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Dye removal from wastewater using the adsorbent developed from sewage sludge

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Abstract: Sewage sludge was used to develop an effective carbon adsorbent. This adsorbent was employed for the removal of azo dye such as Direct Dark Brown M and Acid Mordant Brown RH. The adsorption of dyes on this adsorbent was studied as a function of contact time, concentration, pH and temperature by batch method. The equilibrium adsorption capacity of a carbonaceous adsorbent prepared from city wastewater treatment plant was 502, and 329.7 mg/g of Direct Dark Brown M and Acid Mordant Brown RH, respectively. The experimental data were analyzed by the Langmuir and Freundlich models of adsorption. Equilibrium data fitted well with the Langmuir model. The rates of adsorption were found to conform to the Lagergren second-order kinetics with good correlation. The equilibrium adsorption capacity of the carbonaceous adsorbents was determined with the Langmuir equation as well as the Lagergren second-order rate equation. The most ideal pH for adsorption of two dyes onto adsorbents was found to be 3 and below. The results indicate that the carbonaceous adsorbents could be employed as a low cost adsorbent in the removal of dyes from wastewater.

Keywords: adsorbent; sewage sludge; azo dye; isotherms; kinetics

Introduction

Adsorption is relevant in environmental pollution and protection with reference to water and wastewater treatment (Bowen, 1992). Toxic materials, hazardous ions and dyes from industrial effluents by the way of adsorption are of great significant in connection with environmental and human health safety. Adsorption by solids decreases the toxicity of the wastewater or removes non-safe organic materials from industrial effluents, etc.(Pala, 2002).

Effluent from the dyeing industry contains highly coloured species, such as highly coloured wastes are not only aesthetically displeasing but also hinder light penetration and may in consequence disturb biological processes in waterbodies. In addition, dyes are toxic to some organisms and hence harmful to aquatic animals. Furthermore, some of azo dyes and their reaction products such as aromatic amines are highly carcinogenic. Therefore, removal of dyes before disposal of the wastewater is necessary.

Among various treatment technologies, adsorption onto carbonaceous adsorbent (Haghseresht, 1999; Tsai, 1998; Kumar, 2000) has proven to be one of the most effective and reliable physicochemical treatment methodology. However, commercially available carbonaceous adsorbents are very expensive. Therefore, there is a need to produce low cost and effective carbons applied in water pollution control. If low cost non-conventional sources are used to prepare carbonaceous adsorbents for a specific purpose, then they should be economical for wastewater treatment.

The present investigation reported the results of removal of Direct Dark Brown M and Acid Mordant Brown RH from spent textile dyeing wastewater by the adsorption onto carbonaceous adsorbent prepared from low cost sewage sludge. The objective of the present work was to examine the effectiveness of the prepared carbonaceous adsorbent in removing Direct Dark Brown M and Acid Mordant Brown RH from wastewater. The kinetic data and equilibrium data of adsorption studies were processed to understand the adsorption mechanism of the dye molecules onto the carbonaceous adsorbents.

1 Experimental

1.1 Materials

The sewage sludge used in this project is supplied by the Tianjin Sewage Treatment Plant, China, and characteristics of the dewatered sludge are shown in Table 1. When the dried sewage sludge sample is sieved, it falls into the size fractions shown in Table 1.

Table 1 Constitution and particle distribution of dry sewage sludge

Properties	Dry sewage sludge	Carbonaceous adsorbent
Volatile matter, %	46.00	25.54
Ash, %	29.85	31.57
Fixed carbon content, %	24.15	46.84
Particle size, mesh	60	60—200
BET surface area, m^2/g		173.94
Particle size		
1000—1999 mm, %	45	
500—999 mm, %	30	
< 499 mm, %	25	

It is seen that sewage sludge contains large amounts of ash and a significant amount of volatile matter. It is the volatile matter that will be liberated during high temperature treatment in which processing a rudimentary pore structure is formed in the char. The resulting char can then be activated further to increase the adsorptive capacity. Fixed carbon content of sewage sludge is very low, indicating a high volume reduction. This is favorable because large quantities of wastes can be utilized in this way.

A dyeing wastewater collected from a textile dyeing factory in Tianjin, China was used to evaluate the effectiveness of the prepared carbonaceous adsorbents in the treatment of wastewater. Two different coloured wastewater samples, Samples 1 and 2, were used in this study. Detailed characteristics of the samples are given in Table 2 and Table 3.

Table 2 Characteristics of the wastewater samples

Parameter	Direct Dark Brown M	Acid Mordant Brown RH
PH	8.20	8.12
TSS, mg/L	198	271
COD, mg/L	1477.6	1880.6
TOC, mg/L	559.7	734.6

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Table 3 Properties of dyes

Sample No.	Name	C.I.	Molecular formula	Azo groups	λ_{max}, nm	Type
1	Direct Dark Brown M	22311	$C_{29}H_{19}N_5Na_2O_7S$	2	392	Anionic
2	Acid Mordant Brown Rh	13250	$C_{12}H_{10}N_5NaO_6S$	1	443	Anionic

The sludge were subjected to some treatments prior to determining their adsorption capacity. First, dried in an air oven at 110℃ for overnight, to get the dry sewage sludge; second, treatment involved drying plus chemical activation (zinc chloride solution, 1—5 mol/L) plus pyrolysis to obtain carbonaceous adsorbent. The material was sieved to obtain the desired size fractions, washed thoroughly with hot distilled water. Activation was applied by means of 1.5 kg/cm^2 steam pressure at 550℃ for 1 h. The activated material thus prepared was then ground and dried in an air oven at 110℃ for overnight. Some physicochemical characteristics of the adsorbent are summarized in Table 1. The surface area of the carbonaceous adsorbent was 173.94 m^2/g, it was determined by the BET (Micromeritics ASAP-2010 adsorption analyzer) method. Before utilization, the carbon was thoroughly washed with distilled water several times and then dried in hot air oven at 110℃.

1.2 Methods

Weighed quantity of carbonaceous adsorbent was taken in a standard-joint pyrex glass stoppered bottle (250 ml) containing 100 ml wastewater sample. The pH was adjusted to the desired value(2.0—9.0) and the mixture was shaken for a predetermined period using a thermostatic horizontal shaker operated at 150 r/min. Kinetics of adsorption was determined by analyzing adsorptive uptake of the dye colour at different time intervals. Independent bottles containing 100 ml wastewater sample and 0.06 g carbonaceous adsorbent were used during the kinetic studies to get accurate results for each point on the graph. Isothermal studies were conducted with different doses of adsorbent(0.01—0.3 g) and 100 ml sample by shaking the reaction mixture for equilibrium time. Dye concentration in the reaction mixture was calculated from the calibration curve. The amount of dye adsorbed onto the adsorbents, q_e(mg/g), was calculated by the following mass balance relationship:

$$q_e = (C_0 - C_e)\frac{V}{W}, \quad (1)$$

where C_0 and C_e are the initial and equilibrium liquid-phase concentrations of dye, respectively(mg/L), V is the volume of the solution(L), and W is the weight of the adsorbent used(g).

2 Results and discussion

2.1 Influence of system pH on adsorption capacity

The variations in removal of dye from wastewater at various system pH are shown in Fig. 1. It is evident that the maximum removal of dye colour for both the samples is at pH 3 and below, their removal efficiency were greater than 70% and 65% respectively. Low pH leads to an increase in H^+ concentration in the system and the surface of the carbonaceous adsorbent acquires positive charge by absorbing H^+ ions. As the adsorbent surface is positively charged at low pH, a significantly strong electrostatic attraction appears between the positively charged adsorbent surface and anionic dye molecule leading to maximum adsorption of dye. In alkaline medium, the extent of dye colour removal is increased as the pH is increased from 8 to 9.

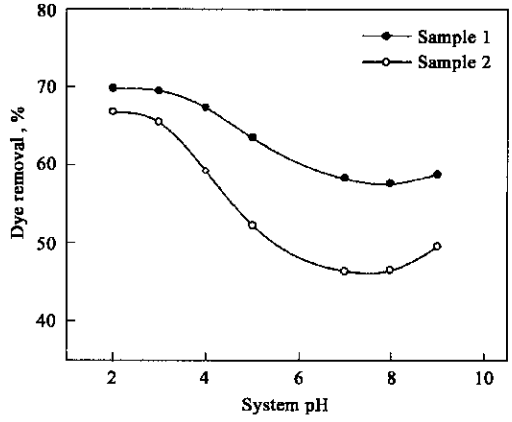

Fig.1 Effect of system pH on removal of two dyes by adsorbents
Experimental conditions: adsorbent = 0.6 g/L; contact time = 150 min and temperature = 30℃

2.2 Adsorption kinetic

The influence of contact time on dye color removal by carbonaceous adsorbent is presented in Fig. 2 It shows that adsorbent is efficient to adsorb Direct Dark Brown M and Acid Mordant Brown RH from wastewater, the process reaches equilibrium gradually. This is due to the fact that carbonaceous adsorbent is composed of porous structure with large internal surface area(Pelekani, 2001; Chiou, 2002). First, the adsorbate migrates to the exterior surface of the adsorbent particles, followed movement from particle surface into interior site and finally the adsorbate is adsorbed into the active sites at the interior of the adsorbent particle. This phenomenon occurs after relatively long contact time. The time profile of dye uptake is a single, smooth and continuous curve leading to saturation, suggesting also the possible monolayer coverage of dyes on the surface of the carbonaceous adsorbents. Fig. 2 shows that the contact time required in attaining equilibrium is almost 120 min for both the samples.

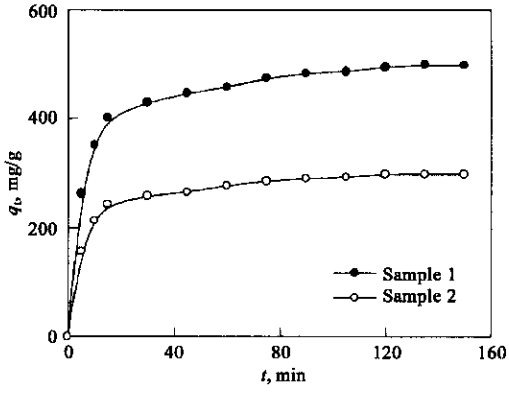

Fig.2 Time profiles of solid-phase concentrations of dyes for adsorbent-dye system
Experimental conditions: carbon = 0.6 g/L; pH = 3 and temperature = 30℃

Kinetic data were treated with the Lagergren-first-order kinetic model (Chiou, 2002; Zümriye, 2001). The differential equation is the following:

$$\frac{dq_t}{d_t} = k_1(q_e - q_t), \quad (2)$$

where q_e and q_t refer to the amount of dye adsorbed(mg/g) at equilibrium and at any time, t (min), respectively, and k_1

is the equilibrium rate constant of Lagergren-first-order sorption (min^{-1}).

Integrating Eq.(2) for the boundary conditions $t = 0$ to t and $q_t = 0$ to q_t, rearranged to obtain a linear form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t. \quad (3)$$

Values of the rate constant, k_1, equilibrium adsorption capacity, q_e, and the correlation coefficient, r^2, were calculated from the plots of $\log(q_e - q_t)$ versus t (inset of Fig.3) for both wastewater samples. Although the correlation coefficients for both samples are found to be higher than 0.98, the calculated equilibrium adsorption capacities do not agree with experimental values(Table 4). This indicates that adsorption of two dyes onto carbonaceous adsorbents is not an ideal Lagergren-first-order reaction.

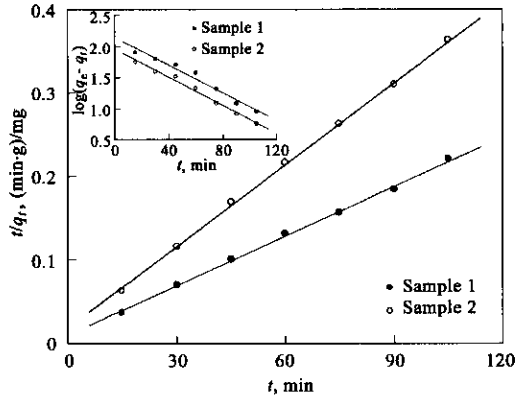

Fig. 3 Lagergren-second-order kinetics for adsorption of two dyes on adsorbents, inset, Lagergren-first-order kinetics for adsorption

Table 4 Lagergren-first-order and Lagergren-second-order adsorption rate constants and the calculated and experimental q_e values for adsorption of two dyes on adsorbent

Sample	First-order kinetic model				Second-order kinetic model		
	q_e(exp), mg/g	k_1, min^{-1}	q_e(cal), mg/g	r^2	k^2, g/(mg·min)	q_e(cal), mg/g	r^2
1	496	0.025	141.6	0.985	0.11	500	0.999
2	298.2	0.026	91.8	0.993	0.09	303	0.999

Kinetic data were further treated with the Lagergren-second-order kinetic model. The differential equation is the following:

$$\frac{dq_t}{d_t} = k_2(q_e - q_t)^2, \quad (4)$$

where k_2 is the equilibrium rate constant of Lagergren-second-order adsorption(g/(mg·min)). Integrating Eq. (4) for the boundary condition $t = 0$ to t and $q_t = 0$ to q_t, rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \cdot t. \quad (5)$$

If Lagergren-second-order kinetics is applicable, the plot of t/q_t versus t should show a linear relationship. The linear plots of t/q_t versus t show a good agreement of experimental data with the Lagergren-second-order kinetic model for both wastewater samples(Fig.3). The correlation coefficients(r^2) for the second-order kinetic model are higher than 0.99. The second order rate constant, k_2, and the equilibrium adsorption capacity, q_e, were calculated from the intercept and slope of the plots of t/q_t versus t. The calculated q_e values agree very well with the experimental data(Table 4). These indicate that the adsorption of two dyes from wastewater on adsorbents obeys Lagergren-second-order kinetic model.

2.3 Adsorption isotherm studies

The adsorption isotherms(Allen, 2004; Wong, 2004) of various classes of compounds(q_e versus C_e) in different surfaces have been classified according to their shapes. Adsorption isotherms expressing the adsorbed amounts as a function of equilibrium concentration for both wastewater samples are presented in Fig. 4. It can be seen that the curves are all likely to be a typical Langmuir-type adsorption isotherm.

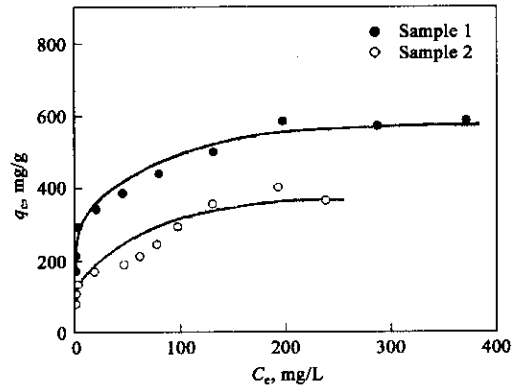

Fig.4 Isotherm for adsorption of two dyes on adsorbent prepared from sewage sludge
Experimental conditions: contact time = 150 min; pH = 3 and temperature = 30℃

The theoretical Langmuir isotherm equation can be represented as(Allen, 2004):

$$q_e = \frac{q_{mon} K_L C_e}{1 + K_L C_e}, \quad (6)$$

where K_L is the Langmuir constant related to the energy of adsorption(L/mg) and q_{mon} is the maximum amount of adsorption corresponding to complete monolayer coverage on the surface(mg/g). The constants K_L and q_{mon} can be determined from the following linearised form of Eq.(6):

$$\frac{1}{q_e} = \frac{1}{q_{mon} K_L} \times \frac{1}{C_e} + \frac{1}{q_{mon}}. \quad (7)$$

The linear plots of $1/q_e$ versus $1/C_e$ for the wastewater samples show that adsorption follows Langmuir isothermal model(Fig.5). Conformation of the experimental data into Langmuir isotherm model indicates the homogeneous nature of carbonaceous adsorbents surface, i.e., each dye molecule/carbonaceous adsorbents adsorption has equal adsorption activation energy; the results also demonstrate the formation of monolayer coverage of dye molecule at the outer surface of carbonaceous adsorbents. Values of q_{mon} and K_L were calculated from the intercept and slope of the linear plots, respectively, and are presented in Table 5. The equilibrium adsorption capacities evaluated from the Langmuir equation and the Lagergren-second-order rate model show that the evaluated values are reasonable. Steep slope of the Langmuir plots is indicative of the usefulness of carbonaceous adsorbents at high concentration and also of the efficiency in column operations.

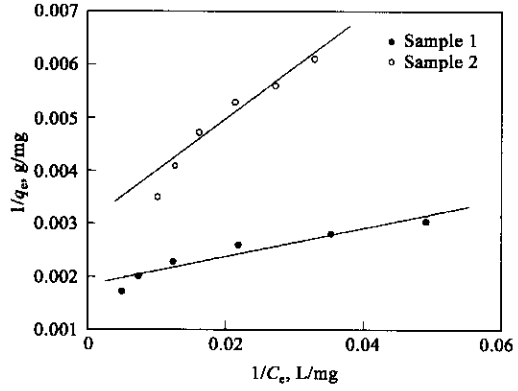

Fig.5 Langmuir plots for adsorption of two dyes on adsorbents.

Table 5 Langmuir and Freundlich constants for adsorption of two dyes on adsorbents

Sample	Langmuir isotherm				Freundlich isotherm		
	q_{mon}, mg/g	K_L, L/mg	R_L	r^2	K_F	n	r^2
1	502	0.08	0.03	0.980	201.8	5.03	0.954
2	329.7	0.03	0.1	0.982	88.3	3.98	0.944

The essential features of Langmuir adsorption isotherm can be expressed in terms of a dimensionless constant called separation factor or equilibrium parameter (R_L), which is defined by the following relationship(Wong, 2004):

$$R_L = \frac{1}{1 + K_L C_0}, \quad (8)$$

where C_0 is the initial dye concentration (mg/L). The R_L value indicates the shape of the isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 0$) or unfavorable($R_L > 1$). By processing the above equation, R_L values for investigated dye-adsorbent system are found to be 0.03 for Sample 1 and 0.1 for Sample 2. From the values of R_L, it is confirmed that prepared carbonaceous adsorbent is favourable for adsorption of two dyes from wastewater under the conditions used in this study.

The Freundlich isotherm(Allen, 2004) is expressed by the following equation:

$$q_e = K_F C_e^{1/n}, \quad (9)$$

where K_F is roughly an indicator of the adsorption capacity and $1/n$ is the adsorption intensity. In general, as the K_F value increases the adsorption capacity of adsorbent for a given adsorbate increases. The magnitude of the exponent, $1/n$, gives an indication of the favorability of adsorption. Values of $n > 1$ represent favourable adsorption condition. Eq.(9) may be linearised by taking logarithms:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e. \quad (10)$$

Linear plots of log q_e versus log C_e show that adsorption of two dyes from wastewater on carbonaceous adsorbents also follow the Freundlich isotherm(Fig.6). Values of K_F and n are calculated from the intercepts and slopes of the plots and are listed in Table 5. The results suggest that two dyes are favourably adsorbed by adsorbent prepared from sewage sludge. However, the values of the correlation coefficient (r^2) (Table 5) indicate that the Langmuir isotherm has been best fitted for the adsorption of two dyes on adsorbents.

3 Conclusions

In this study, it is shown that carbonaceous adsorbent prepared from sewage sludge, with BET surface area of 173.94 m^2/g, is considerably efficient for removal of Direct Dark Brown M and Acid Mordant Brown RH from wastewater. The adsorption is highly dependent on contact time, adsorbent dose and pH. Experimental conditions are contact time 150 min; pH 3 and temperature 30℃. The most ideal pH is 3 and below, their removal efficiency were greater than 70% and 65% respectively, the contact time required in attaining equilibrium is almost 120 min for both dyes. The kinetics of dye adsorption on carbonaceous adsorbents follows the Lagergren-second-order model. The equilibrium data fit well in the Langmuir model of adsorption, showing monolayer coverage of dye molecules at the outer surface of carbonaceous adsorbents. The value for the maximum adsorption capacity is 502 mg/g and 329.7 mg/g respectively. The result would be useful for fabrication and designing of spent textile dyeing wastewater for the removal of dyes. Since the raw material, sewage sludge, is freely available the treatment method seems to be economical.

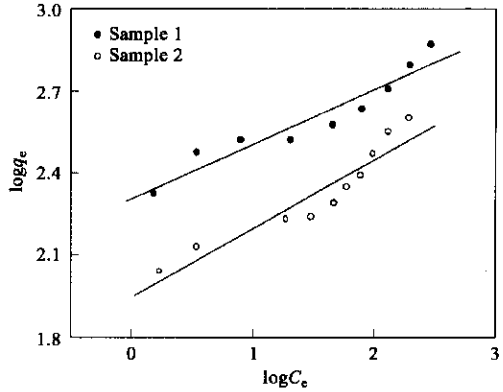

Fig. 6 Freundlich plots corresponding to adsorption of two dyes on adsorbents.

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