

## Acid dye removal by using modified activated carbon encapsulated with nano particles

S. Daniel\*, P.S. Syed shabudeen

Department of Chemistry, Kumaraguru College of Technology, Coimbatore-641049.

**Abstract:** Colors can cause major environmental pollutions and are responsible for the carcinogenic and mutagenic risks. Textile industries are responsible for producing large amounts of highly contaminated effluents that contain synthetic dyes which are characterized by being toxic and reactive. Adsorption technique has been used as a promising treatment method to remove the pigments that do not adhere to fibers during dyeing process. Modified adsorbent has been prepared by coating nano metal oxide particles on the adsorbent prepared from the pods of *delonix regia*. The adsorption behaviour of acid orange-7 (AO-7) on nano MgO composite has been investigated to understand the physicochemical process involved and to explore the potential use of nano particles in textile effluent treatment. Effects of initial dye concentration, pH, contact time and temperature have been investigated. Chemical and morphological characteristics of the nano coated adsorbent has been evaluated using methods such as Scanning Electron Microscopy and Fourier Transformed Infrared Spectroscopy. Sorption kinetics are conducted and followed pseudo-first order kinetic model. Equilibrium data are well represented by Langmuir model. The results indicate that the modified composite is a promising low cost technology adsorbent for the removal of waste dyes.

**Key words:** sorption kinetics, acid orange-7, *delonix regia*, nano metal oxide composite.

### Introduction

Several industries such as textile, paper and plastics use dyes to colour their materials, as a result these dyes are invariably released as waste water into the water bodies<sup>1</sup>. Uptake of these effluents through food chain in aquatic organisms will cause various physiological illnesses such as hypertension, sporadic fever, renal damage and muscle cramps<sup>2</sup>. Several physical and chemical treatment methods including coagulation, adsorption, filtration and precipitation have been used for the removal of the dye from industrial wastewater. Unfortunately, these methods are not totally efficient, and the difficult in the treatment consists in the stability of these dyes, as they are kind of organic compounds that usually have a synthetic origin and complex molecular aromatic structures letting them difficult to be biodegraded<sup>3</sup>. Among all treatment techniques, adsorption has been shown to be superior to the other techniques because of its simplicity of design, low cost and high efficiency. Adsorption is a conventional technology for dye removal with very high efficiency and simple process and activated carbon is used for the removal of azo dye, acid orange-7 from aqueous solution<sup>4</sup>. The adsorbent prepared from *delonix regia* has been investigated for its suitability and found to be on par with any other low cost adsorbent<sup>5</sup>. The coating of nanoparticles on activated carbon and used as an adsorbent has come up as an interesting area of research because of their small particle size and high surface area. The active sites are also more and capable of interacting with pollutant species<sup>6,7</sup>. A previous studies indicate that adsorption capacity remains unchanged after regeneration of nanosized adsorbent<sup>8,9</sup>.

## Experimental

### Preparation of dye solution

Acid orange-7 is procured from Thirupur, Tamil Nadu, an Indian town of Textiles and used as a commercial dye without any purification. Acid orange-7(AO7) is an anionic azo dye and its IUPAC name is sodium 4-[(2-hydroxy-1-naphthyl)azo]benzene sulfonate. It is used for dyeing variety of materials of nylon, silk, and wool. It is highly toxic and may cause cancer due to its carcinogenic nature<sup>10</sup>. The stock solution of 1000ppm of dye AO7 is prepared by using double distilled water and a number of standard solutions of various concentrations ranging from 10 to 100 mg/L are made up from the stock solution. The dye absorbs  $\lambda_{\max}$  at 542 nm.

### Preparation of modified activated carbon encapsulated nano particles

The small pieces of dried *delonix regia* pods are made charcoal by the process of concentrated Sulphuric acid pickling for 48 hours. This material is then washed in distilled water and treated with 5% sodium bicarbonate solution for neutralization. This is kept for drying at 120°C for an hour and shifted to a tubular furnace in Nitrogen current and heated up to 700 °C for an hour. A carbonaceous material is grounded in the ball mill, washed with the distilled water and dried at 120 °C in a furnace. This dried powder is sieved into various particle sizes range from 70-150 BSS<sup>11</sup>. The activated carbon is encapsulated with nano particle of MgO prepared by chemical method<sup>12</sup>.

### Batch mode of adsorption studies

This composite adsorbent material is tested in batch mode of experiments using mechanical shaker. The adsorption capacity  $q_e$  is calculated from the difference between the initial and final absorbance values obtained from the calibration curve drawn by measuring the absorbance for various concentrations ranging from 20mg/L to 100 mg/L at  $\lambda_{\max}$  542 nm by using the UV Visible Spectrophotometer

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

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

## Results and Discussions

### Characterization of the adsorbent:

The TEM (Fig.1), SEM (Fig.3), images infer the presence of larger surface area available for adsorption. The XRD (Fig.4) studies reveal 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 show that the unadsorbed activated adsorbent posses more active sites (Fig 2.a) and it has been occupied with the dye stuff after adsorption and its adsorption capacity becomes saturated as per the FTIR studies (Fig 2.b).

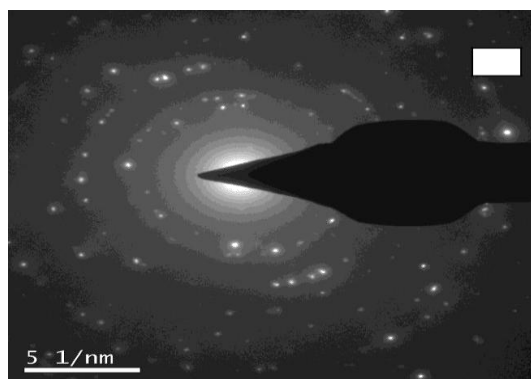


Fig. 1. TEM images of Magnesium oxide nano composite

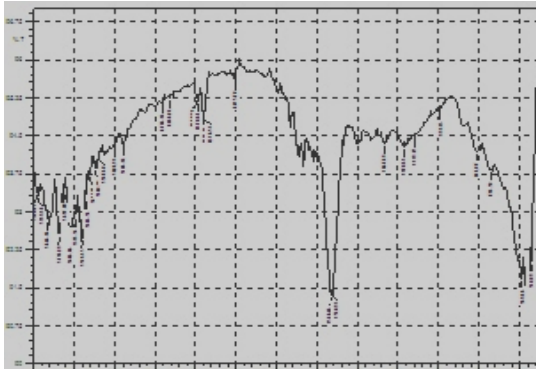


Fig. 2a. FTIR spectrum of Magnesium oxide nano composite (before adsorption)

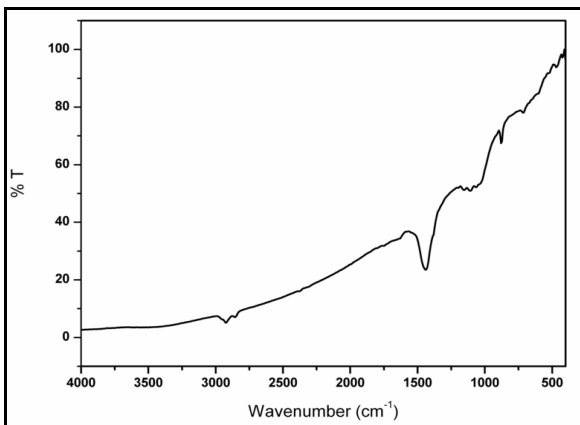


Fig. 2b. FTIR spectrum of Magnesium oxide nano composite (after adsorption)

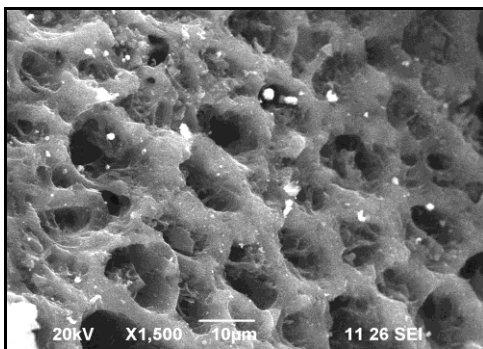


Fig. 3. SEM images of Magnesium oxide nano composite

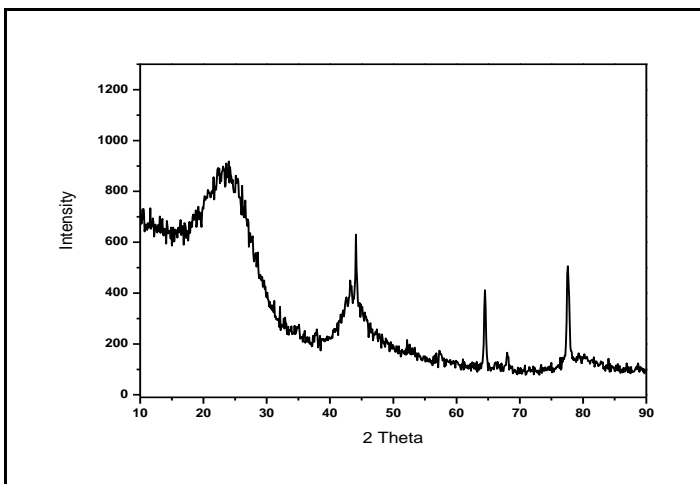
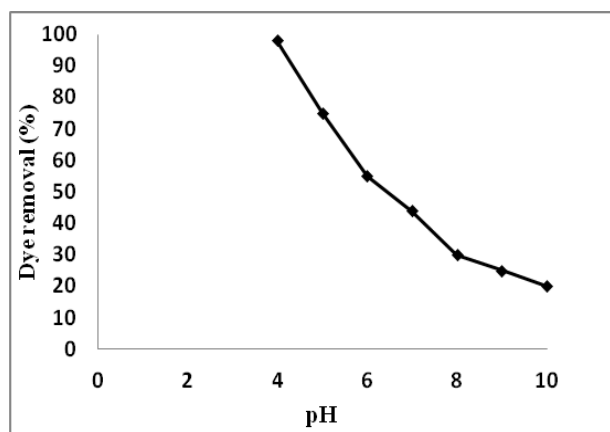


Fig. 4. XRD pattern of the Magnesium oxide nano composite

### Effect of adsorbent dosage

The effect of the various adsorbents dosages on the adsorption are tested with various amounts of adsorbents with the masses range 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 UV Visible spectrophotometer. These studies reveal that the adsorption is maximum at 0.1g of adsorbent dosage<sup>9</sup>.

### Effect of solution pH



**Fig. 5. Effect of initial pH on percentage dye removal, AO-7 concentration 100mg/L and 303 K**

The dye removal is affected by the solution pH and the effect has been shown in (Fig. 5). It is observed that the adsorption capacity decreases when pH increases. The maximum adsorption of AO7 occurs at pH 4. This is ascribed to the reason that in the aqueous medium the functional groups on the surface are protonated in acidic medium causing more electrostatic interactions between the protonated adsorbent and the anionic dye. As the pH increases, the number of active sites which are protonated decreases, and hence the adsorption of anionic dye also decreases.

A positively charged site on the adsorbent favors the adsorption of anionic dyes due to electrostatic attractions.

### 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 4.0. The dye uptake capacity at different time intervals of 10 minutes, and tested up to 240 minutes. It is observe from these testes that at 120 minutes of contact time, the removal efficiency of this adsorbent material is more than 90%. The optimum value of contact time is 120 minutes.

### Adsorption isotherm

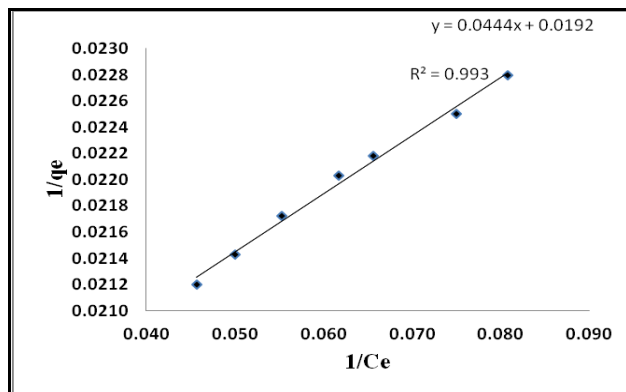
The Freundlich, Langmuir and Temkin isotherm models have been applied for this system at temperature 303K and parameters are calculated accordingly.

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. 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  $Q_0$  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. The values of  $q_0$  and  $b$  are calculated from the intercept and slope respectively and the results are presented in Table 1.



**Fig. 6. Langmuir adsorption isotherm for the adsorption of AO-7 onto nano composite**

**Table 1: Adsorption isotherm parameters for the adsorption of Acid orange-7 dye onto nano composite**

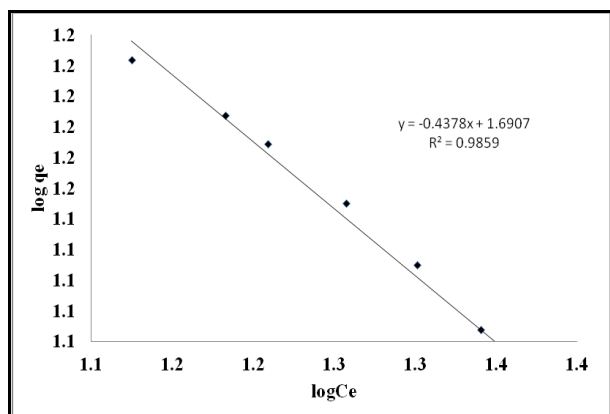
Langmuir			Freundlich			Temkin	
Qo	b	R <sup>2</sup>	KF	n	R <sup>2</sup>	B	R <sup>2</sup>
2.08	0.4324	0.9930	2.0169	0.3156	0.9859	17.002	0.9921

The data related to the equilibrium fit very well with the Langmuir adsorption isotherm models. The  $R^2$  factor is 0.9915 which suggests that Langmuir isotherm provides a good fit to the isotherm data<sup>13</sup>. The value of  $R_L$ , the separation factor is 0.0226 and indicates that this adsorption is favourable adsorption with monolayer formation of Acid orange-7 on the new nano composite adsorbent material.

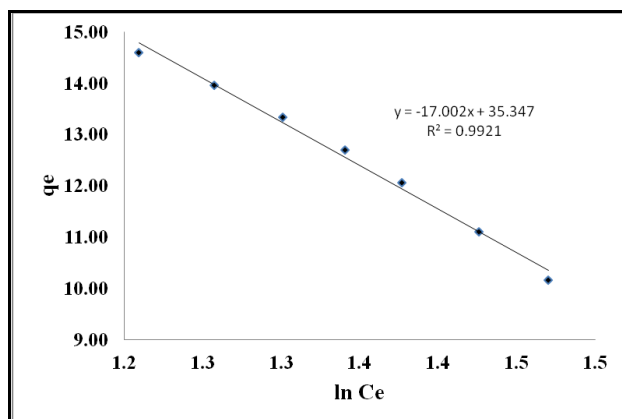
The Freundlich equation is used to determining the applicability of heterogeneous surface energy in the adsorption process. The empirical Freundlich equation is expressed as:

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

Where  $K_F$  is measure of adsorption capacity ( $\text{mg g}^{-1}$ ) 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 ( $1/n > 1$ )<sup>11</sup>. The plots of  $\ln q_e$  Vs  $\ln C_e$  showed good linearity ( $R^2$  0.9859) Fig.7. 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  $K_F$  2.0169 indicates higher affinity for Acid orange-7 in the adsorption process. The results clearly infer that both of these models are well suited for the adsorption of Acid orange-7 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 Acid orange-7 forms a monolayer upon the surface of nano composite activated carbon material.



**Fig. 7. Freundlich adsorption isotherm for the adsorption of AO-7 onto nano composite**

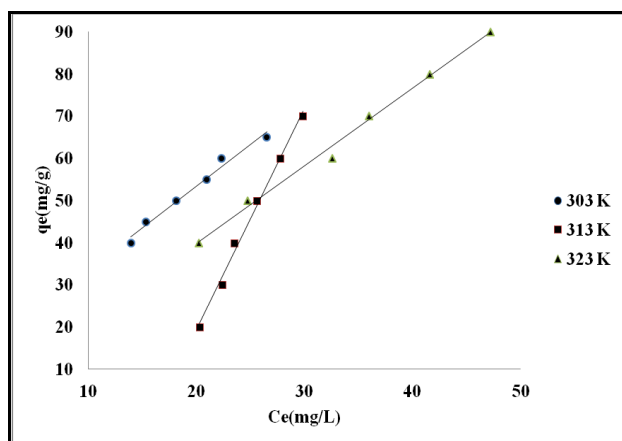


**Fig. 8. Temkin adsorption isotherm for the adsorption of AO-7 onto nano composite**

Temkin isotherm model (Fig. 8) 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  $q_e$  ( $\text{mg g}^{-1}$ ) and  $C_e$  ( $\text{mg L}^{-1}$ ) are the amount of adsorbed dye per unit weight of adsorbent and unadsorbed dye concentration in solution at equilibrium respectively. Therefore, a plot of  $q_e$  versus  $\ln C_e$  enables one to determine the constants  $A$  and  $B$ . The value for constant  $B$  is  $17.002 \text{ J mg}^{-1}$  is heat of adsorption and shown in Table 1. The correlation coefficient of 0.9921 obtained shows that adsorption of AO7 also follows the Temkin model.



**Fig. 9. Adsorption isotherm plot of  $C_e$  vs  $q_e$  of AO-7 at 303 K, 313 K and 323 K**

In order to investigate the effect of temperature on the uptake of Acid orange-7, the process was carried out at different temperatures ranging from 303K, 313K and 323K (Fig. 9). For the equilibrium concentration of the adsorbate ( $C_e$ ) and the amount of dye adsorbed ( $q_e$ ), various parameters of adsorbent is better at higher temperatures as the adsorbed amount of Acid orange-7 increase with rise in temperature. The changes in the dye removal expected during the process require the values of thermodynamic parameters which are calculated using the following equations.

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

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

The Gibbs free energy changes ( $\Delta G^0$ ) are calculated from above the equation, and the values of  $\Delta G^0$ ,  $\Delta H^0$ , and  $\Delta S^0$  for the adsorption of Acid orange-7 onto nano composite at 303K, 313 K and 323 K are given in Table 3. The negative values of  $\Delta G^0$  indicate the spontaneous nature of the adsorption process. The magnitude of  $\Delta G^0$  also increase with increasing temperatures indicate that the adsorption is more favorable at higher

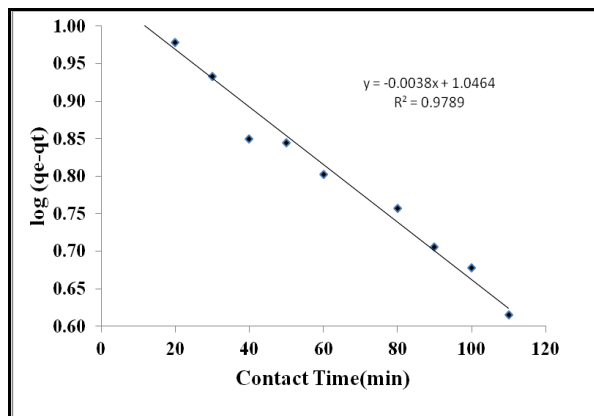
temperatures. The negative values of  $\Delta H^\circ$  indicate that the exothermic nature of the adsorption of Acid orange-7 onto nano composite.

**Table 3: Thermodynamic parameters for the adsorption of Acid orange-7 dye onto nano composite**

Conc. (mg/l)	T (K)	$K_d$	$\Delta G^\circ$ (J mol <sup>-1</sup> )	$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )
20	303	18.2	-1644.3	64.42	-21.8
	313	19.2	-2389.4		
	323	20.1	-3022.8		
40	303	3.8	-1172.5	55.08	-14.7
	313	4.7	-1463.2		
	323	6.4	-1913.3		
60	303	3.2	-944.7	38.57	-11.0
	313	3.9	-1238.1		
	323	5.1	-1771.7		
80	303	2.6	-552.5	22.14	-6.3
	313	3.0	-734.4		
	323	3.5	-1033.6		
100	303	2.4	-421.6	14.27	-3.2
	313	2.8	-653.3		
	323	3.2	-940.7		

## Kinetic studies

### Pseudo first order kinetic model

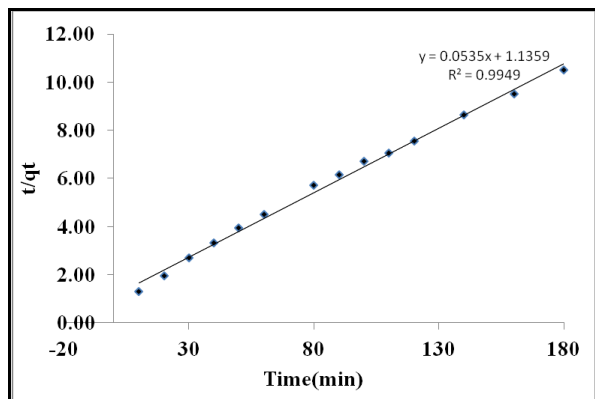


**Fig. 10. Pseudo first order for the adsorption of AO-7 onto nano composite**

The rate of removal of AO7 has been observed as a function of time (Fig. 10). Lagergren proposed a pseudo-first order kinetic model as given below

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

Where  $k_1$  (min<sup>-1</sup>) is the rate constant of the pseudo-first order adsorption and  $q_t$  is the adsorption capacity at time 't' (mg g<sup>-1</sup>). The rate parameters  $k_1$  and  $q_e$  can be directly obtained from the intercept and slope of the plot of  $\log(q_e - q_t)$  vs time t. The correlation value of  $R^2$  is 0.9789 for 100 mg L<sup>-1</sup> and the equilibrium constant  $k_1$  is  $1.65 \times 10^{-3}$  s<sup>-1</sup>. The observed experimental results reveal that this adsorption phenomenon follows the pseudo-first order kinetics.



**Fig. 11. Pseudo second order for the adsorption of AO-7 onto nano composite**

The pseudo-second-order kinetic model (Fig. 11) is based on the assumption that the sorption follows second order chemisorption<sup>5</sup>. Pseudo-second-order kinetic model is given as

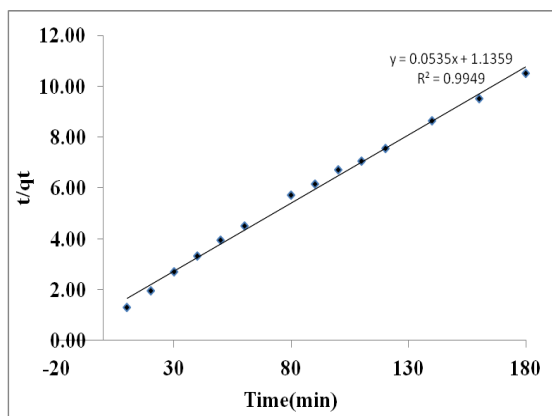
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Where  $k_2$  [ $\text{g mg}^{-1} \text{min}^{-1}$ ] is the rate constant of the pseudo-second order adsorption and  $q_t$  is the adsorption capacity at time 't' ( $\text{mg g}^{-1}$ ). The correlation value of  $R^2$  is 0.9949 for  $100 \text{ mg L}^{-1}$  and the equilibrium constant  $k_2$  is  $2.5198 \times 10^{-3} \text{ s}^{-1}$ . The correlation constant of pseudo second order is higher than the first order and hence second order model fits better than Lagregren model.

Elovich model has been applied to evaluate the possibility of chemisorptions by the formula

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

The plot between  $q_t$  versus  $\ln t$  (Fig. 12) is a straight line. The values are given in Table 2. The correlation coefficient is found to be 0.9533.



**Fig. 12. Elovich adsorption of dye onto AO-7 composite**

**Table 2: Kinetic parameters for the adsorption of Acid orange-7 dye onto nano composite**

Pseudo first order		Pseudo second order		Elovich		
$k_1$	$R^2$	$k_2$	$R^2$	$\alpha$	$\beta$	$R^2$
$1.65 \times 10^{-3}$	0.9789	$2.5198 \times 10^{-3}$	0.9949	42.24	0.0643	0.9533



## 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 Acid orange-7 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 are contributed only by the nano particles of MgO coatings. The batch mode of experiments show that the adsorption of Acid orange-7 over modified adsorbent of *delonix regia* is dependent on pH, adsorbent concentration, contact time and temperature. The results confirm that maximum dye removal can be accomplished. The Freundlich, Langmuir and Temkin isotherms are aptly fit the data well. The kinetic studies reveal that the adsorption data is better fitted with pseudo second order kinetic model than Lagergren kinetic model. The adsorption capacity of this modified nano composite activated carbon is higher than the activated carbon.

## References

1. Syed Shabudeen PS, Venckatesh R and Pattabhi S, Preparation and Utilization of Kapok Hull Carbon for the Removal of Rhodamine-B from Aqueous Solution, E-Journal of Chemistry, May 2006, 3(11), 83-96
2. O'Neil C, Hawkes F, Hawkes DL, Lourenco ND, Pinheiro HM and Dele'e W. Colour in textile effluents D sources, measurement, discharge consents and simulation: a review, Journal of Chemical Technology, 1999, **74**, 1009-1018.
3. Hameed BH, Ahmad AL, Latiff KNA, Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust. Dyes Pigments. 2007, 75, 143-149.
4. Quan X, Liu X, Bo L, Chen S, Zhao Y, and Cui, Regeneration of acid orange 7-exhausted granular activated carbons with microwave irradiation, Water Research, 2004, 38(20), 4484-4490.
5. Indhumathi P, Syed Shabudeen PS, Saraswathy CP, The identification and Characterization of activated carbon. International Journal of Advanced Engineering Technology, 2011, 2(3) 78-84.
6. Khaled A., Kapoor P N and Klabunde KJ, Nanocrystalline metal oxides as new adsorbents for air purification, Nano structured Materials, 1999, 11, 459-468.
7. Hristovski K, Baumgardner A and Westerhoff P, Selecting metal oxide nanomaterials for arsenic removal in fixed bed columns: from nanopowders to aggregated nanoparticle media, Journal of Hazardous Materials, 2007, 147(1-2), 265-274.
8. Hu J, Lo IMC, and Chen G, Fast removal and recovery of Cr(VI) using surface-modified jacobsite (MnFe<sub>2</sub>O<sub>4</sub>) nanoparticles, Langmuir, 2005, 21(24), 11173-11179.
9. Daniel S Syed shabudeen PS, Sequestration of carcinogenic dye in waste water by utilizing an encapsulated activated carbon with nano MgO, International Journal of Chem Tech Research, 2014-2015, 7(5), 2235-2243.
10. Gupta V. K, Mittal A, Gajbe V, and Mittal J, Removal and recovery of the hazardous azo dye acid orange 7 through adsorption over waste materials: bottom ash and de-oiled soya, Industrial and Engineering Chemistry Research, 2006, 45(4), 1446-1453.
11. Ozacar M, and Sengil IA, Adsorption of metal complex dyes from aqueous solutions by pinesaw dust, Bioresources Technology, 2005, 96, 91-95.
12. Senthil Kumar P and Kirthika K, Equilibrium and Kinetics studies of Ni onto bael leaf Powder, Journal of Engineering Science and Technology, 2009, 4, 396.
13. Srivastava R, and Rupainwar DC, Removal of hazardous triphenylmethane by mango bark Powder, Indian Journal of Chemical Technology, 2011, 18, 67.

\*\*\*\*\*