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Studies on characterization and removal of methylene blue with *Delonix regia* plant litters activated carbon encapsulated nano metal oxide

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Abstract

An advanced adsorbent material prepared by encapsulating nano-metaloxide on an activated carbon of *Delonix regia* plant litters was tested for its efficiency and superiority as an improved, advanced activated carbon material. It was subjected to modern instrumental techniques to evolve its morphology and its structure by FTIR, SEM, TEM, XRD, EDAX and BET studies. The size of MgO particles was in the range of 20nm-25 nm. The surface area of nano composite was 632 $m^2 g^{-1}$. Experimental results, based on batch mode of experiments, indicated that the adsorbent could remove 90% dye for the adsorbent dosage of 100 mg, at pH 7.0 and contact time of 120 min. The adsorption equilibrium data were well correlated for both, Langmuir and Freundlich isotherms. The monolayer adsorption capacity Qo was found to be 14.425 mg g^{-1} for the composite. The kinetic adsorption data fitted the pseudo first order modeled by Lagergren and also intra particle diffusion. Removal efficiency of the composite adsorbent was higher than the uncoated adsorbents. Regeneration of exhausted adsorbent showed considerable improved variation in comparison to normal activated carbon materials.

Key words

Delonix regia, Nano metal oxide composite, Scanning Electron Microscopy, X-Ray Diffraction

Introduction

All the flow process industries are based on certain synthetic chemicals which are used in textiles, paper and plastic industries and consume various types of dyes to colour the materials in order to increase their marketing. This will subsequently generate a large volume of effluent and pollute the surface water bodies and affect the environment and cause sudden depletion in aquatic living organisms (Banat *et al.,* 1996) namely fish, prawn, snails etc,. Several methods have been adopted for removal of dye in which adsorption has given the best possible results (Jain and Gupta, 2003) and activated carbon has been cited by US Environmental Protection Agency as one of the best dye removers (Derbyshire *et al.,* 2001). However, the cost factor (Babel and Kurniawan, 2003) of commercial activated carbon limits its usage. This leads to investigation of various non-conventional adsorbents for dye removal which have been reported. Carbon prepared from agricultural waste such as bagasse (Valix *et al.,* 2004) coir pith (Namasivayam and Kadirvelu, 1994) silk cotton waste or Kapok Hull (Syed Shabudeen *et al.,* 2006), *Delonix regia* (Syed Shabudeen and Daniel, 2013) and activated carbon from industrial wastes such as waste tyres (Nakagawa *et al.,* 2004), waste news paper (Okada and Yamamoto, 2003), waste carbon slurries (Jain and Gupta, 2003) has also been used for dye removal. Solid wastes such as fly ash and red mud are also used as low cost adsorbents for dye removal (Gupta *et al.,* 2003; Wang *et al.,* 2005) and saw dust (Garg *et al.,* 2004), activated fly ash, (Rastogi, 2008), palm kernel fiber (El-Sayed, 2011) silkworm exuviae (Chen, 2011), carbon nano tubes (Madrakiana *et al.,* 2011) graphene (Liu, 2012) has also been utilized. These dyes are considered to be the major water pollutants and are toxic and even, carcinogenic due to bioaccumulation and pose serious threat to aquatic organisms (OÕNeill and Hawkes, 1999).

Cationic dye, Methylene Blue is commonly used for dying cotton and silk (Deng, 2011) fibers. After dying, fibers are washed in fresh water bodies to stabilize the colours. During this process, excess colour present in the textile fibers is dissolved in water bodies. This results in surface water pollution. Methylene Blue and its decomposed residues cause diarrhea and jaundice, the most feared water borne viral diseases. Only limited work is available with composite material used as adsorbent. Moreover adsorption technique has proved its efficiency over other dye removal methods. After the advent of nanotechnology, nano materials have been incorporated (Hu *et al*., 2010) onto the adsorbent or the activated carbon are made into carbon nano tubes (Zhang *et al*.,2010). The nano composites have proved for their large surface area (Alexander *et al*., 2012), higher dye removal capacity (Ranjithkumar *et al*., 2014) and capacity of reusable (Yuvaraj Haldorai *et al*., 2014). So, an attempt was made to enhance dye removal capacity of activated carbon prepared from *Delonix regia* by incorporating nano particles. *Delonix regia* is a botanical name of a flowering plant 'Flame tree' which originated in Madagasker and grows worldwide. It is commonly known as 'Gulmohar' in Hindi. It is a popular street tree and due to its wide spread canopy and litters from leaves, flowers and thick pods form solid wastes which are used to prepare the precursor of the composite adsorbent.

Materials and Methods

Preparation of composite of nano MgO encapsulated *Delonix regia* adsorbent : Dried *Delonix regia* pods were cut into small pieces and then activated with concentrated sulphuric acid for 48 hrs. Carbonized material was washed with excess quantity of distilled water and dried at 120°C for 1 hr and the material obtained was soaked in 5% sodium bicarbonate solution and allowed to stand overnight to remove any residual acid. This activated mass was then thoroughly washed with distilled water and dried. This carbonized material was kept at 700 ºC for 60 min in a tubular furnace under controlled nitrogen flow. The resulting carbons were ground in a ball mill, washed with pure water and finally dried at 120 ºC. The dried powder was sieved into various sizes (Range from 70-150 BSS).

The feasible method to encapsulate nano metal oxide was attempted by chemical method in which 6 g of $MgCl_2$ and 2 g of surfactant SDS (Sodium dodecyl sulphate) was dissolved in 100 ml of distilled water and taken in an additionally 1.6 g of NaOH (0.4N) in 100 ml of distilled water taken in a separate beaker. Magnesium oxide solution was slowly poured into the NaOH beaker. This mixture was slowly and constantly stirred by a magnetic stirrer at pH 11 for about 2 hrs. A white $Mg(OH)_2$ precipitate was formed and it was washed thoroughly with distilled water. This $Mg(OH)_2$ precipitate was dried at 120 ºC for 2 hrs and calcined at 800ºC for 5 hrs in an Muffle furnace and finally granular nano MgO was prepared.

Initially, 0.02 g MgO was dispersed in 50 ml methanol and using magnetic stirrer, this mixture was stirred well for 2 hr. During this process the volume of methanol was maintained at 50 ml mark. Then 1g of activated pods of *Delonix regia* carbon particles of mesh size 150 BSS were added to dispersed MgO solution and stirring was continued for another 2 hrs. Finally, nano MgO encapsulated carbon particles was filtered out and washed with methanol for 2-3 times. It was then dried at 60^0C in a hot air-oven and then kept at 400^0C under nitrogen atmosphere.

Characterization technique : Fourier Transform Infrared Spectroscopy (FT-IR, Thermo NICOLET Corporation, 5DX-FT-IR) was made at ambient temperature with 8 cm^{-1} resolution. Powder X-ray diffraction (XRD) analysis was performed on Xpert PROPA Nalytical PW3040/60'X'PertPRO with Cu-Kα X-ray radiation source (λ = 1.5418 Å). Morphological characterization of the adsorbent was performed employing a SEM Hitachi S-3000H scanning electron micro-scope (SEM, max magnification of 1.5 × 105) equipped with an Everhardt Thornley secondary electron detector (ET-SED). TEM image of nano MgO was recorded using the selected area electron diffraction (SAED) technique. Specific surface area (BET) of the adsorbent before activation, after activation and nano/AC composite were determined by Nitorgen physisorption at 25 ºC. EDX spectrum (Thermo Electron Corporation, USA) was collected at an accelerating voltage of 20.0 kV and magnification of ×700. Brunauer-Emmett-Teller (BET) surface area and pore volumes (Barrett-Joyner Halenda, BJH method) were evaluated by using nitrogen adsorption-desorption isotherms measured at 77 K on an ASAP 2020 V3.00H Micrometrics apparatus. Prior to adsorption, approximately 50.0 mg of solid was placed in cell and evacuated at about 250 °C for 3 hr. Thermal stability of nano metal oxide sample was tested by thermo-gravimetric analysis (TGA), with a Q 500 instrument from Mettler, over a temperature range of 25ºC-1000°C under N_2 flux at a heating rate of 10 °C min^{-1}.

Preparation of methylene blue solutions: The value of absorbance for different concentration of the dye solution was measured using Double Beam UV Spectrophotometer at maximum wavelength of 665 nm. As methylene blue dye is water-soluble and basic in nature, a stock solution of 1000ppm was prepared by using double distilled water. This dye solution was taken for adsorption studies with normally activated and nano metal oxide encapsulated adsorbent prepared from the pods of *Delonix regia*. Dye was procured from NICE CHEMICALS Pvt. Ltd, India. Experimental solutions were prepared by diluting stock solution of MB with distilled water to the desired concentration level. The pH of test solution was varied by adding dilute HNO_3 or NaOH.

Results and Discussion

Transmission Electron Microscopy analysis revealed that the synthesized MgO particles were crystalline, hexagonal and

on nano meter scale measure about 20-100 nm. Energy Dispersive X-ray spectrum show that the synthesized product was mainly composed of Mg, O and their respective atomic content was very high. It confirms the high purity of synthesized material without any other impurities like SDS etc. EDX spectrum of nano MgO encapsulated activated carbon composite clearly indicated the presence of carbon with MgO nanoparticles without any other impurities.

Thermal Gravimetric Analysis curve indicated two weight loss regions, the first one correspond to the loss of adsorbed solvents molecules and the second weight region above 330 ºC attributes to the decomposition of $Mg(OH)_2$ followed by crystallisation of MgO particles which is in good agreement with differential thermal analysis.

Fig. 1 a, b shows FTIR spectrum of both activated carbon and the composite, the peaks around 3300 cm^{-1} and 3900 cm^{-1} showed the presence of O-H stretching vibrations due to the existence of surface hydroxyl group and chemisorbed H_2O molecules. Peaks between 1600 cm^{-1} and 3000 cm^{-1} were due to C-H bonds. The band at 1700 cm^{-1} in case of composite was due to C=O stretching which was absent in case of activated carbon which is ascribed to coupling of anti symmetrical vibration modes of Oxygen atoms (Moreno-Castilla *et al.,* 2000). The peak at 1060 cm^{-1} for composite represents C-O of oxygen related groups present in the adsorbent (Abdel-Nasser and El-Hendawy, 2003).

Morphological studies based on SEM of samples of adsorbent before activation, after activation and composite material exhibited porous nature which resembles caves with deep depth and is shown in Fig. 2. SEM morphological image of composite material (Ning Wanga *et al.,* 2013) revealed that nano magnesium oxide particles were deposited inside the microphores structure and formed extra new pores on AC which formed an extra surface area for adsorption (Gholamreza Moussavi). X-ray diffraction pattern (Fig. 3) clearly proved that the synthesized material was MgO of hexagonal phase and all the peaks present in spectra were in with reported JCPDS data (JCPDS 89-9746). No impurity peak was observed in this pattern (Richards *et al.,* 2001), which clearly implies hexagonal phase MgO could be obtained from the above synthetic route. EDAX studies (Fig. 4) of carbon coated with MgO showed only three peaks corresponding to C, Mg and O. From the particle size analysis studies, it evident that the particles of MgO were in the range of 20nm-25 nm.

Adsorption reactions for adsorbents were carried out using 100 ml solution containing 100 mg l^{-1} of dye and 0.1g of adsorbent at room temperature with pH adjusted to 7.0. The dye uptake capacity was measured at different time intervals, 10 min until 240 min. The results of analysis showed that after around 180 min the adsorbents removed 90% of the dye from solution. Therefore, the optimum value was considered to be 120 min, but for guarantee the maximum adsorption and a complete equilibrium condition, the subsequent experiments were performed with 180 min of contact time. The experiment carried out for various adsorbent dosage and the optimum condition was fixed at 100 mg of adsorbent.

The pH of aqueous solution is an important factor that affects dye adsorption process through changing the surface charge of an adsorbent and ionization behavior of adsorbent and dye (Qada, 2006). The effect of solution pH on MB removal by adsorbents showed that the dye removal efficiency increased with increasing pH in the acidic range and reached maximum at pH 7.0 and then decreased in the alkaline range. It was also seen that the dye removing capacity of composite 93% which was much higher than AC and raw carbon.

Linear plot of C_e/q_e Vs C_e (Fig. 6 a) showed that the adsorption followed Langmuir isotherm model. The values of monolayer capacity 'Q_0' and Langmuir constant 'b' was evaluated from the intercept and slope of these plots by using graphical techniques.

The essential features of Langmuir isotherm may be expressed in terms of equilibrium parameter R_L, which is a dimension less constant and referred as separation factor or equilibrium parameter (Rajeswari and Subburam, 2003). $R_L=1/(1+bC_0)$, where C_0 is the initial concentration and 'b' is the constant related to the energy of adsorption (Langmuir constant). The values of R_L indicate the nature of isotherm. If the conditions are $R_L>1$, $R_L=1$, $0<R_L<1$ and $R_L= 0$ are unfavorable, linear, favorable and irreversible respectively. The value of monolayer capacity (Qo) between 8.67 mg g^{-1} and 14.245 mg g^{-1} and calculated R_L value between 0.0612 and 0.0965 from the results showed that dye uptake followed the Langmuir adsorption isotherm and was favourable. Moreover, the correlation coefficients (R^2) was between 0.9848 and 0.9974 which confirms that the novel nano metal oxide encapsulated adsorbent followed Langmuir adsorption isotherm.

Based upon the experimental values, Freundlich adsorption isotherm plot was obtained by plotting log qe Vs log C_e and shown in Fig. 6b. The slope and intercept of this linear portion of isotherm plots were determined by adopting graphical methodology. These slope values indicated adsorption intensity (n) between 0.452 and 0.485 and the intercept values between 5.604 and 12.705 indicated an idea about adsorption capacity K_F. It was observed that the adsorption capacity of the adsorbent for removal of methylene blue increased in the following order: carbon<activated carbon<nano/composite.

As 1/n is a measure of adsorption intensity, if n = 1 then that the partition between the two phases was independent of the concentration. If the 1/n value was below 1, it indicates normal adsorption. On the other hand, 1/n being above 1 indicates

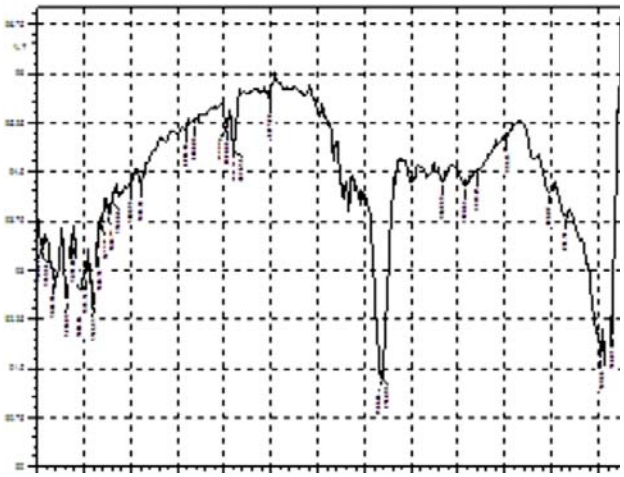

Fig. 1 (a) : FTIR spectrum of activated carbon

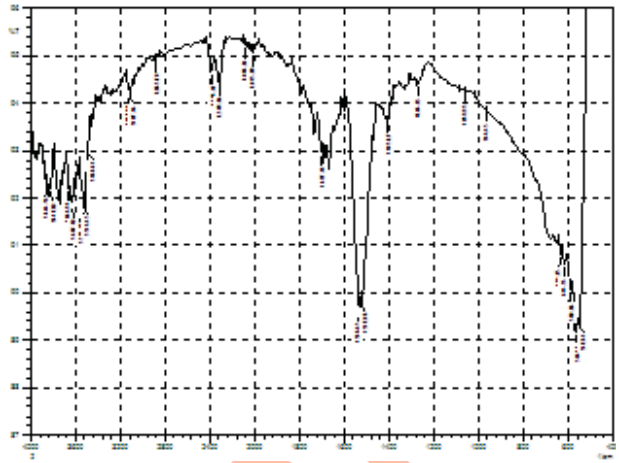

Fig. 1 (b) : FTIR spectrum of nano/composite

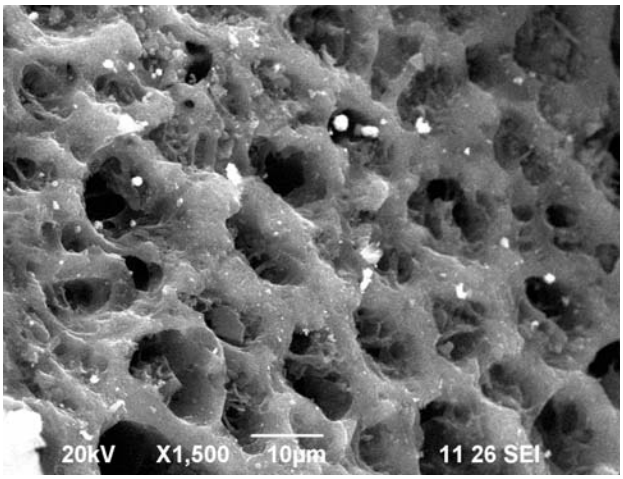

Fig. 2 : SEM images of nano MgO / AC composite

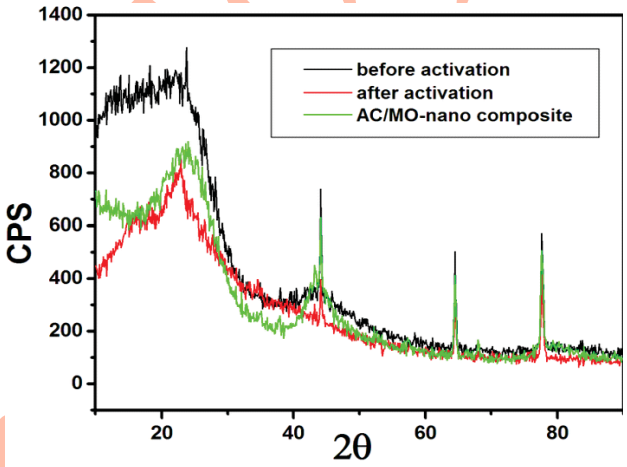

Fig. 3 : XRD patterns of the adsorbents C, AC and composite

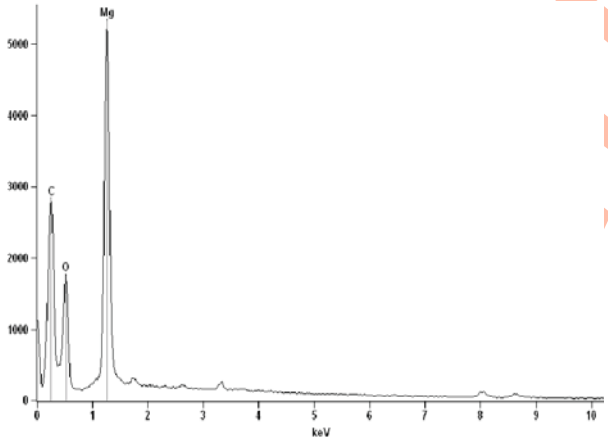

Fig. 4 : EDAX of nano MgO/AC composite

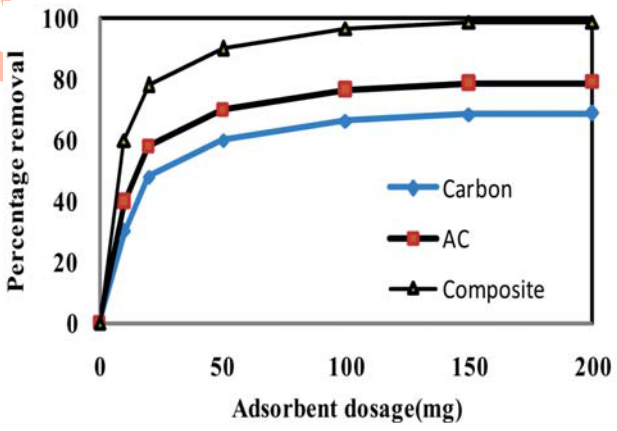

Fig. 5 : Effect of adsorbent dosage on methylene blue adsorbed by C, AC and composite (Adsorbent 100 mg, room temperature 300K and pH 7.0).

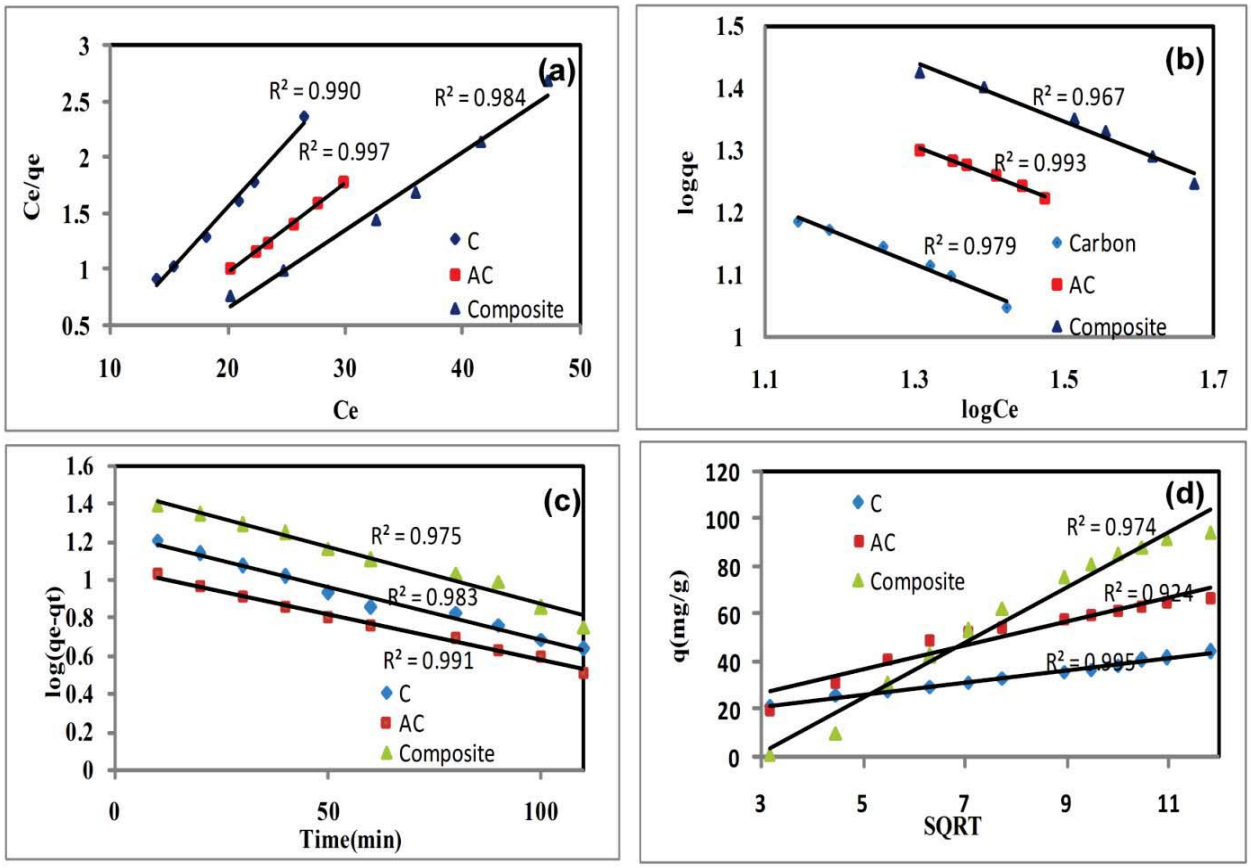

Fig. 6 : Values of methylene blue adsorbed by C, AC and composite by (a) Langmuir isotherm, (b) Freundlich isotherm, (c) Lagergren pseudo first order kinetics isotherm and (d) Intra particle diffusion isotherm

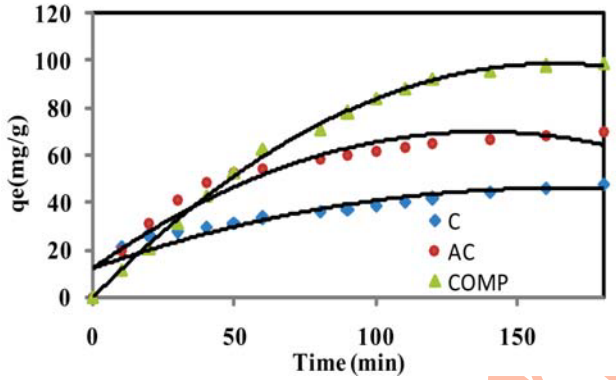

Fig. 7 : Effect of contact time on adsorption capacity of MB adsorbed by C, AC and Composite

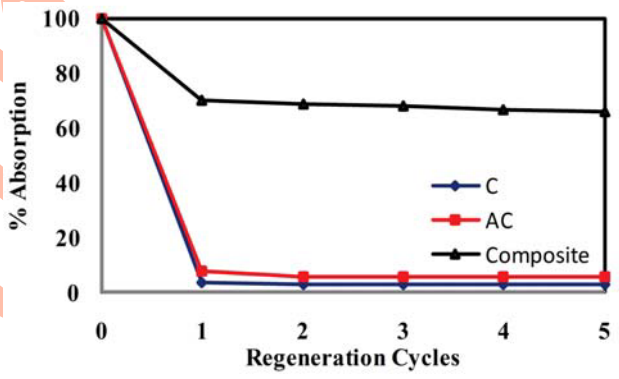

Fig. 8 : Adsorption capability of MB in each of five regeneration cycles with C, AC and Composite

cooperative adsorption (Ozacar and Sengil, 2005). It is generally stated that the value of 'n' in the range of 2 to 10 represents good adsorption isotherm. It was also observed that the 'n' values of the adsorbent for dye at various temperature and particle sizes were found out and this value ranged from 2 to 10, which confirmed that the activated carbon was favourable for Freundlich isotherm. The experimental data were attempted to fit into Freundlich adsorption isotherms, and it was efficiently and most effectively fitted. It clearly indicated that the system followed Freundlich adsorption isotherm model and the adsorbent's surface under study was heterogeneous. The correlation coefficient, evolved with graphical techniques, was found to be between 0.9713 and 0.9972.

Table 1 : Adsorption kinetic data for methylene blue dye removal with various particle sizes, equilibrium time (180 min)

Particle size (BSS mesh No.)	Dye conc. (mg 100ml^{-1})	q_e	g x10^{-5}	Kad	K_P	D_PX10^{-10}
70	5	0.45	9.00	0.0216	0.033	
	10	0.83	8.30	0.0173	0.074	
						0.164
	15	1.29	8.60	0.0188	0.097	
	20	1.66	8.30	0.0255	0.102	
90	5	0.48	9.60	0.017	0.035	
	10	0.92	9.20	0.019	0.066	
	15	1.35	9.00	0.028	0.098	
						0.109
	20	1.70	8.50	0.026	0.135	
150	5	0.48	9.6	0.018	0.036	
	10	0.93	9.3	0.018	0.067	
						2.58
	15	1.38	9.2	0.030	0.105	
	20	1.74	8.7	0.026	0.138	

These values exhibited some deviation from linearity and tried to form curves as clearly indicated in the graphs under observations. The reason for this behaviour was that the initial curve portion represented formation of monolayer followed by intra particle diffusion at later stages and final plateau portion indicated saturation of the adsorption process. It was summarized that methylene blue followed Freundlich adsorption isotherm model, the derived 'n' value being ranging from 1 to 10. The graphical studies showed small deviation from linearity, the mechanism of adsorption followed formation of monolayer, Intra particle diffusion and saturation in a favourable pattern.

The adsorption kinetic study is quite significant in wastewater treatment as it describes the rate of solute uptake, which in turn controls the residence time of adsorbate uptake at the solid-solution interface (Lakshmi Narayanan Rao *et al*., 1994). Dosage study is an important parameter because it determines the capacity of adsorbent for a given initial concentration of dye solution. In the present study, the kinetics of adsorption system was studied by plotting the amount of dye adsorbed on the adsorbent with time for different adsorbent dosages at constant initial concentration (100mg l^{-1}) on different carbonaceous materials. In all the experiments, from the nature of the curves and smoothness of the curves for dye adsorption, it was found that the process of adsorption was continuous and involved either monolayer formation on the adsorbent surface or monolayer coupled with other mechanism, predominantly intra particle diffusion (Ismail *et al.,* 2013). Since with increase in active adsorption sites increased with adsorbent dosage, the amount of dye adsorbed increased with sorbent dosage. High availability of adsorption sites with higher adsorption dosage had positive effect on the initial rate of dye uptake. Lagergren plot of dye is presented in Fig. 6c. The linear plot of log (q_e - q_t) Vs t showed that adsorption followed pseudo first order rate expression given by Lagergren.

The values of pore diffusion coefficients were calculated on the particles size for dye and these inferences were compared with the results and it was inferred that pore diffusion was not the rate-limiting step. Based upon different ideas available in literature, it is possible to determine the nature of adsorption process with reference to pore diffusion coefficient. If the values fall between 10^{-11} to 10^{-13} (cm^2/sec), the process is said to be controlled due to intra particle diffusion coefficient (Namasivayam and Kadirvelu, 1994), but the dye system in the present study showed values within the limit (10^{-11}cm^2/sec). It confirmed that the process was controlled due to intra particle diffusion (Table 1).

Intra particle diffusion rate constant can be given as follows, $q = K_p T^{½}$; K_p values for the adsorption of the dye are presented in the (Table 1) and the plot is given in (Fig.6 d). The rate constant for intra particle diffusion K_p was calculated from the slope of the linear equation by q (mg g^{-1}) Vs $T^{½}$ (sec). The Kp value generally increases withincrease of dye concentration (Fig. 1) and can be related to concentration diffusion.

Initial adsorption coefficients increased with increase in initial dye concentration and therefore it was concentration dependent. From the results, an overall examination of effect of dye concentration on rate constant K_{ad} described the mechanism of adsorption. In case of strict surface adsorption, a variation of rate should be proportional to concentration. The relationship between initial solute concentration and rate of adsorption was not linear. This was due to limitation caused by pore diffusion of adsorption. It was concluded that pore diffusion also limited the overall rate of adsorption.

To evaluate the effectiveness of three adsorbents, the plots for the amount of methylene blue adsorbed (q_e), as a function of time, is presented in Fig. 7. Initial adsorption was quick for all adsorbents, due to adsorption of molecule on the external

surface of carbon particles. The process was slow adsorption process due to the fact that the dye molecules got into the porous structure of the adsorbent. Nano composite showed fast adsorption because it had large surface area.

(Fig. 8) shows percentage adsorption capacity of C, AC and composite in each of the five regeneration cycles. It was seen that nano encapsulated composite had higher regeneration efficiency as compared to C and AC, implying that the presence of MgO nano particles was beneficial for achieving high regeneration efficiency by hydrogen peroxide. The adsorption capacity of composite decreased as the number of regeneration cycle increased. However 70% of regeneration efficiency of the composite at fifth cycle was still achieved.

The results of this study showed that nano magnesium oxide encapsulated compostite of D*elonix regia* could be successfully used for removal of methylene blue dye from the aqueous medium. Desorption experiments showed that even after five adsorption-desorption of cycles, the composite could be reused without significant loss of its initial properties. The adsorption capacity of nano composite was higher than that of normally activated carbon.

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