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Sequestration of carcinogenic dye in waste water by utilizing an encapsulated activated carbon with nano MgO.

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Abstract: The sequestration of the carcinogenic dye Congo red in the textile processing effluents is vital for environmental safety of the human population and all living organisms in water bodies. In order to mitigate this carcinogen in water bodies, a new composite material is prepared from the wooden waste from the pods of *delonix regia*. These pods are activated to form an activated carbon and are loaded with magnesium oxide nano particles to form a new composite material. This composite material is utilized as an adsorbent for Congo red dye sequestration studies of waste water. The FTIR, SEM, TEM, and XRD studies are carried out with this newly formed composite adsorbent-nano MgO encapsulated activated carbon. The kinetic studies with respect to adsorbent dosage, contact time, the effect of pH, adsorption capacities are investigated and these studies revealed that this encapsulated new adsorbent favorably adopts to the Freundlich and Langmuir models on adsorption and it follows the pseudo first order rate kinetic. These studies on the new nano MgO encapsulated activated carbon prepared from the pods of *delonix regia* proves its efficiency in adsorbing the pollutant load of a carcinogenic dye stuff in the waste water bodies.
Key words: Adsorbent dosage, Congo red dye, *Delonix regia*, Nano metal oxide composite.

Introduction

The mitigation of toxic dye house effluents with molecular fragments remains a major problem with reference to bio-accumulation in Indian context[1]. Dyes impart the desired colour fashionably upon the materials by chemical adsorption phenomenon[2]. Nearly 15% of the dyes are left out into the environment during the processing and results in polluting the clean water bodies and creates a lot of miseries to the water consumers and administrators, the honorable Supreme Court of India intervened in this issue and order for even to the closer of these pollution causing industries. As per the existing statistics the textile processing units around the world are consuming 60% of the total dye stuff produced and the remaining stock is utilized by other industries in imparting the desired colors. Several methods are attempted to remove the pollutants from the effluents among them the phenomenon of adsorption has been proved it as an effective and becomes economical. In order to fulfill the commitments laid down by the Pollution control boards in India, attempts are already made with several commercially available activated carbons but they are very expensive[3]. In an effort to find an alternative to this high cost adsorbent, several attempts have been made, in which activating the agricultural solid waste material in to an activated carbon is attempted. In this attempt a new novel composite material is prepared by activating the carbon and identifying its complexity, the larger area of this composite activated carbons ignite the desire to initiate an investigation about this material. Several tests are made to determine the efficiency of this material in up taking the dye residues from the waste waters. A very limited work has been carried out and reported with the composite adsorbents. Thus a new composite material is prepared by coating a nano metal oxide coat over an activated carbon formed from the pods of *delonix regia* an agricultural wooden waste. This nano encapsulated activated carbon material is investigated for its efficiency in adsorbing the dye congo red dye (1- Naphthalenesulfonic acid, 3, 3'-(4, 4' biphenylene bis (azo) bis 4-amino) di sodium salt) benzedene based. The bioaccumulation of these benzedene molecular compounds will create the tissues causing cancer; this is due to the consumption of water from polluted water bodies. Even the exposure of these dye molecules will create allergic reactions possibly anaphylactic shock. The sequestration of this dye from industrial waste waters becomes inevitable before discharging them into water bodies on health, hygienic points for environmental protection[4]. Already activated carbons have proved their efficiencies over these types of dye removal techniques[5]. By using a composite adsorbent material due to its complexity and larger area of adsorbent with lot of active sites results an improved efficiency to remove the carcinogenic dye Congo red.

Experimental

Preparation of nano MgO encapsulated activated pods of *delonix regia* adsorbent

Delonix regia pods are collected and dried, cut into small pieces and activated in the concentrated sulphuric acid pickling for 48 hours. This material is washed in distilled water and treated with 5% sodium bicarbonate solution for neutralization, washed with distilled water and kept for drying at 120°C for an hour and shifted to a tubular furnace in nitrogen current and heated in tubular furnace up to 700 ºC for an hour. A carbonaceous material is resulted is grounded in the ball mill and washed with the distilled water, dried at 120 ºC. This dried powder is sieved into various particle size ranges from 70-150 BSS[6].

A solution consists of 6 g of $MgCl_2$ with 2 g of Surfactant SDS (Sodium Dodecyl Sulphate) is made up to100 ml in a standard flask and this solution is added to 100 ml 0.04N NaOH solution with constant stirring for 2 hours by using a magnetic stirrer at 11 pH, a white $Mg(OH)_2$ is precipitate out and this is washed with distilled water, dried for 2hours at 120 ^{0}C. This white solid mass is kept at 800^{0}C for 5 hours in a muffle furnace, and it is grounded to a granular MgO powder. A 0.02gm of MgO powder is dispersed into a 50 ml methanol and stirred for 2 hours by maintaining a constant volume of 50 ml mark. One gram of activated pods of *delonix regia* carbon particles of mesh number 150 BSS is added and dispersed in MgO continuing solution and is stirred for 2 hours which results a nano MgO encapsulation over the activated carbon particle is filtered, washed with methanol, dried at 60^{0}C and heated to 400^{0}C in a tubular furnace in nitrogen atmosphere.

The preparation of stock solution of dye for 1000ppm by using double distilled water. A number of Congo red standard solutions are made up as stock solutions with various concentrations ranging from 10 to 100 mg/L

Batch mode of adsorption studies

This composite adsorbent material is tested in batch mode of experiments using mechanical shaker. The Calibration curves were obtained with standard Congo red dye solution. Mass capacity of adsorption q_e was calculated from the difference between the initial and final absorbance values from the calibration curve drawn by measuring the absorbance at λ max at 497nm by using the spectrophotometer.

$$q_e = \frac{C_e - C_o}{W} V$$

Where, C_0 and C_e (mg L^{-1}) are concentrations of the dye solution at initial and final equilibrium state. V is the volume of the solution in liter, and W is the mass of dry adsorbent used (g).

Results and Discussions

Effect of adsorbent dosage

The effect of the various adsorbents dosages on the adsorption are tested with various amounts of adsorbents with the masses in between 0.02 and 0.2g. These tests are carried out at room temperature, at neutral pH the samples are constantly stirred for 180 minutes. The concentration of the remaining solution is observed with spectrophotometer. These studies revels that the adsorption is maximum at 0.1g of adsorbent dosage.

Effect of solution pH

The pH of the aqueous dye solution is an important factor of dye adsorption process. This is due to the ionization behavior of adsorbent and the dye. The effect of pH on Congo red adsorption by the adsorbents are tested in acidic and in basic ranges the adsorption remains constant and it attains the maximum at a pH of 7.0.

It is reveled that the dye adsorbing capacity of this new composite material becomes maximum of 93% at a neutral pH.

Effect of contact time

Adsorption studies for the adsorbents are carried out by using 100ml of the solution containing 100 mg/L of dye and 0.1g of adsorbent at room temperature at a pH of 7.0. The dye uptake capacity at different time intervals of 10 minutes, and tested up to 240 minutes. From theses testes at 120 minutes of contact time, the removal efficiency of this adsorbent material is 90%. The optimum value of contact time is 120 minutes. The TEM (Fig.1), SEM (Fig.3), images infer the presence of larger surface area available for adsorption. The XRD (Fig.4) studies reveals with the presence of active sites in this nano particle encapsulated activated carbon with more active sites for adsorption. The FTIR studies of the encapsulated adsorbent reveals that the unabsorbed activated adsorbent posses more active sites which is in the FTIR studies (2.a) figure and it has been occupied with the dye stuff and its adsorption capacity becomes saturated as per the FTIR studies (2.b) figure.

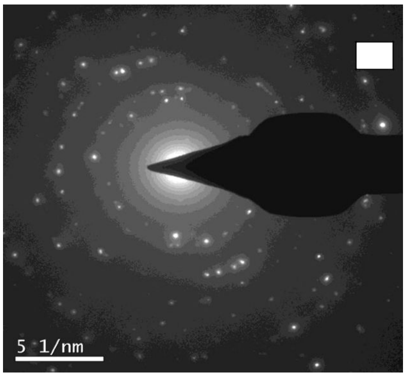

Fig 1. TEM images of MgO Nanoparticles

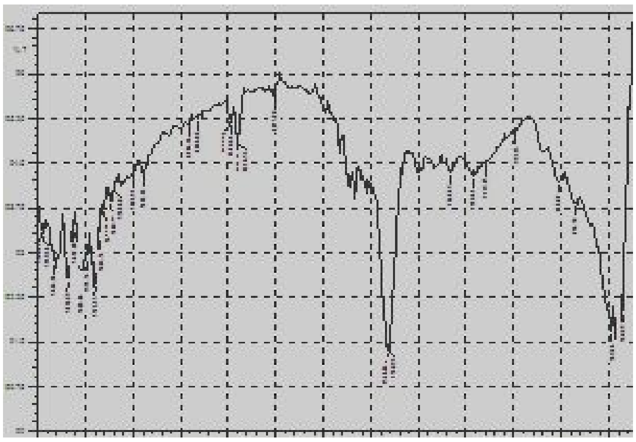

Fig 2a. FTIR Spectra for nano composite(Before asorption)

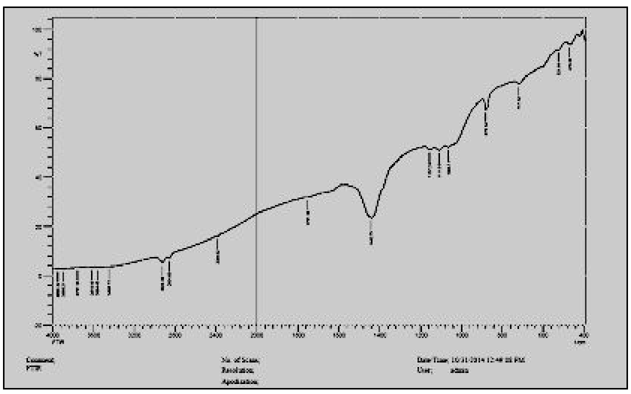

Fig 2b. FTIR Spectra for nano composite(After adsoprtion)

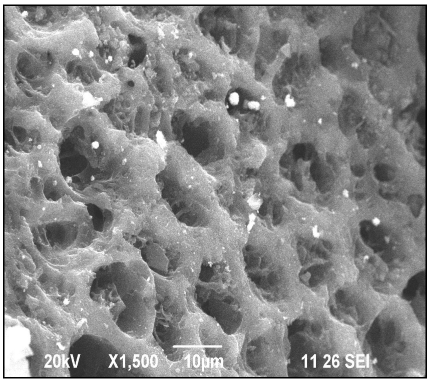

Fig 3. SEM images of magnesium oxide nano composite

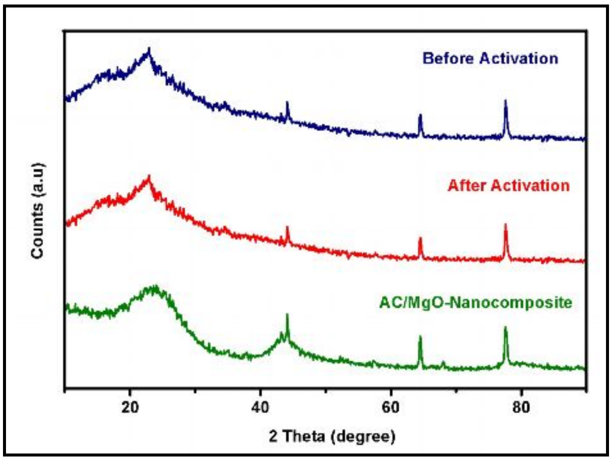

Fig 4. XRD patterns of the adsorbents C, AC and Composite

Effect of initial dye concentration

The study on initial dye concentration was studied by varying the dye concentration from 5 to 20 mg L^{-1} leads to a decrease in the percentage of the Congo red dye removal. The rapid adsorption takes place in the first 30 min and the adsorption rate decreased gradually and the adsorption reached equilibrium at an optimum contact time. This is because at low adsorbate/adsorbent ratio, the number of sorption sites in the composite material decreases with increase of adsorption at beginning and the adsorption sites are saturated and results a decrease in the adsorption. At high initial concentration, the gradient between the solution sample and the particles enhances dye diffusion through the film surrounding encapsulated particle and also in the porous network of the composite material which contains more active sites during the adsorption.

Langmuir Adsorption isotherm

Langmuir isotherm model is based upon the 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 plane of the surface during a maximum adsorption capacity occurs[7]. The linear transformation of the Langmuir equation is given by

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

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.5. The values of q_0 and b were calculated from the intercept and slope respectively and the results are presented in Table 1. 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.

$$R_L = \frac{1}{(1+bC_0)}$$

The data related to the equilibrium fit very well with the Langmuir adsorption isotherm models. The maximum adsorption capacity of this adsorbent to the Congo red by Langmuir isotherm is 52.63 mg g^{-1}. The R^2 factor is 0.9915 which suggests that Langmuir isotherm provides a good fit to the isotherm data. The value of R_L is 0.83 and indicates that this adsorption is favourable adsorption with monolayer formation of Congo red on the new nano composite adsorbent material.

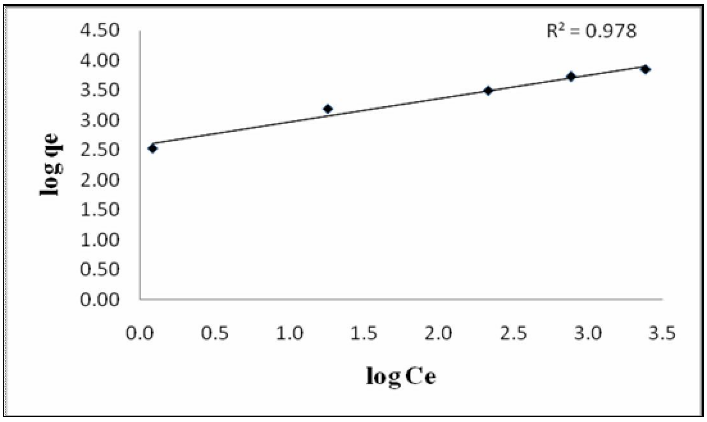

Fig5. Freundlich adsorption isotherm for the adsorption of dye onto nano composite

Table 1: Kinetic Parameters for the adsorption of Congo red dye onto nano composite

Kinetic model	Model coefficients	
	C_0 = 100 mg L^{-1}	
Pseudo-first order	q_{cal} (mg g^{-1})	37.65
	k_1(min^{-1})	0.1819
	R^2	0.9859
Intra-Particle diffusion	k_{int} (mg g^{-1} $min^{-0.5}$)	2.588
	C	1.653
	R^2	0.9948
Langmuir	q_0 (mg g^{-1})	52.63
	R_L	0.8333
	b(L mg^{-1})	0.225
	R^2	0.9931
Freundlich	k_f (mg g^{-1})	13.219
	n	2.557
	R^2	0.9784

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^{-1}) 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)[8]. The plots of ln q_e Vs ln C_e showed good linearity (R^2 0.9784) Fig.6. The values of K_f and n given in the Table 1. The values of n lies in between 1 to 10 indicate that it is an effective adsorption. This value also indicates degree of favorability of the adsorption. Higher value of k_f 13.219 indicates higher affinity for Congo red in the adsorption process. The results clearly infer that both of these models are well suited for the adsorption of Congo red over the nano-composite material, the regression factor, the values calculated from the experimental values of the Langmuir adsorption isotherm values, gives as an evident with the factors that Congo red forms a monolayer upon the surface of nano composite activated carbon material.

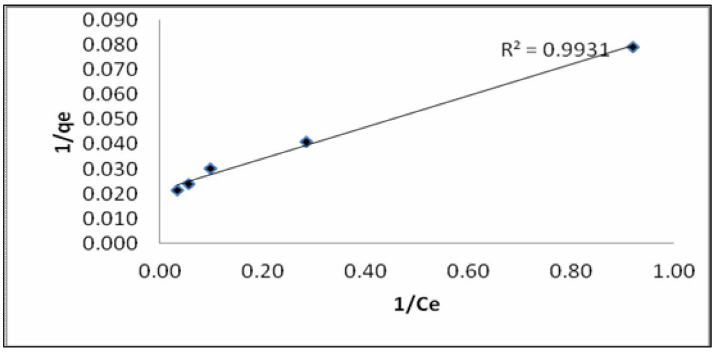

Fig 6. Langmuir adsorption isotherm for the adsorption of dye onto nano composite

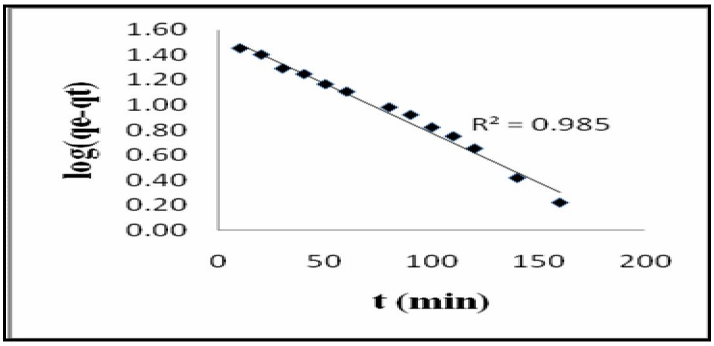

Fig 7. Pseudo first order for the adsorption of dye onto nano composite

Adsorption kinetics

Pseudo first order kinetic model

Lagergren proposed a pseudo-first order kinetic model as given below[9]

$$\log(q_e - q_t) = \log q_e - \left[\frac{k_1}{2.303t}\right]$$

Where k_1 (min^{-1}) is the rate constant of the pseudo-first order adsorption and q_t is the adsorption capacity at time 't' (mg g^{-1}) .The rate parameters k_1 and q_e can be directly obtained from the intercept and slope of the plot of $\log(q_e - q_t)$ V_s time t in Fig-7. The correlation value of R^2 was 0.9859 for 100 mg L^{-1}. The equilibrium adsorption capacity is is 37.65 mg g^{-1}. The observed experimental results reveal that this adsorption phenomenon follows the pseudo-first order kinetics.

Intra-particle diffusion Studies

There are three consecutive mass transport steps associated with the adsorption of solute from the solution by an adsorbent. They are (i) film diffusion, (ii) intra-particle or pore diffusion[10], 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 analyzed with the application of intra-particle diffusion model proposed by Weber and Morris. The intra-particle diffusion equation is given as

$$q_t = k_{id} t^{0.5} + C$$

Where q_t is the amount of dye adsorbed (mg g^{-1}) k_{id} the intra-particle diffusion rate constant (mg g^{-1} $min^{0.5}$) and C is the intercept is listed in Table 2. k_{int} is determined from the slope of the plot of q_t versus $t^{0.5}$ in Fig. 8. The calculated value of k_{id} is 2.58 mg g^{-1} $min^{0.5}$ and C is 1.65. The correlation coefficient (R^2) value was 0.9948. The higher R^2 value indicates that intra-particle diffusion plays a significant role in the initial stage of the adsorption and the values of the intercept give the nature of the thickness of the boundary layer. If larger value of the intercept, the greater is the boundary layer.

Table 2: Thermodynamic Parameters for the adsorption of Congo red dye onto nano composite

Conc. (mg/l)	T (K)	K_d	ΔG◦ (J mol^{-1})	ΔS◦ (J mol^{-1} K^{-1})	ΔH◦ (kJ mol^{-1})
20	300	18.2	-1501.7	74.42	-23.8
	310	19.2	-1999.4		
	320	20.1	-2805.8		
40	300	3.8	-1062.5	52.08	-16.7
	310	4.7	-1393.2		
	320	6.4	-1813.3		
60	300	3.2	-820.7	40.57	-13.0
	310	3.9	-1128.1		
	320	5.1	-1501.7		
80	300	2.6	-452.5	22.82	-7.3
	310	3.0	-694.4		
	320	3.5	-965.6		
100	300	2.4	-311.6	16.23	-5.2
	310	2.8	-553.3		
	320	3.2	-820.7		

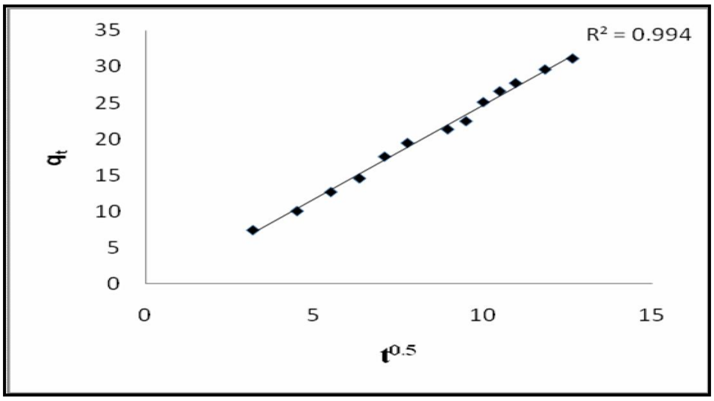

Fig 8. Intra particle diffusion of dye onto nano composite

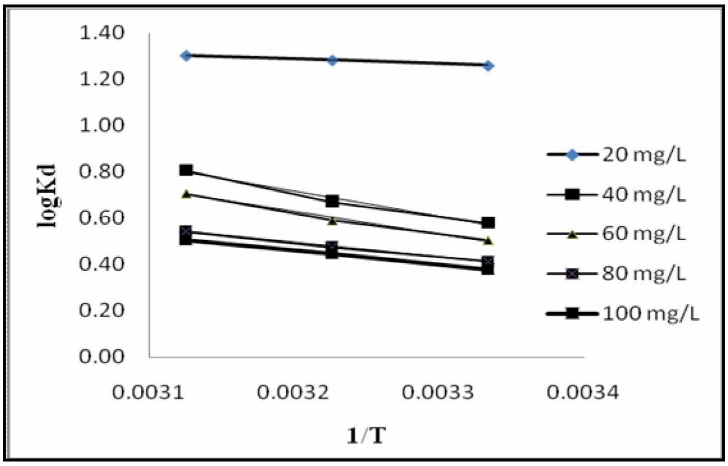

Fig 9. Vant-Hoff isotherm plot for the adsorption of Congo red dye onto nano composite

Thermodynamic studies.

In order to investigate the effect of temperature on the uptake of Congo red the process was carried out at different temperatures ranging from 300K, 310K and 320K. The temperature affected the equilibrium uptake as shown in Fig.9. The equilibrium Congo red adsorption capacity of both the adsorbents were better at higher temperatures as the adsorbed amount of Congo red increased 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 and related to several thermodynamic parameters including free energy change (ΔG^0), enthalpy (ΔH^o), and entropy (ΔS^0) which are used to decide whether the adsorption is a spontaneous or non spontaneous. The Thermodynamic parameters are calculated from the following equation

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

Where R is the universal gas constant (8.314 $Jmol^{-1}$ K^{-1}), T the temperature (K), and K_d is the distributioncoefficient. If the value of ΔG^o is negative, the chemical reaction can occur spontaneously at a given temperature. The K_d value was calculated using the following Equation $K_d = \frac{C_e}{q_e}$

Where: The q_e and C_e are the equilibrium concentrations of Congo red (mg L^{-1}) on adsorbent and in solution. The enthalpy change (ΔH^0) and entropy change (ΔS^0) can be calculated from the following equation. $\Delta G^0 = \Delta H^0 - T\Delta S^0$ can be expressed as follows,

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

The thermodynamic parameters of ΔH° and ΔS° were obtained from the slope and intercept of the plot between log K_d versus 1/T respectively from the Fig.9. The Gibbs free energy changes (ΔG^0) were calculated from above the equation, and the values of ΔG^0, ΔH^0, and ΔS^0 for the adsorption of Congo red onto nano composite were given in Table 2. The negative values of ΔG^0 indicated the spontaneous nature of the adsorption process. The magnitude of ΔG^0 also increased with increasing temperature indicating that the adsorption was more favorable at higher temperatures. The negative values of ΔH^o indicate that the exothermic nature of the adsorption of Congo red onto nano composite. Further, negative ΔG^0 values indicate spontaneous nature of the adsorption process and positive ΔS^0 values indicate the affinity of the adsorbent of dye.

Conclusion

The results of this study show that the new composite material of nano magnesium oxide encapsulated activated carbon of *delonix regia is* successful in removing the carcinogenic dye Congo red from the waste water. The morphological study confirms that the surface of the composite is very active owing to the larger surface area with more active sites is contributed only by the nano coatings. Both the Freundlich and Langmuir isotherms are aptly fit and to obtain equilibrium state. The kinetic studies revealed that the adsorption data is best fitted with pseudo first order kinetic model. Lagergren kinetic model found to be effective to know about the intra particle diffusion mechanism. The adsorption capacity of this nano composite activated carbon is higher than the activated carbon.

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