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**Research Article** 

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# Synthesis, characterization and adsorption behaviour of MgO nano particles on Rhodamine B dye

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## ABSTRACT

The efficient removal of various dyes from the waste waters of textile industries is an important and challenging task. In the present study, it is attempted to validate the applicability of a new nanocomposite adsorbent for the removal of a cationic dye Rhodamine B from the effluent wastewaters. Magnesium oxide nano particles are encapsulated on a low cost activated carbon prepared from delonix regia and used for sorption study. The nano composite is characterized using FTIR, SEM, TEM, XRD, EDAX and BET. The effect of parameters like adsorbent dosage, contact time, pH, adsorption capacity and desorption have been studied. The adsorption studies indicate that Langmuir and Temkin isotherms are found to be the apt models due to their higher correlation coefficients. It fits well with pseudo first order kinetics having good agreement with the experimental values.

Key words: delonix regia, Rhodamine B, nano magnesium oxide composite, adsorbent dosage

# INTRODUCTION

Dyes are chemicals, which on binding with a material will give colour to them. New dyes are synthesized and they have several applications as they are gorgeously colourful. Textile is one of those industries where more and more dyes and pigments are used to color the products. In recent years, it is estimated that more than 100,000 dyes are available commercially[1] and their global production exceeds 800,000 tons per year[2]. The effluent water discharged from these textile industries is a major concern as several water bodies present in and around these industries are used as open reservoirs for domestic purposes. Colour is one of the characteristics of an effluent, which affects the nature of the water and inhibits sunlight penetration into the stream and reduces photosynthetic action[3,4]. Dye-containing wastewater as an important cause of environmental contamination has aroused more attention because most of the dyes molecules have complicated structures and they are photolytically stable, which render them resistant towards conventional biochemical decomposition[5,6]. Moreover, discharge of such contaminated water into public streams is a great environmental challenge not only due to its treatment for reuse but also its toxicity to human beings and animals by contaminating underground water reservoirs[7]. Some dyes are carcinogenic and mutagenic, and they are stable to biological degradation. The presence of a very small amount of dye in water (<1 mg/L for some dyes) is highly visible and enough to present an aesthetic problem[8]. Hence, waste water from dyeing industry is one of the major causes of environmental problems. Rhodamine B is an important dye, which is widely used in textile industry for dyeing silk, wool, jute leather and cotton. It causes carcinogenic and teratogenic effects on public health[9]. It has been medically proven that drinking water contaminated with Rhodamine B dyes could lead to subcutaneous tissue borne sarcoma which is highly carcinogenic[10]. In addition, others kinds of toxicity such as reproductive and neurotoxicity have been widely and intensively investigated and proved as well by exposure to these dyes. Various natural or wasted materials have been extensively explored and

investigated for the adsorption removal of different contaminants from aqueous solutions[11-14]. But these methods suffer with a major drawback of sludge formation and also adsorbent regeneration is relatively difficult, which makes them unsuitable for commercialization. But there is still a demand for an effective method to treat these dyes economically. Few methods were studied to remove it from wastewater; Libanori et al.[15] used TiO2-coated activated carbon catalyst; Wang et al.[16] reported its degradation by using swirling jet-induced cavitations combined with H<sub>2</sub>O<sub>2</sub>; Chang et al.[17] also reported its removal by fly ash adsorption with Fenton pre-oxidation. However, problems correspondent with these methods exist such as secondary pollution, high operational costs and long reaction time. Adsorption has time and again proved several advantages over other dye removal methods. Increase in population, westernization that leads to fashion world and subsequent usage of dyes, pigments and colourants has lead to quantitatively increase of effluents. So, the need of the hour is either to explore a new removal technique or enhance the absorptivity of a sorbent and the second one is practically viable by latest nano technology. The nano materials are incorporated onto the adsorbent[18] or the activated carbon are made into carbon nano tubes[19]. The nano composites thus prepared have proved for their large surface area [20], higher dye removal capacity[21] and capacity of reusable[22]. To enhance their dye removal capacity, applications have been attempted in this present study by using the impregnating technique of nano metal oxides on activated carbon of *delonix* regia to form an advanced composite material for the waste water treatment process.

## **EXPERIMENTAL SECTION**

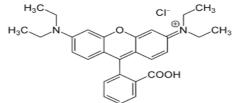
**Preparation of delonix regia adsorbent:** The dried *delonix regia* pods are cut into small pieces and the small pieces are then pickled with concentrated sulphuric acid for 48 hours. After ensuring that all the materials are carbonized completely, the excess sulphuric acid is washed with sufficient quantity of distilled water several times and dried at 120°C for 1 hour. The material thus obtained is soaked in 5% Sodium bicarbonate solution and allowed to stand overnight to remove any residual acid. This activated mass is then thoroughly washed with distilled water and dried. This carbonized material is kept at 700 °C for one hour in a tubular furnace under controlled N<sub>2</sub> flow. The resulting activated carbon is ground in a ball mill, washed with pure water and finally dried at 120° C. The dried powder is sieved into various sizes ranging from 70-150 BSS.

**Preparation of nano magnesium oxide particles:** Nano magnesium oxide is prepared by a chemical method. In a beaker 6 g of MgCl<sub>2</sub> and 2 g of surfactant SDS (Sodium dodecyl sulphate) are mixed in 100 ml of distilled water. This mixture is added into the 0.4N NaOH solution by stirring constantly with magnetic stirrer for about 2 hours by maintaining the pH 11. A white precipitate of Mg(OH)<sub>2</sub> is precipitated which is washed thoroughly with distilled water. This Mg(OH)<sub>2</sub> precipitate is then dried at  $120^{\circ}$ C for 2 hours and calcined at  $800^{\circ}$ C for 5 hours in an muffle furnace. It is then allowed to cool to reach room temperature to obtain granular nano MgO.

**Nano MgO encapsulation on activated carbon:** To coat the nano particles on the activated carbon, initially 0.02 g nano MgO is dispersed in 50 ml of methanol taken in a beaker by constant stirring for 2 hours. During this process the volume of methanol is maintained at 50 ml mark till the end of the experiment. One gram of powdered activated carbon of *delonix regia* of mesh size 150 BSS is added slowly with continued stirring for another 2 hours. Finally the nano MgO encapsulated carbon particles are filtered and washed with excess methanol for 2-3 times. The carbon sample is dried at  $60^{\circ}$ C in a hot air-oven, calcined at  $400^{\circ}$ C under nitrogen atmosphere and preserved in air tight container to carry out the tests.

#### **Preparation of Rhodamine B dye solutions**

The dye Rhodamine B is procured from one of the Textile industries in Tirupur Town situated in India. The stock solution is prepared by dissolving 1 g of Rhodamine B in 1000 ml of double distilled water. The aqueous solution of the dye is adjusted to pH 7.0. A number of standard solutions are prepared from the stock solution of 1000 ppm for the various concentrations range from 10 to 100 mg/L to use it in the dye removal experiment. Rhodamine B dye structure is given below



#### **Experimental methods and measurements**

**Characterization Techniques:** The following techniques are used to characterize the newly prepared adsorbent. The Fourier transform infrared spectroscopy (FT-IR, Thermo NICOLET Corporation, 5DX-FT-IR) is made at ambient temperature with a 8 cm<sup>-1</sup> resolution. Powder X-ray diffraction (XRD) analysis is performed on a Xpert PROPA Nalytical PW3040/60'X'PertPRO with Cu-Ka X-ray radiation source ( $\lambda = 1.5418$  Å). Morphological characterization of the adsorbent is performed employing SEM Hitachi S-3000H scanning electron micro-scope (SEM, mo ax magnification of 1.5 × 105) equipped with an Everhardt Thornley secondary electron detector (ET-SED).

#### **Batch mode experiment**

Dye removal experiments with the nano MgO coated carbon composite are carried out as batch tests in 250 ml Borosil conical flasks under uniform stirring in a magnetic shaker. Calibration curves are obtained with standard Rhodamine B dye solution using distilled water as a blank. Mass capacity of adsorption  $q_e$  is calculated from the difference between the initial and final absorbance values and a calibration curve was drawn by measuring the absorbance at  $\lambda max = 560$  nm using UV-Visible Spectrophotometer.

$$q \quad = \quad \frac{(C_o-C_e)}{W}V_e$$

Where  $C_0$  and  $C_e$  (mg L<sup>-1</sup>) are the liquid-phase concentrations of dye at initial and equilibrium respectively. V is the volume of the solution (l), and W is the mass of dry adsorbent used (g). The pH of the aqueous solutions of Rhodamine B is approximately 6.7 which does not change much with dilution, therefore all experiments are done without adjusting the pH. The batch adsorption is carried out by mixing a pre-weighed amount of the composite with 100 ml of aqueous dye solution of a particular concentration. The conical flasks are kept on a magnetic shaker and agitated for a pre-determined time interval at a constant speed. The system parameter such as adsorbent amount, agitation time and temperature are controlled during the experiments. After adsorption is over, the mixture is allowed to settle for 10 min. The supernatant liquid portion is centrifuged and the dye remaining unadsorbed is determined spectrophotometrically. Each experiment is carried out duplicate and the average results are calculated.

## **RESULTS AND DISCUSSION**

#### SEM morphology and XRD

It is widely used to study the morphological features and surface characteristics of the adsorbent materials. Typical SEM photographs are shown in Fig.1. It reveals that the nano composite has a rough surface with more porous and caves like structure.

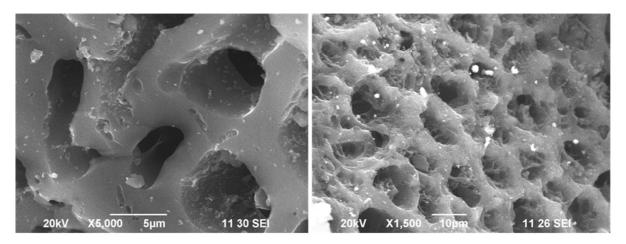


Fig.1. SEM images of nano MgO composite

The X-ray diffraction pattern (Fig.2) clearly proves that the synthesized materials is MgO of hexagonal phase and all the peaks present in the spectra agreed with reported JCPDS data (JCPDS 89-9746). No impurities peak is

observed in this pattern which clearly implies hexagonal phase MgO could be obtained from the above synthetic route.

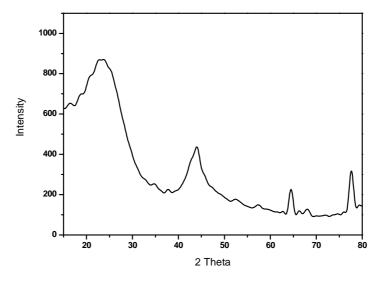


Fig.2. XRD patterns of nano MgO composite

# **Determination of functional group**

The FTIR spectrum of Rhodamine B on nano composite before and after adsorption is in the range of 4000 to 400 cm<sup>-1</sup> is presented in Fig.3. The peaks around 2900 cm<sup>-1</sup> and 3400 cm<sup>-1</sup> show the presence of O-H stretching vibrations due to the existence of surface hydroxyl group and chemisorbed H<sub>2</sub>O molecules. The peaks between 1600 cm<sup>-1</sup> and 3000 cm<sup>-1</sup> are due to C-H bonds. The peaks at 1710 cm<sup>-1</sup> and 1610 cm<sup>-1</sup> are due to C=O stretching. The peak at 1219 cm<sup>-1</sup> for Composite repsresents the C-O of Oxygen related groups present in the adsorbent. The band around 453.08cm<sup>-1</sup> which was associated with the in-plane and out-of-plane aromatic ring deformation vibration common that is quite common for activated carbon.

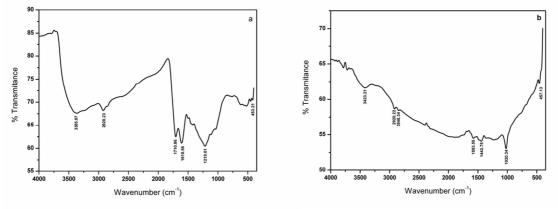


Fig.3. FTIR Spectrum of nano MgO composite(a.before adsorption; b.after adsorption)

## Effect of particle size

The adsorption of Rhodamine B is investigated at particle size 70, 90 and 150 BSS mesh of the nano composite and the results are represented in Fig.4(a). With increase in particle size, there is increase in adsorption. It appears that large dye molecules are able to penetrate to some of the interior pores of the particles when their size is large. Apparently access to all pores is facilitated as particle size becomes larger resulting in higher adsorption. As the particle of size 150 BSS mesh exhibit maximum adsorption capacity, all further detailed studies were done with this size only.

#### Effect of adsorbent dosage

The dependence of dye adsorption on carbon dose is studied by varying the amount of carbon from 50 to 150 mg / 100ml of the solution, keeping other parameters (pH, agitation speed and contact time) constant for the initial dye concentration of 100 mg L<sup>-1</sup> and which show the Rhodamine B removal efficiency for different carbon doses. From Fig.4(b) it can be observed that removal efficiency is generally improved with increasing the carbon concentration upto a certain value and then, there is no further increase of adsorption. The removal efficiency of Rhodamine B with the increase in carbon concentration is due to the greater surface area with more functional groups consequent to the increase in the number of carbon particles with more number of exchangeable sites for adsorption and saturation which occur as a result of non-availability of exchangeable sites on the adsorbent. The high removal at higher dosage is expected due to the increased adsorbent surface area and availability of more adsorption sites. The removal of Rhodamine B from the solution is noted at a initial concentration of 100 mg L<sup>-1</sup>. The percentage of dye adsorbed increases along with the increase of adsorbent dosage from 50-150 mg L<sup>-1</sup>. Above 100 mg of adsorbent dose the equilibrium of dye is reached and no increase in the % removal of dyes at this point and so the nano composite of 100mg is chosen for subsequent experiments.

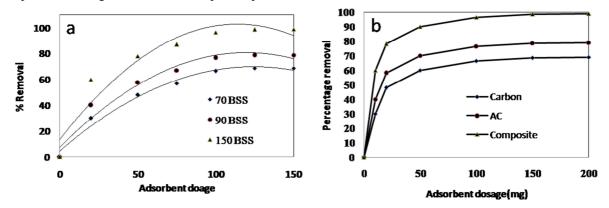


Fig.4. (a) Effect of particle size and (b) adsorbent dosage for adsorption of Rhodamine B dye on nano MgO composite

#### **Effect of Contact time**

The adsorption experiments are carried out for different contact times with a fixed adsorbent dose (0.100g) at room temperatures. It is observed that the uptake of the dye increases with time. The extent of adsorption is rapid in the initial stage and becomes slow in later stage till saturation is attained around 2 hours. This shows that equilibrium can be assumed to be achieved by 2 hours of contact time. It is basically due to saturation of the active site which does not allow further adsorption. The adsorption rate is found to decrease with increase in time.

### Effect of Initial dye concentration

The study of initial dye concentration is studied by varying the dye concentration from 20 to 100 mg  $L^{-1}$ . The rapid adsorption takes place in the first 30 min. Then the adsorption rate decreases gradually and the adsorption reaches equilibrium. This is because at low adsorbate/adsorbent ratio, the number of sorption sites in the nano composite but as the ratio increases the adsorption sites are saturated, resulting to decrease in the sorption efficiency. At high initial concentration, the gradient between the solution sample and the centre of particle enhances dye diffusion through the film surrounding the particle and in the porous network of the nano composite.

#### Effect of pH

The pH of the dye solution plays an important role in the whole adsorption process. There is an increase in adsorption capacity of the nano composite is noticed as the pH increases from 2 - 6, whereas above 6 the adsorption amount was only slightly affected by pH. As pH of the system decreases, the number of negatively charged adsorbent sites decreases and the number of positively charged surface sites increases. This favours the adsorption of positively charged dye cations due to electrostatic repulsion. In addition, lower adsorption of Rhodamine B at acidic pH might be due to the presence of excess H<sup>+</sup> ions competing with dye cations for the available adsorption sites.

### **Adsorption kinetics**

The study of adsorption kinetics describes the solute uptake rate and evidently these rate controls the residence time of adsorbate uptake at the solid-solution interface including the diffusion process. The adsorption study is tested for

four models i.e. pseudo first order, pseudo second order, intra- particle diffusion and Elovich model. The experiments are carried out for time intervals varied from the 0 to 120 min at constant temperature, with 100 mg  $L^{-1}$  of Rhodamine B by keeping other parameters constant.

#### Pseudo first order kinetic model

Lagergren proposed a pseudo-first order kinetic model as given below

$$\log(\mathbf{q}_{\mathrm{e}} - \mathbf{q}_{\mathrm{t}}) = \log \mathbf{q}_{\mathrm{e}} - \frac{\mathbf{\kappa}_{1}}{2.303}\mathbf{t}$$

Where  $k_1 (min^{-1})$  is the rate constant of the pseudo-first order adsorption and the rate parameters  $k_1$  can be directly obtained from the intercept and slope of the plot of  $log(q_e - q_l) V_s$  time t(Fig.5.a). The correlation value of  $R^2$  is 0.9926 for 100 mg L<sup>-1</sup> of the dye. The equilibrium adsorption capacity is 20.27 mg g<sup>-1</sup>. And the calculated equilibrium adsorption capacity is 21.25 mg g<sup>-1</sup> for 100 mg L<sup>-1</sup>. The calculated and experimental results reveal that, the pseudo-first order model provides a good approximation to the experimental kinetic data for the adsorption of Rhodamine B from aqueous solution.

## Pseudo-second-order kinetic model

The pseudo-second-order kinetic model is based on the assumption that the sorption follows second order chemisorption. Pseudo-second-order kinetic model is given as

$$\frac{\mathrm{d}\mathbf{q}}{\mathrm{d}\mathbf{t}} = \mathbf{k}_2(\mathbf{q}_{\mathrm{e}} - \mathbf{q}_{\mathrm{t}})^2$$

Where  $k_2$  is the pseudo-second order rate constant of dye adsorption. The plot of t/q versus t (Fig.5.b) should give a linear relationship, from which  $k_2$  can be determined from the slope and intercept of the plot are listed in the Table 1. The correlation value  $R^2$  is 0.9754. The rate constant  $k_2$  is  $4.97 \times 10^{-4}$  g mg<sup>-1</sup> min<sup>-1</sup>. So, when the correlation value of pseudo-second order is compared with pseudo-first order, it is concluded that the pseudo-second order is not totally adequate to describe the adsorption process.

#### Intra-particle diffusion model

There are essentially three consecutive mass transport steps associated with the adsorption of solute from the solution by an adsorbent. These are (i) film diffusion, (ii) intra-particle or pore diffusion, and (iii) sorption into interior sites. The third step is very rapid and hence film and pore transports are the major steps controlling the rate of adsorption. In order to understand the diffusion mechanism, kinetic data is further analyzed using the intra-particle diffusion model based on the theory proposed by Weber and Morris. The intra-particle diffusion equation is given as

# $q_t = K_{\rm int} t^{0.5} + C$

Where  $q_t$  is the amount of nano composite adsorbed (mg g<sup>-1</sup>)  $k_{int}$ ,the intra-particle diffusion rate constant(mg g<sup>-1</sup> min<sup>0.5</sup>) and C is the intercept and  $k_{int}$  is determined from the slope of the plot of  $q_t$  versus  $t^{0.5}$  (Fig.5.c). The calculated value of  $k_{int}$  is (0.52 - 0.88) mg g<sup>-1</sup> min<sup>0.5</sup> and C is (0.85 - 0.93). The correlation coefficient (R<sup>2</sup>) value is 0.9930 for the nano composite. The high R<sup>2</sup> value indicates that intra-particle diffusion might play a significant role in the initial stage of the adsorption. The value of intercept gives an idea about the thickness of boundary layer ie., larger the intercept greater is the boundary layer. The double nature of plot may be explained by the fact that the initial portion is boundary layer diffusion effect while the final linear portion is the result of intra particle diffusion.

#### **Elovich model**

Elovich equation is also used successfully to describe second order kinetic assuming that the actual solid surfaces are energetically heterogeneous, but the equation does not propose any definite mechanism for adsorbate–adsorbent. It has extensively been accepted that the chemisorption process can be described by this semi-empirical equation. The linear form of this equation is given by:

$$q_t = \frac{1}{\beta} \ln \alpha \beta + \frac{1}{\beta} \ln t$$

Where  $\alpha$  is the initial adsorption rate (mg g<sup>-1</sup> min<sup>-1</sup>), and the parameter  $\beta$  is related to the extent of surface coverage and activation energy for chemisorption (g mg<sup>-1</sup>). The Elovich coefficients could be computed from the plots q<sub>t</sub> v<sub>s</sub> lnt. The initial adsorption rate  $\alpha$  and desorption constant  $\beta$  are calculated from the intercept and slope of the straightline plots of q<sub>t</sub> against lnt as shown in Fig.5.d. The kinetic constants obtained from the Elovich equation were presented in table 1. It will be seen that applicability of the simple Elovich equation for the present kinetic data indicates that the Elovich equation is able to describe properly the kinetics of Rhodamine B onto nano composite.

Pseudo first order		Pseudo second order		Elovich		
k1	$R^2$	k <sub>2</sub>	$\mathbb{R}^2$	α	β	$\mathbb{R}^2$
1.15x10 <sup>-1</sup>	0.9926	4.97x10 <sup>-4</sup>	0.9754	1.722	1.919	0.9895

Table 1: Kinetic Parameters for the adsorption of Rhodamine B dye onto nano composite

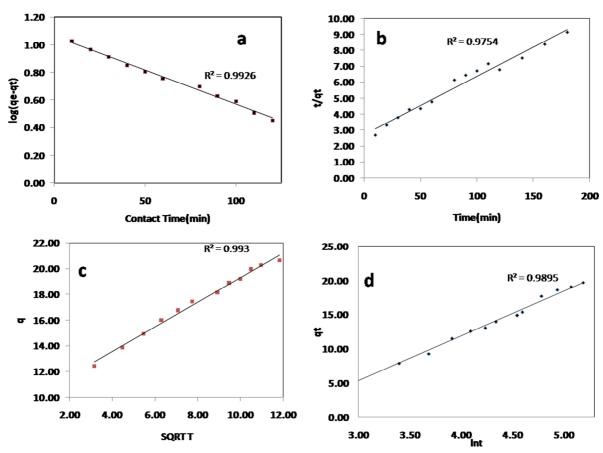


Fig.5(a). Pseudo first order (b) Pseudo second order (c) Intra particle diffusion (d) Elovich isotherm for the adsorption of Rhodamine B dye onto nano composite

## Adsorption isotherm

#### Langmuir isotherm

Langmuir isotherm model is based on assumption that a saturated monolayer of adsorbate molecules is present on the adsorbent surface, the adsorption energy is constant and there is no migration of adsorbate molecules in the surface plane when maximum adsorption capacity occurs. The linear transformation of the Langmuir equation is given by

$$\frac{1}{q_e} = \frac{1}{q_0 b C_e} + \frac{1}{q_e}$$

Where  $q_o$  is the maximum amount of adsorbate per unit mass of adsorbent form a complete monolayer on the surface (adsorption capacity),  $C_e$  denotes equilibrium adsorption concentration in solution,  $q_e$  is the amount adsorbed per unit mass of adsorbent and b is the binding energy constant. A plot of  $1/C_e$  versus  $1/q_e$  is graphically represented in Fig.6.a. The values of  $Q_0$  and b are calculated from the intercept and slope respectively and the results are presented in Table 2. A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter,  $R_L$  also known as the separation factor that is given by the following equation.

$$\mathbf{R}_{\mathrm{L}} = \frac{\mathbf{1}}{(\mathbf{1} + \mathbf{b} \ \mathbf{C}_{\mathbf{0}})}$$

The data related to the equilibrium obeys well with the Langmuir models. The maximum adsorption capacity of adsorption of Rhodamine B by Langmuir isotherm is 16.20 mg g<sup>-1</sup>. The R<sup>2</sup> value 0.9908 suggests that the Langmuir isotherm provides a good fit to the isotherm data. The value of  $R_L$  was 0.2026 which favours adsorption i.e. formation of monolayer of Rhodamine B on the surface of nano composite.

#### Freundlich isotherm

The Freundlich equation is used to determining the applicability of heterogeneous surface energy in the adsorption process. The empirical Freundlich equation is expressed as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

Where  $k_f$  is measure of adsorption capacity (mg g<sup>-1</sup>) and n is adsorption intensity. 1/n values indicate the type of isotherm to be irreversible (1/n = 0), favorable (0 < 1/n < 1), unfavorable (1/n > 1). The plots of ln q<sub>e</sub> vs ln C<sub>e</sub> (Fig.6.b) shows linearity (R<sup>2</sup> = 0.9825). The values of K<sub>f</sub> and n given in the Table 2. Values of n lies 1 to 10 indicate an effective adsorption. It also indicates degree of favorability of adsorption. The Freundlich adsorption capacity by this plot is 13.48 mg g<sup>-1</sup>. Higher value of k<sub>f</sub> indicates higher affinity for Rhodamine B adsorption. From the results it was clearly observed that both models were well suited for adsorption of Rhodamine B on nano composite, but the regression factor as well as the calculated and experimental values correlates more correctly with the Langmuir values, on this basis it could be concluded that, Rhodamine B form monolayer on the surface of nano composite.

#### Temkin isotherm

Temkin isotherm model predicts a uniform distribution of binding energies over the population of surface binding adsorption. Linear form of Temkin equation is expressed as:

#### $q_e = B \ln A + B \ln C_e$

Where B = RT/b, b is the Temkin constant related to heat of sorption  $q_e (mg g^{-1})$  and  $C_e (mg L^{-1})$  are the amount of adsorbed dye per unit weight of adsorbent and unabsorbed dye concentration in solution at equilibrium, respectively. Therefore, a plot of  $q_e$  versus ln  $C_e$  (Fig.6.c) enables one to determine the constants A and B. From Table 2, nano composite has maximum binding energy which is uniformly distributed. The value for constant B is 0.0749 J mg<sup>-1</sup> is heat of adsorption. The correlation coefficient of 0.9906 obtained shows that adsorption of Rhodamine B also follows the Temkin model.

Table 2: Isotherm Parameters for the adsorption of Rhodamine B dye onto nano composite

Langmuir			Freundlich			Temkin	
$Q_0$	В	R <sup>2</sup>	KF	n	R <sup>2</sup>	В	$\mathbb{R}^2$
16.2	3.401	0.9908	13.48	2.123	0.9825	0.0749	0.9906

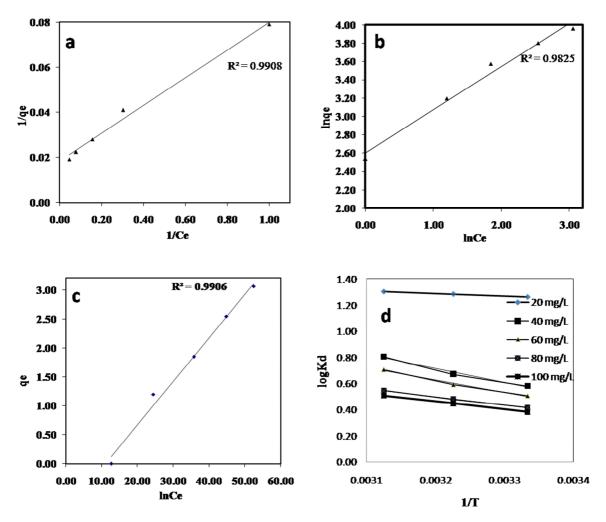


Fig.6(a). Langmuir adsorption isotherm (b) Freundlich adsorption isotherm (c) Temkin adsorption isotherm (d) Vant-Hoff isotherm for the adsorption of Rhodamine B dye onto nano composite

#### Thermodynamic study

In order to investigate the effect of temperature on the uptake of Rhodamine B the process is carried out at different temperatures ranging from 300K, 310K and 320K. The temperature affected the equilibrium uptake. The equilibrium of Rhodamine B adsorption capacity of both the adsorbents are better at higher temperatures as the adsorbed amount of Rhodamine B increases with the rise in temperature. Higher uptake at high temperature is due to the increase in molecular diffusion or may be attributed to the availability of more active sites on the surface of the related with several thermodynamic parameters including free energy change ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ), and entropy ( $\Delta S^0$ ) which is used to decide whether the adsorption is a spontaneous process or not. Thermodynamic parameters can be calculated from the following equation

# $\Delta G^0 = -RT \ln K_d$

Where R is the universal gas constant (8.314  $\text{Jmol}^{-1} \text{ K}^{-1}$ ), T the temperature (K), and K<sub>d</sub> is the distribution coefficient. If the value of  $\Delta G^{\circ}$  is negative, the chemical reaction can occur spontaneously at a given temperature. The K<sub>d</sub> value is calculated using the equation

$$K_d = \frac{C_e}{q_e}$$

Where  $q_e$  and  $C_e$  are the equilibrium concentrations of MG (mg L<sup>-1</sup>) on the adsorbent and in the solution, respectively. The enthalpy change ( $\Delta H^0$ ) and entropy change ( $\Delta S^0$ ) can be calculated from the following equation.

$$\Delta G^0 = \Delta H^0 - T \Delta S^0$$

This equation can be written as

$$\ln K_{d} = \frac{\Delta S^{0}}{R} - \frac{\Delta H^{0}}{RT}$$

The thermodynamic parameters of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  are obtained from the slope and intercept of the plot between log  $K_d$  versus 1/T respectively from the Fig.6.d. The Gibbs free energy changes ( $\Delta G^0$ ) were calculated from the above equation and the values of  $\Delta G^0$ ,  $\Delta H^0$ , and  $\Delta S^0$  for the adsorption of Rhodamine B onto nano composite are given in Table 3. The negative values of  $\Delta G^0$  indicates the spontaneous nature of the adsorption process. The magnitude of  $\Delta G^0$  also increases with increasing temperature indicates that the adsorption is more favorable at higher temperatures.

Conc. (mg/L)	T(K)	K <sub>d</sub>	∆G°	$\Delta S^{\circ}$	ΔH∘
Cone. (mg/L)	1(1)	<b>n</b> d	$(J \text{ mol}^{-1})$	$(J \text{ mol}^{-1} \text{ K}^{-1})$	$(kJ mol^{-1})$
20	300	18.2	-1501.7		
	310	19.2	-1999.4	74.42	-23.8
	320	20.1	-2805.8		
40	300	3.8	-1062.5		
	310	4.7	-1393.2	52.08	-16.7
	320	6.4	-1813.3		
	300	3.2	-820.7		
60	310	3.9	-1128.1	40.57	-13.0
	320	5.1	-1501.7		
80	300	2.6	-452.5		
	310	3.0	-694.4	22.82	-7.3
	320	3.5	-965.6		
	300	2.4	-311.6		
100	310	2.8	-553.3	16.23	-5.2
	320	3.2	-820.7		

Table 3: Thermodynamic Parameters for the adsorption of Rhodamine B dye onto nano composite

The negative values of  $\Delta H^{\circ}$  indicate that the exothermic nature of the adsorption of Rhodamine B onto nano composite. Further, negative  $\Delta G^{\circ}$  values indicate spontaneous nature of the adsorption process and positive  $\Delta S^{\circ}$  values indicate the affinity of the adsorbent of dye.

#### CONCLUSION

The current study investigates the equilibrium and the dynamics of the adsorption of Rhodamine B onto nano MgO activated carbon prepared from *delonix regia*. The adsorption capacity of the adsorbent is considerably affected by initial concentration, adsorbent dose, particle size, contact time, temperature and initial pH. The adsorption of Rhodamine B is exothermic in nature with the adsorption capacity increasing with increasing temperature. The Langmuir, Freundlich and Temkin models are used for the mathematical description of the adsorption equilibrium of Rhodamine B onto nano composite. The experimental data fitted well to Langmuir and Temkin adsorption isotherms. The kinetics of adsorption Rhodamine B on nano composite is studied by using four kinetic models. The adsorption proceeds according to the pseudo-first order model and Elovich which provide the best correlation of the data in all cases and diffusion was not the only rate-controlling step. According to Elovich model, the results show that the rate could be enhanced by increasing the adsorption temperature. The enhanced adsorption is due to the chemical adsorption of the dye on the nano coated sorbent. Negative  $\Delta H$  and positive  $\Delta S$  values indicate that the adsorption of Rhodamine B onto nano composite is exothermic. Rhodamine B has good affinity towards the adsorption proceeds.

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