the dye is investigated and shown in Figure 3b-c. As can be seen from Figure 3b-c, the dye removal is increased with increasing contact time upto 140 min and endsup with negligible dye removal. The increase in removal of the dye during the initial period may be due to large available amount of surface area of the adsorbent. As the surface area became gradually filled up, the removal rate decreased. It can be observed from results that the sorption capacity of dye increased in time and at a certain time (140 min) reached to constant value where no more dyes removed from the solution[17]. Perturbation plot is also shown in Figure 5, which is close agreement with trends obtained in Figure 4.

Isotherm models

In this study, various isotherm equations are used to find out the best fit of isotherm model to describe the adsorption process among Langmuir (Type I – IV) and Freundlich[18]. The results are shown in TABLE 4. For the several Langmuir isotherm models, the separation factor (R_L) is used to verify whether the adsorption process is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).The a separation factor R_L is defined in the following equation:

$$R_L = \frac{1}{1 + bC_o} \quad (7)$$

In this study, the lower R_L value indicates that the adsorption process is favourable. For the Freundlich isotherm, the K_F parameter, known as the heterogeneity factor, can be used to indicate whether the adsorption is linear ($K_F = 1$), whether the adsorption is a chemical process ($K_F < 1$), or physical process is favorable ($K_F > 1$). The values of K_F obtained is 2.58, indicated that the physical process is favorable. However, all the parameters predicted by various isotherm models did not explain the behavior of presnt adsorption process adequately. To study the isotherm equations more undeniably, correlation coefficient (R^2) is employed to determine the best-fitting isotherm model. From the analysis of TABLE 4, the Langmuir type I isotherm model showed the highest R^2 values among all the isotherms. The results obtained showed that the Langmuir type I isotherm is the best model to describe the adsorption process[19].

Adsorption kinetics

The study of adsorption kinetics is a key factor to identify the changes in adsorption process with respect to time. Hence, in this study two kinetic models, namely, pseudo- first- order and pseudo-second- order models (Type I –Type IV) were investigated and results are shown in TABLE 5. From the results, it is found that the experimental q_e values of the pseudo-first-order kinetic model is very close to calculated q_e values. But calculated q_e values of pseudo-second -order kinetic model did not fit well

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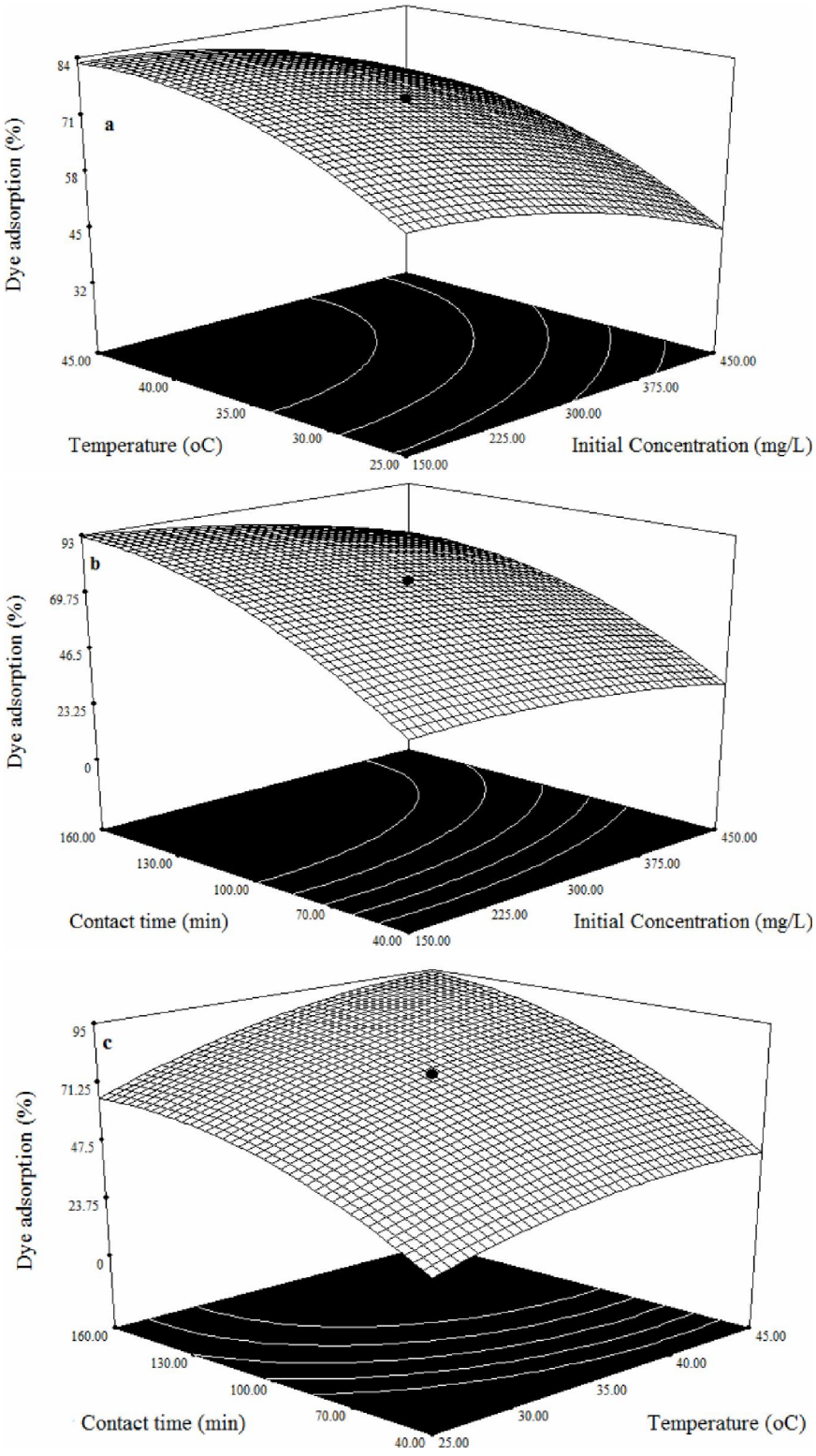

Figure 4 : 3D response surface and contour plot for dye adsorption

with experimental q_e values than pseudo-first-order kinetic model. This findings shows the adsorption process follows approximately pseudo-first-order kinetic model. To determine the exact kinetic model, all the kinetic models are analyzed using R^2 value. From the findings, it is found that R^2 of pseudo-first-order kinetic model has greater (R^2<0.99) than pseudo-second-order kinetic model and indicates the

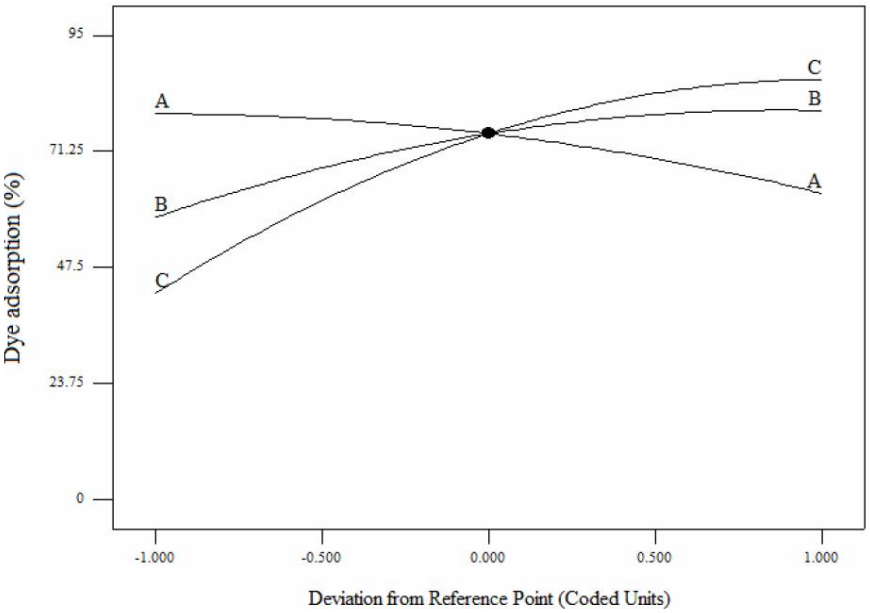

Figure 5 : Perturbation plot for dye adsorption process

TABLE 4 : Adsorption isotherm parameters

	R^2	K	Slope	Intercept	R_L
Langmuir 1	0.99578	0.12846	0.0236	0.18372	0.004922
2	0.96647	13.1672	0.2422	0.01839	0.000048
3	-0.823	42.0209	-7.5465	42.0209	0.000015
4	-0.823	-8.9899	8.98991	4.4836	-0.000070
Freundlich	0.90163	2.5879	0.37986	0.95086	n=2.6325

TABLE 5 : Kinetic parameters of adsorption process

Kinetic model	Dye Concentration (mg/L)	q_e exp	q_e cal	R^2
Pseudo -first-order				
Lagergran	150	13.23	17.08	0.9984
	300	26.45	34.18	0.9943
	450	36.41	51.26	0.9985
Pseudo -second-order				
Type I	150	13.23	24.31	0.9858
Type II			0.04	0.9658
Type III			24.28	0.9758
Type IV			21.58	0.9658
Type I	300	26.45	48.63	0.9888
Type II			0.02	0.9568
Type III			48.56	0.9587
Type IV			47.52	0.9786
Type I	450	36.41	83.85	0.9832
Type II			0.01	0.9584
Type III			84.37	0.9687
Type IV			82.56	0.9785

best of pseudo-first-order kinetic model to experi- mental data[20].

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Thermodynamic studies

In order to better understand the effect of temperature on the adsorption dye on AgNP, three basic thermodynamic parameters were studied: the Gibbs free energy of adsorption (ΔG), the enthalpy change (ΔH), and the entropy change (ΔS). The Gibbs free energy of adsorption related to the equilibrium constant K_c is calculated from the equation[21]

$$\nabla G = -RT \ln K_c \quad (8)$$

The thermodynamic adsorption equilibrium constant, K_c, was calculated by determining the apparent equilibrium constants at different initial concentration of dye solutions and extrapolating to zero,

$$K_c = \frac{C_a}{C_e} \quad (9)$$

where R is the universal gas constant (8.314 J/mol K), T is the reaction temperature in K, C_a is the equilibrium concentration of the dye adsorbed onto AgNP (mg/L) and C_e is the equilibrium concentration of the dye solution (mg/L).

The changes in enthalpy and entropy were determined using the following equation:

$$\nabla G = \nabla H - T\nabla S \quad (10)$$

The values of ΔH and ΔS were obtained from the slope and intercept of the plots of ΔG versus T and found to be 3.25 kJ/mol and 0.03 kJ/mol K, respectively. The positive values of ΔH revealed that the adsorption process is endothermic and physical in nature; hence with increasing temperature the adsorbed amount at equilibrium increased. Whereas, the positive ΔS corresponded to an increase in the degrees of freedom of the solid–liquid interface during adsorption process. Therefore, the values of ΔH and ΔG both suggested that adsorption of dye onto AgNP is a physisorption process. Generally, the value of ΔG for physisorption is in the range from -20 to 0 kJ/mol, but chemisorption is between -400 and -80 kJ/ mol. The calculated ΔG values were -2.53, -3.04, and -3.26 kJ/mol, respecthively, corresponding to temperatures of 298, 308, and 318 K. The ΔG values were found to be negative, indicating that the adsorption process is spontaneous and thermodynamically favorable.

Desorption studies

In order to find out the mechanism of adsorption and recovery of the adsorbate and adsorbent, desorption studies were conducted[22] and 92 % of the dye was removed in the first cycle. Then, the used adsorbent was treated with 0.05 N HNO_3 which resulted in 97 % stripping of dye. For obtaining the reusability of the AgNPs beads desorption cycle was repeated 20 times and the removal of dye decreased nominally per cycle up to 19 cycles suggesting high efficiency of the adsorbent. In the last cycle 56% of dye was removed.

CONCLUSIONS

In this study, microwave green method was used to prepare the silver nano particle (AgNP) for the adsorption of dye. Different adsorption conditions such as initial condcentration, temperature and contact time were investigated using three factors three level central composite response surface design (CCD). The isothermal data obey the Langmuir model better compared to Freundlich model for the adsorption of dye. The data on kinetic studies indicated that the adsorption kinetics of dye on adsorbent beads followed the pseudo-first-order kinetics indicating physicosorption process. Thermodynamic data shows the favourable and spontaneuous adsorption process. The regeneration of the spent adsorbent is easily performed with HNO_3 and the composite adsorbent can be effectively reused for 20 cycles consecutively. Overall, AgNPs showed excellent adsorptive characteristics for the removal of dye from aqueous solution.

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