Active manganese oxide: a novel adsorbent for treatment of wastewater containing azo dye

S. Chakrabarti, B. K. Dutta and R. Apak

ABSTRACT

A new variety of active manganese oxide was prepared, characterized, and tested for its potential of adsorbing Congo Red, a dis-azo dye, from aqueous solutions. Both equilibrium and kinetics were investigated over different values of process parameters such as temperature (25–45°C), adsorbent loading (0.4–0.6%), initial dye concentration (50–500 mg/L), presence of salts (sodium sulphate, 500 mg/L) and the oxygen content (MnO$_x$, x = 1.2, 1.33 and 2) of the adsorbent. The equilibrium adsorption data were fitted to Langmuir and Freundlich isotherms. Langmuir adsorption capacity of the sorbent (x = 1.33) for *Congo Red* was 38.6 mg/g at room temperature which is substantially higher than those for commercial manganese dioxide, red mud, coir pith, activated carbon, and fly ash. The kinetic data were best interpreted using a pseudo-second order model. The results show that the active manganese oxide used in this work removes the dye by reversible adsorption and has the potential for practical use for remediation of textile industry effluents.

Key words | adsorption, Congo red, dye removal, effluent treatment, manganese oxide

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INTRODUCTION

Wastewater from textile, paper, leather and allied industries sometimes contains residual azo dyes which are not easily biodegradable and produce carcinogenic amines on degradation. Though some countries imposed ban on the use of selected azo dyes (Geisberger 1997), these dyes are still used in many others and development of suitable techniques for their removal from wastewater still remains a challenging problem.

Conventional coagulation and activated sludge processes are not always effective for removal of these dyes for their high water solubility and low biodegradability (Crini 2006). Adsorption is an effective and clean technique for this purpose. Commercial activated carbon is the most commonly used adsorbent but it is relatively expensive (Jain *et al.* 2003). Activated carbon prepared from various cheap raw materials including rice husk (Singh & Srivastava 2001), jackfruit peel (Inbaraj & Sulochana 2002) and bagasse pith (McKay *et al.* 1987) has also been found suitable for the

removal of dyes and other contaminants from wastewater. Adsorption of dyes from wastewater using sulphonated coal (Mittal & Venkobachar 1996) and fly ash (Mohan *et al.* 2002) has been reported in the literature.

Manganese dioxide is a well-known solid-phase oxidant that exists in different forms. Mn-oxides in soils and sediments participate in a wide variety of redox as well as cation-exchange reactions. For example, *birnessite* is capable of oxidizing Se(IV), Cr(III) and As(III) (Post 1999). Degradation of toxic organics such as atrazine and hydroxylamines has been reported by Cicchi *et al.* (2001). Zhang *et al.* (2008) observed that manganese dioxide formed *in situ* had a significantly higher adsorption capacity for several hazardous aromatics. There are a few literature reports on the reactivity of naturally occurring Mn(III/IV) oxides towards organic substances (Ulrich & Stone 1989) and to dye pollutants (Ge & Qu 2003). Liu & Tang (2000) made a detailed investigation on oxidative

decoloration of direct red F3B dye using one such variety of manganese oxide.

The present work originated from our observation that active manganese oxide, prepared by us, had a considerably better capacity to chemisorb SO_2 gas compared to technical grade MnO_2 (Basu *et al.* 1989). In the mentioned work, the reaction of sulphur dioxide on the surface of active manganese oxide ($MnO_{1.44}$) was investigated. The rate of reaction was found to be pseudo-first order with significant product layer diffusional resistance. In preliminary experiments, we found that a bis-azo dye, *Congo Red* was also efficiently removed from aqueous solution by active manganese oxide. As the solid had a variable composition and contained non-stoichiometric amounts of oxygen, one could attribute a redox reaction for the removal of color. We conducted the experiment in an oxygen-free atmosphere and checked for an oxygen-balance for reduction in the chemical oxygen demand (COD) of the dye solution against the oxygen content of the spent activated oxide. We did not find any measurable decrease in the oxygen content of the activated manganese oxide, but the COD decreased to a considerable extent. Moreover the dye leached out of the used adsorbent on treatment with acetone, so one can conclude that the removal of dye was by adsorption only.

In the above context, we have explored in this work, the effectiveness of active manganese oxide for the removal of *Congo Red*, a dis-azo dye, by adsorption from aqueous solutions. Preparation and characterization of the material are also described. Influences of process parameters like oxygen content of the adsorbent, adsorbent loading, temperature, presence of salts in the solution, and the initial dye concentration on adsorption equilibrium and kinetics were investigated. The equilibrium and kinetic parameters have been evaluated using suitable models.

METHODS

Materials

Preparation of active manganese oxide

Active manganese oxide (MnO_x, $1 < x < 2$) was prepared from Mn(II) sulphate. A 20% solution of the $MnSO_4$ was

mixed with 25% aqueous NaOH and the pH was adjusted to 5.5–6 by adding sulphuric acid. The slurry of precipitated $Mn(OH)_2$, diluted by adding an equal volume of distilled water, was aerated at a rate of 8.5 L/min through a sparger. The color of the precipitate turned brown. For $MnO_{1.33}$, the time of passing air was 3 h and for $MnO_{1.2}$ $1\frac{1}{2}$ h at the same air flow rate. After aeration, the hydrated oxide was washed repeatedly with hot distilled water to make it free from salts, centrifuged, dried in a hot air oven at 105 to 110°C, cooled in a dessicator, powdered, sieved and stored.

Chemicals used

Spectroscopic grade *Congo Red* dye (C.I. Number: 22120) was procured from LOBA-Chemie, India. The chemicals such as technical grade Manganese dioxide MnO_2, sulphuric acid H_2SO_4, sodium sulphate Na_2SO_4 etc. were procured from E. Merck/International Chemicals, India.

Analytical methods

Aqueous dye samples were analyzed using a Shimadzu UV-160A UV–vis spectrophotometer with maximum absorption wavelength at 500 nm. The X-ray diffraction (XRD) study was done using a Philips X'Pert (model no. PW 3040/60) instrument with Cu–K_α radiation ($\lambda = 1.504060\,\text{Å}$). Scanning Electron Microscopy (SEM) was employed using a Hitachi S-3400N instrument at 15 kV SE; 10,000X. For calculating the oxygen content, a sample of active oxide was reacted with a known excess of oxalic acid in the presence of 1 M sulphuric acid, and the excess oxalic acid was back-titrated with standard $KMnO_4$ solution.

Experimental procedure

For equilibrium studies, dye solutions of concentrations ranging from 50 to 500 mg/L were taken in batches of 50 mL in 125 mL airtight borosilicate glass bottles. A mass of 0.2 g of the activated MnO_x (here, $MnO_{1.33}$) was added to each bottle and the contents were allowed to attain equilibrium at constant temperature in a shaker bath at about 150 strokes per minute. From initial experiments, a contact time of 3 h was found sufficient for attainment

of adsorption equilibrium. Three different temperatures (25°, 35° and 45°C) were used for equilibrium study. The content of each bottle was centrifuged twice at 8,000 rpm in a REMI R-24 Research Centrifuge and the supernatant liquid was analyzed spectrophotometrically using a 1 cm light path quartz cell.

For time–concentration experiments, measured weights of MnO_x were contacted with 50 mL dye solution in a set of bottles shaken in a constant temperature shaker bath. The supernatants were analyzed at regular time intervals for the residual dye. The experiments were repeated thrice and the standard deviations were within 3%.

RESULTS AND DISCUSSION

Characterization of activated manganese oxide

Active MnO_x prepared by us is a dark brown powder insoluble in water. It was characterized by particle size distribution (PSD), Fourier tranformed infra-red spectroscopy (FTIR), XRD and SEM. PSD was obtained by dynamic light scattering instrument (Zeta Plus, Brookhaven Instruments Corporation) using a scattering angle of 90°. The mean particle diameter noted was 669.6 nm. The BET (Brunauer, Emmett and Teller) specific surface area (Brunauer *et al.* 1938; Ruthven 1984) was determined as 9.55 m²/g. The FTIR spectrum (Figure 1a) of

activated MnO_x matches the IR spectrum of hausmannite, which re-confirmed the empirical formula obtained from oxygen analysis. The values for 2θ and d in the XRD matched with those of standard Mn_3O_4 reported in JCPDS Card no.80-0382. The powder diffraction pattern (Figure 1b) indicates presence of some crystals of Mn_3O_4. SEM shows that the particles are mixed agglomerates of submicron sized amorphous materials and crystals (Figure 1c).

Adsorption equilibrium

The equilibrium adsorption isotherms are generally smooth and concave to the concentration axis. Such adsorption processes are generally 'favorable' (Sposito 1982; Apak 2002). The equilibrium data could be satisfactorily fitted to both Langmuir and Freundlich isotherm equations, which can be represented as follows:

$$q_e = q_0 \frac{K_L C_e}{1 + K_L C_e} \tag{1}$$

$$q_e = K_F (C_e)^{1/n} \tag{2}$$

where q_e = quantity of dye adsorbed in mg/g on activated MnO_x at equilibrium; C_e = Concentration of the solution in mg/L at equilibrium; q_0 = Maximum adsorption capacity (Langmuir) in mg/g of activated MnO_x; K_L = Langmuir constant in L/mg, related to 'intensity' of adsorption; K_F, n are Freundlich constants related to the strength of the
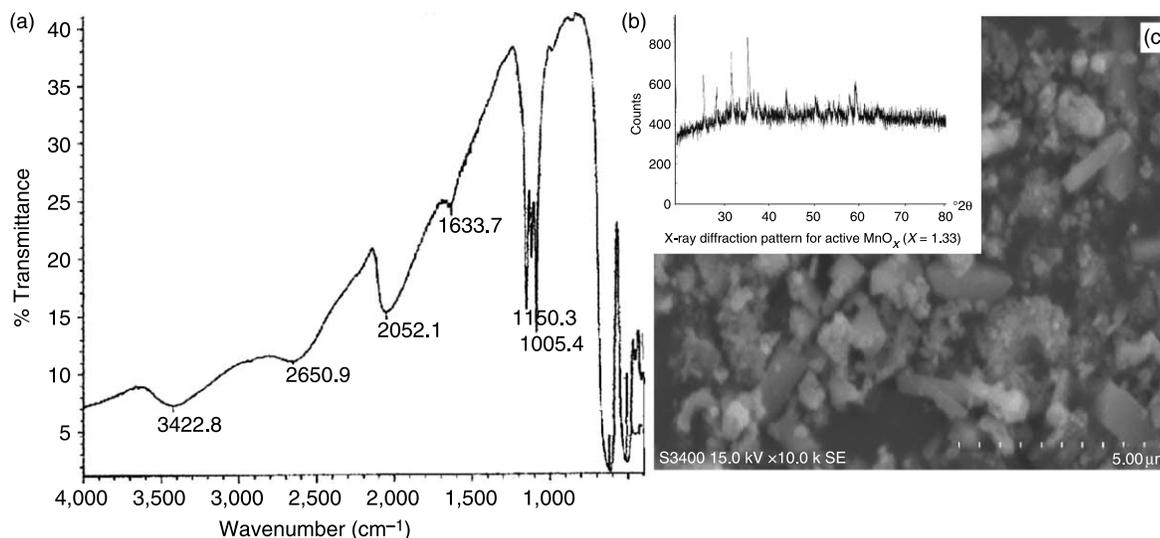
Figure 1 │ Characterization of the adsorbent by FTIR, XRD and SEM. (a) FTIR of the sample; (b) XRD of the sample; (c) SEM picture for [15 kV SE at $10^4 \times$].

adsorbate-adsorbent interaction and to the distribution of bond strengths among the surface sites of a heterogeneous sorbent, respectively (Reed & Cline 1994).

Adsorption isotherms were obtained for Congo-Red–activated MnO_x system at three temperatures (Figure 2). The values of the constants in Langmuir and Freundlich equations at different temperatures are given in Table 1. The observed Langmuir adsorption capacity of the sorbent for *Congo Red* was 38.6 mg/g at 25°C which is an order of magnitude higher than those for red mud, (4.05 mg/g, Namasivayam & Arasi 1997), coir pith activated carbon (6.7 mg/g, Namasivayam & Kavitha 2002), and fly ash (9.8 mg/g, Acemioglu 2004). In general, exothermic adsorption processes (i.e. $\Delta H_{ads} < 0$) are adversely affected by a rise in temperature, and the Langmuir constant (K_L) decreases with increasing temperature. For endothermic adsorption processes (i.e. $\Delta H_{ads} > 0$), K_L increases with temperature (Baker & Khalili 2004). Increase in the value of percentage removal (from 31.8% to 54.2%) and maximum adsorption capacity with temperature indicates endothermic adsorption and possibly chemisorption, where increasing numbers of dye molecules as well as adsorption sites acquire the necessary energy for adsorption with increase in temperature (Asfour *et al.* 1985; Mohan *et al.* 2002). Both Namasivayam & Kavitha (2002) and Purkait *et al.* (2007) and have also indicated endothermic
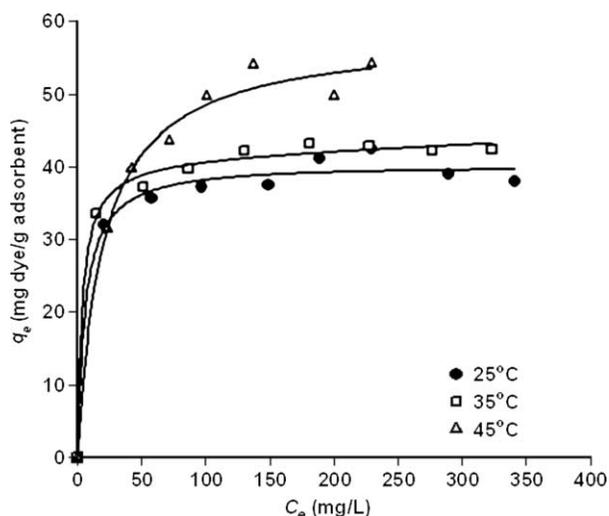
Figure 2 │ Effect of temperature on adsorption isotherm of Congo Red on activated manganese oxide (MnO_x) [Adsorbent loading = 0.4% w/v; x = 1.33; pH = 7.5].

adsorption phenomena for *Congo Red* retention by various activated carbons.

Since Glauber's salt is often used as mordant for dyeing, its effect on adsorption was studied. Presence of 500 mg/L Na_2SO_4 marginally decreased the percentage removal from 30.7 to 28. The isotherms at 25°C (not shown) are quite close to each other. The equilibrium adsorption capacity with salt was 35.94 mg/g whereas the same without salt was 37.97 mg/g, the variation remaining within relative error of measurement. The intensity of adsorption (K_L) also decreased from 0.2225 to 0.0581 L/mg by addition of salt. The effect of salt on the adsorption phenomenon may be qualitatively explained in terms of surface charge of the adsorbent. Kirillov *et al.* (2009) cited uncertainties in the point of zero charge (pzc) of hausmannite reported by a number of researchers. Ocaña (2000) reported a pzc of 5.7, whereas Kosmulski (2006) indicated a value greater than 10. Ignoring the variability reported by different workers, if we accept the pzc value of 5.7 suggested by Ocaña, then at the experimental working pH of 7.5, the adsorbent surface would acquire a homogeneously negative charge and anions like sulfate would not expectedly influence the adsorption capacity (Aguedach *et al.* 2008).

Oxygen content of active MnO_x could be tailored during sorbent preparation by varying the duration of aeration of the suspended manganese hydroxide. Therefore, the effect of oxygen content on the adsorption behaviour of the sorbent with respect to that of technical grade manganese dioxide (MnO_2) was worth investigating. The percentage removal of the dye from a 500 mg/L solution was 50.6% in case of $MnO_{1.2}$, 30.7% for $MnO_{1.33}$ and 2.9% in case of technical grade MnO_2. Maximum adsorption capacities obtained from Langmuir isotherm equation also decreased with increasing oxygen content. The technical grade MnO_2 had the minimum adsorption capacity.

Adsorption kinetics

The experimental data of adsorption vs time were analyzed by first and pseudo-second order kinetic equations. We first analyzed the kinetic data using the most widely used Lagergren equation, Equation (3) (Ho 2004) where first order adsorption rate constant

Table 1 | Effect of temperature on Langmuir and Freundlich constants [pH = 7.5, x = 1.33, adsorbent loading: 0.4% w/v]

Temp (°C)	q_0 (Equation 1) mg/g	K_L (Equation 1) L/mg	R^2	n (Equation 2)	K_F (Equation 2)	R^2
25	38.61	0.2350	0.9949	8.65	22.38	0.9886
35	43.47	0.2293	0.9900	10.26	25.74	0.9784
45	58.13	0.0505	0.9889	3.3886	12.66	0.9857

lumps together the liquid phase mass transfer and the solid phase diffusion phenomena.

$$\log(q_e - q_t) = \log q_e - \frac{K_{ad}}{2.303}t \tag{3}$$

Here q_t is the amount of dye adsorbed in mg/g onto activated MnO_x at any time t, q_e is the equilibrium concentration of the adsorbate on the sorbent in mg/g and K_{ad} is the global adsorption rate constant in time^{-1} that can be evaluated from the slope of the linear plot of log $(q_e - q_t)$ against t.

The rate constants obtained from the Lagergren equation varies nonlinearly with increase in the adsorbent loading and initial dye concentration. This indicates a complex mechanism and model of adsorption of the dye on this particular adsorbent. We then analyzed the data using the pseudo-second order model proposed by Ho & McKay (1999) based on the temporal deviation of solute loading from the equilibrium adsorption as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{4}$$

where k_2 is the pseudo-second order rate constant, g/(mg h). Integrating Equation (4) and applying initial condition, we get:
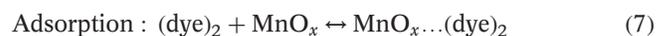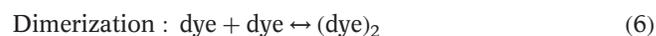
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{5}$$

The values of k_2 and q_e could be obtained from a plot of t/q_t against t, using the slope and intercept of the linearized model Equation (5) such that q_e = slope^{-1}, and k_2 = (slope)^2(intercept)$^{-1}$.

Table 2 shows the values of the adsorption rate constant as a function of various parameters. Higher correlation coefficients were obtained for the pseudo-second order model compared to those obtained from first order kinetics.

Furthermore, the experimental q_e values were closer to the calculated ones obtained from the second-order kinetic plots, and the values showed consistent trends of variation with the relevant parameters. Purkait *et al.* (2007) have also reported that the adsorption of *Congo Red* onto activated carbon is better represented by pseudo-second order kinetics. Similar results of adsorption kinetics for *Congo Red* retention by activated carbon prepared from coir pith was observed by Namasivayam & Kavitha (2002).

Congo Red is a disazo dye with a high self-assembling tendency. If the slow step in *Congo Red* adsorption involves dimerization (Skowronek *et al.* 1998) of the dye, which is very common for such dyes in aqueous solutions at moderate concentrations, then this would manifest itself in a second-order kinetics of adsorption with respect to the dye concentration. Thus, the basis of the second order model may be interpreted as follows:

$$\text{Dimerization}: \text{dye} + \text{dye} \leftrightarrow (\text{dye})_2 \tag{6}$$

$$\text{Adsorption}: (\text{dye})_2 + MnO_x \leftrightarrow MnO_x...(\text{dye})_2 \tag{7}$$

As increase in adsorbent loading generally means increase in the sites for adsorption, percent removal of *Congo Red* dye expectedly increased from 32% to 46% when adsorbent loading increased from 0.4% to 0.6% w/v at 25°C and pH 7.5. The active reagent was $MnO_{1.33}$ and initial dye concentration was 500 mg/L. The pseudo-second order rate constant values also increased concomitantly (Table 2).

Percentage removal of *Congo Red* dye increased from 32% to 64% as the concentration of dye decreased from 500 to 200 mg/L. However, the adsorption rate constant was the highest for 500 mg/L (0.2585 g mg/h) and the lowest for 200 mg/L (0.1707 g mg/h). The adsorbent might not be saturated in the mentioned range of concentration, and therefore, the more was the availability of dye molecules, the more was the rate of adsorption.

Table 2 | Effect of various parameters on the rate constants

Parameter	Value	K_{ad} h^{-1}	R^2	k_2 g mg^{-1} h^{-1}	R^2
Adsorbent loading (% w/v), g	0.4	0.9810	0.9071	0.1620	0.9973
[Initial concentration 300 mg/L, temperature 25°C]	0.5	1.3127	0.9856	0.1662	1.0
	0.6	0.8152	0.9340	0.2134	0.9989
Initial dye concentration (mg/l)	500	0.9810	0.9071	0.2585	0.9964
[Adsorbent loading 0.4% w/v, temperature 25°C]	300	2.1832	0.9696	0.2020	0.9951
	200	1.7687	0.9050	0.1707	0.9923
Temperature (°C)	25	2.1832	0.9696	0.1246	0.9979
[Initial dye concentration (mg/L) 300; $x = 1.33$; adsorbent loading: 0.4% w/v]	35	1.0916	0.9812	0.0967	0.9988
	45	1.2298	0.9613	0.1131	0.9981
Oxygen content	MnO_2	0.6218	0.8515	5.06×10^{-3}	0.8811
[Initial dye concentration (mg/L) 300; $x = 1.2$–2.0 adsorbent loading: 0.4% w/v]	$MnO_{1.3}$	2.1832	0.9696	0.2020	0.9951
	$MnO_{1.2}$	1.6443	0.9679	0.3141	0.9989

With increase in temperature from 25°C to 45°C, the percent removal of *Congo Red* dye from 300 mg/L initial solution increased from 47% to 53%. The pseudo-second order rate constant, however, was observed to remain almost unaffected with increase in temperature in the range of 25 to 45°C (Table 2).

Like equilibrium, the adsorption kinetics was also affected marginally by the addition of salts (Figure 3a). Percentage removal remained approximately unaltered at 47 compared to 43 in presence of 500 mg/L Na_2SO_4 salt at 25°C temperatures after 3 h (180 minutes).

Like the equilibrium studies, the batch-contact time experiments were also conducted with the three varieties of manganese oxides with different oxygen content. Percentage of dye removed was very low (5%) with technical grade MnO_2. With $MnO_{1.2}$ it was 55% whereas with $MnO_{1.33}$ it was 47% under otherwise similar experimental conditions. Figure 3b shows the linear plots for the pseudo-second order model showing the effect of the oxygen content in the activated sorbent. Value of the adsorption rate constant was the highest for $MnO_{1.2}$.
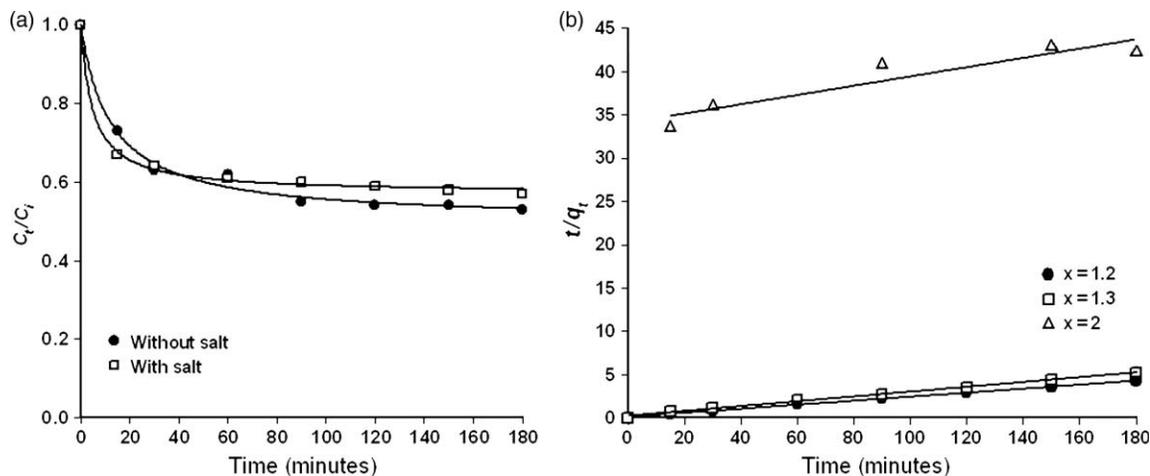
Figure 3 | Effects of (a) addition of salt and (b) oxygen content (x) on adsorption.

CONCLUSIONS

Active manganese oxide adsorbent was prepared in the laboratory by hydrolysis of Mn(II) sulphate with alkali and subsequent aeration of the precipitated manganese hydroxide. XRD studies indicate that this active oxide was mainly Mn_3O_4. The high adsorption capacity and 'favorable' nature of the isotherm indicate its potential of use for the removal of *Congo Red*, a dis-azo dye, from aqueous solution by adsorption. The equilibrium adsorption pattern followed both Langmuir and Freundlich equations, to which, Langmuir isotherm fits better. Langmuir adsorption capacity of the sorbent for *Congo Red* was 38.6 mg/g, which was higher than those of most sorbents reported in literature. The adsorption kinetics followed a pseudo-second order rate equation indicative of the self-assembling tendency of *Congo Red*. The effect of either temperature or salt (Na_2SO_4) addition on both adsorption equilibrium and kinetics was small. The rate of adsorption increased with an increase in both adsorbent loading and initial concentration of dye solution. The oxide of empirical formula $MnO_{1.2}$ showed the highest value of both adsorption capacity and pseudo-second order rate constant among the three varieties of manganese oxides used, possibly due to the unsaturated valency of manganese in this oxide. The relatively high adsorption capacity and rate of the proposed Mn-oxide sorbent for the dye is suggestive of its potential use in the sorptive treatment of textile industry effluents.

ACKNOWLEDGEMENTS

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