

Removal of hazardous dye conged from waste material

Rajeev Jain*, Shalini Sikarwar

Department of Environmental Chemistry, Jiwaji University, Gwalior 474011, India

Received 7 March 2007; received in revised form 15 June 2007; accepted 23 July 2007

Available online 28 July 2007

Abstract

The present paper is aimed to investigate and develop cheap adsorption methods for color removal from wastewater using waste material sawdust as adsorbent. Sawdust, a biosorbent, was successfully utilized in removing a water soluble azo dye, conged from wastewater. The paper incorporates effect of pH, temperature, amount of adsorbent, contact time, concentration of adsorbate, particle size on adsorption. Specific rate constants of the processes were calculated by kinetic measurements and a first order adsorption kinetics was observed in each case. Langmuir and Freundlich adsorption isotherm models were then applied to calculate thermodynamics parameters as well as to suggest the plausible mechanism of the ongoing adsorption processes. In order to observe the quality of wastewater COD measurements were also carried out before and after the treatments. A significant decrease in the COD values was observed, which clearly indicates that adsorption method offer good potential to remove conged from wastewater.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Sawdust; Congored; Adsorption; Kinetics; Waste material

1. Introduction

The effluents from textile, leather, food processing, dyeing, cosmetics, paper and dye manufacturing industries are important sources of dye pollution [1]. Many dyes and their breakdown products may be toxic for living organisms [2]. Therefore, decolorization of dyes are important aspects of wastewater treatment before discharge. It is difficult to remove the dyes from the effluent, because dyes are not easily degradable and are generally not removed from wastewater by conventional wastewater systems [3]. Generally, biological aerobic wastewater systems are not successful for decolorization of majority of dyes. Therefore, in order to achieve the desired degree of treatment, it is necessary to integrate biological, chemical and physical processes as coagulation, ultra-filtration, electro-chemical adsorption and photo-oxidation [4].

Adsorption techniques have potential for removing organics from water due to their high efficiency and ability to separate a wide range of chemical compounds [5,6]. Activated carbon has been widely used as an adsorbent in wastewater treatment to remove organic and inorganic pollutants [7–14]. Possessing

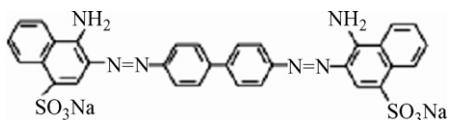
high specific surface area, activated carbon frequently exhibits high removal efficiency for most dissolved compounds. It has a good capacity for the adsorption of many organic molecules. In spite of this it suffers from few disadvantages. Activated carbon is quite expensive, and its regeneration produces additional effluent and results in considerable loss (10–15%) of the adsorbent. Thus, the use of several low cost adsorbents has been studied by many researchers. They have studied the feasibility of using low cost materials, such as waste orange peel [15], banana pith [16], cotton waste, rice husk [17], betonite clay [18], neem leaf powder [19], powdered activated sludge, perlite [20], bamboo dust, coconut shell, groundnut shell, rice husk, and straw, duck weed [21], sewage sludge [22], sawdust carbon [23] and gram husk [24] as adsorbents for removal of various dyes from wastewaters.

The object of the present investigations has been to evaluate the efficiency of removal of conged using activated carbon (AC) and activated sawdust. Activated sawdust (ASD) is, a wood based industrial waste material, is easily available, cheap, and economically advantageous. In the present study, application of activated sawdust for the removal of dyes from aqueous solution has been studied and activated carbon was used as a conventional adsorbent to compare the results. The effect of adsorbent dose, pH, particle size, temperature, initial dye concentration, and equilibrium time has been studied.

* Corresponding author. Tel.: +91 75124016766; fax: +91 7512346209.
E-mail address: rajeevjain54@yahoo.co.in (R. Jain).

2. Materials and methods

The dye congorod (A) was obtained from M/s Merck and its 0.01 M stock solution was prepared in double distilled water. To prepare various solutions at desired concentrations from the stock solution, double distilled water was used for necessary dilutions. All reagents used in the present work were of analytical grade.



Adsorbent activated carbon was purchased from M/s Merck and used as received, while sawdust was collected from the local wood based industries. The dose of adsorbent was varied from 0.06 to 0.33 g/L for activated carbon and from 0.5 to 3.5 g/L for activated sawdust. All pH measurements were carried out with a decibel DB 1011 digital pH meter, fitted with a glass electrode and COD digestion apparatus (Spectra-Lab-2015 S) was used for determining COD of the solutions. Absorbance measurements were recorded on a spectronic 20D+ thermospectronic spectrophotometer over the wavelength range 200–600 nm.

2.1. Adsorbent development

Sawdust was cleaned, thoroughly washed with distilled water, and then dried in an oven. It was further treated with hydrogen peroxide (100 volumes) for about 24 h to remove all adhering organic particles and dried at 110 °C for 1 h in the vacuum oven. The material was grounded and sieved to desired particle sizes such as (<106 BSS mesh), (106–125 BSS mesh), (125–180 BSS mesh), (180–212 BSS mesh), (212–250 BSS mesh), (250–300 BSS mesh), (>300 BSS mesh)). Finally, granules of activated sawdust thus obtained were stored in separate vacuum desiccators until required.

2.2. Adsorption studies

The adsorption experiments were carried out in a batch process by using aqueous solution of congorod with both the adsorbents and experiments were conducted to observe the effect of various parameters such as pH, temperature, particle size, amount of adsorbent, concentration, and contact time. Adsorption isotherms were recorded at equilibrium conditions for the concentration of dye over range 1×10^{-5} to 9×10^{-5} M at a fixed pH. The selected concentration was ascertained after a good deal of examination. Each adsorption study was made in a mechanically agitated 100 mL volumetric flask filled with 30 mL of a dye solution of desired concentration along with a known amount of adsorbent. When the equilibrium was established, supernatant was carefully filtered through Whatmann filter paper (No. 1) saturated with distilled water. To further confirm the adsorption of dye on the filter, a comparative study was done by taking a known amount of the dye. Adsorption of dye on filter paper was not observed.

2.3. Kinetic studies

For kinetic studies, the batch technique was used due to its simplicity. A series of conical flasks of 100 mL capacity and containing a definite volume of solutions of congorod of known concentrations were kept in a thermostat shaking water bath. After attaining the desired temperature, a known amount of the adsorbent was added to each flask and the flasks were allowed to agitate mechanically. At given time intervals the adsorbent was separated by filtration and the filtrate thus obtained was analyzed spectrophotometrically at 498 (λ_{max}) to determine the equilibrium concentration of the dye. The kinetic studies were also carried out under different adsorbate concentrations.

3. Results and discussion

3.1. Effect of contact time on adsorption process

The effect of contact time on the amount of dye adsorbed was investigated at the optimum initial concentration of dye 6×10^{-5} M. The extents of removal (in terms of q_e) of congorod by both the adsorbents increases in Fig. 1, and reach a maximum value with increase in contact time. Based on these results, 20 min for AC and 60 min for ASD was taken as the equilibrium time in adsorption experiments. The removal of congorod from aqueous solutions by adsorption on both the adsorbents increases with time, till the equilibrium is attained. Similar results have been reported in literature for adsorption of dyes [25].

3.2. The effect of pH

The pH is one the most important factors controlling the adsorption of dye on to adsorbent. To determine the optimum pH conditions for the adsorption of congorod over AC and ASD, the effect of pH was observed over the entire pH range (2.0–9.0). The studies were conducted at a fixed concentration of adsorbate (6×10^{-5} M) and contact time (20 min for AC and 60 min for ASD). The results obtained are presented in Fig. 2, which describes maximum adsorption around 99 and 88% for activated carbon and activated sawdust, respectively, at pH 6.5. Hence, all the succeeding investigations were performed at pH 6.5 for both adsorbents.

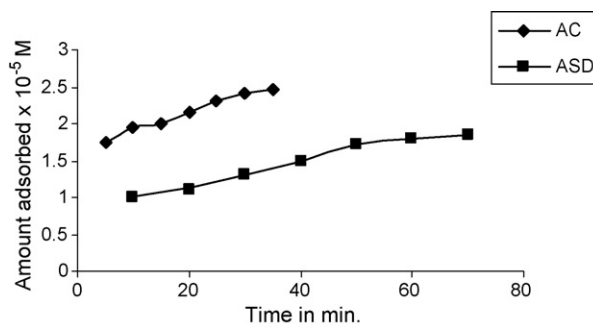


Fig. 1. Effect of contact time on adsorption of congorod (6×10^{-5} M) by (a) AC and (b) ASD at 30 °C and pH 6.5.

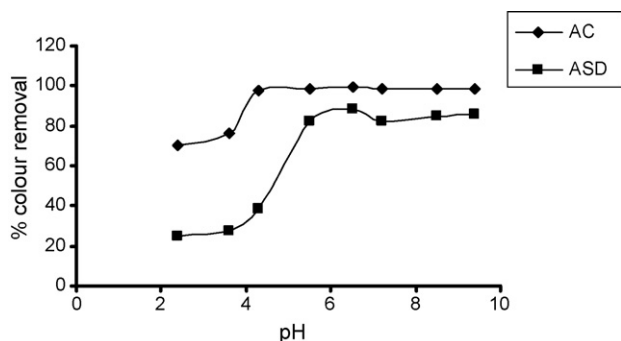


Fig. 2. Effect of pH on amount adsorbed of congored (6×10^{-5} M) by AC and ASD at 30°C .

3.3. The effect of adsorbent dose on adsorption process

To optimize the adsorbent dose for the removal of congored from its aqueous solutions, adsorption was carried out with different adsorbent dosages at different temperatures. The amounts of the dye removed by adsorption on AC and ASD are presented in Fig. 3. The dose of adsorbent was varied from 0.06 to 0.33 g/L for AC and from 0.5 to 3.5 g/L for ASD at fixed pH 6.5, and adsorbate concentration. The study shows an increase in adsorption with the increase in dosage of the adsorbent. As the adsorbent dosage increases, the adsorbent sites available for the dye molecules also increase and consequently better adsorption takes place [26]. In case of AC at initial temperature the uptake of dye increases from 54.7% at 0.06 g/L to 90.7% at 0.33 g/L, whereas, for ASD percentage removal increases from 30% at

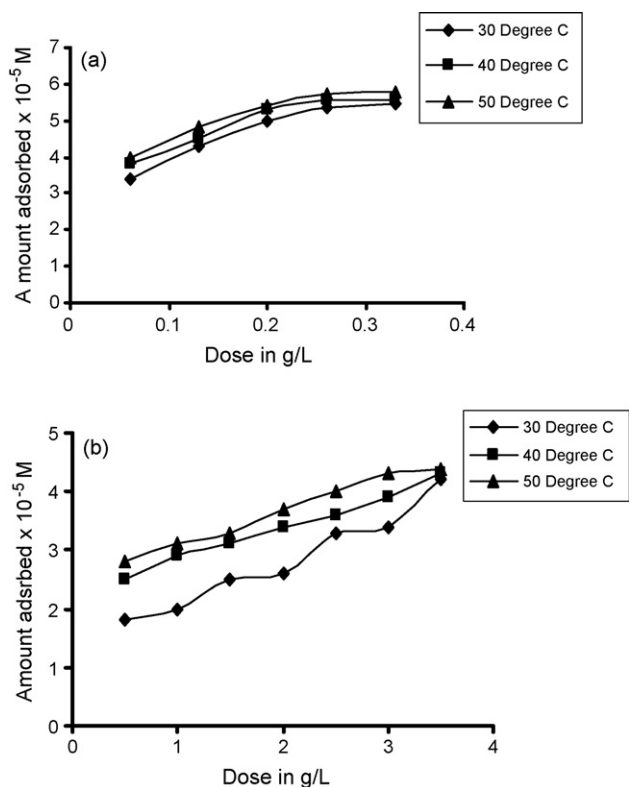


Fig. 3. Effect of adsorbent dose on the uptake of congored (6×10^{-5} M) by (a) AC and (b) ASD at pH 6.5 and different temperatures.

0.5 g/L to 70.1% at 3.5 g/L. It was observed that adsorption of congored over AC increases from 0.06 to 0.2 g/L and then it remains constant whereas adsorption over ASD increases from 0.5 to 2.5 g/L and then it becomes constant and thereafter it further increases at initial temperature. Thus, in all subsequent studies the optimum amounts of AC and ASD were chosen as 0.2 and 2.5 g/L, respectively. At this amount the adsorption over both adsorbents is efficient and save unnecessary use of excess of adsorbent quantity wise. The half life of the process was also determined at varying doses for each adsorbent and it was specified that the half life increases with increasing amount.

3.4. Effect of initial adsorbate concentration on adsorption process

Initial concentrations of congored were changed in order to determine proper congored adsorption keeping the contact time 20 min for AC and 60 min for ASD at a fixed dose 0.2 g/L for AC and 2.5 g/L for ASD at pH 6.5. Fig. 4 showed that the amount adsorbed q_e increased with an increase in the dye concentration. However, percentage removal rate decreased with an increase in the dye concentration. It is also noted that the rate of removal the dye is faster at lower concentration and decreases with increasing concentration. It is apparent from the figure that with increasing concentration of the dye from 1.0×10^{-5} to 9×10^{-5} M, the percentage removal decreases from 99 to 82% for AC and 80 to 55.4% for ASD. Adsorption of the dye was found to increase linearly with increasing concentration of adsorbate for AC in the concentration range from 1×10^{-5} to 9×10^{-5} M whereas for ASD it increases from 1×10^{-5} to 6×10^{-5} M and then it becomes constant indicating the maximum adsorption capacity of the adsorbent at 6×10^{-5} M for ASD. Hence, all further studies were carried out at concentration 6×10^{-5} M for both the adsorbents.

3.5. Effect of particle size on adsorption process

The variation of the rate of adsorption of the substrate with different particle size of adsorbent is another method that is useful for the characterization of the rate-limiting mechanism of a particular system. In the present investigations different particle sizes were taken at a fixed dose (0.5 g/L for AC and 2.5 g/L for

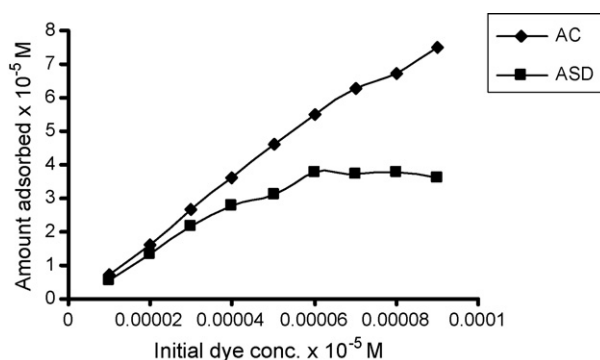


Fig. 4. Effect of initial dye concentration on the adsorption of congored (6×10^{-5} M) by AC and ASD at 30°C and pH 6.5.

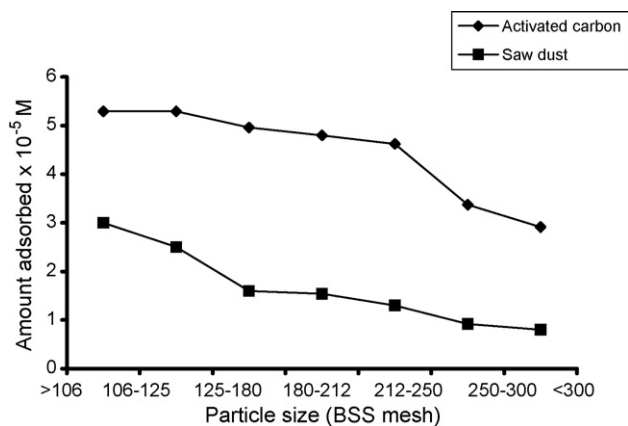


Fig. 5. Effect of particle size on the adsorption of conged (6×10^{-5} M) by AC and ASD at 30°C and pH 6.5.

ASD) and pH (6.5) and adsorption of the dye over both the adsorbents was monitored (Fig. 5). For both AC and ASD, adsorption decreased with increasing particle size. Maximum adsorption (about 94.5% for AC and 76.6% for ASD) could be achieved at the particle size (<106 BSS mesh). High adsorption by both adsorbents with smaller particle sizes is due to the availability of more specific surface area on the adsorbent [27]. Hence, all further studies were carried out using (<106 BSS mesh) size of granules of both adsorbents (Fig. 5).

3.6. Effect of temperature on adsorption process

Temperature has important effects on the adsorption process. As the temperature increases, rate of diffusion of adsorbate molecules across the external boundary layer and internal pores of the adsorbent particle increases. Changing to temperature will change the equilibrium capacity of the adsorbent for particular adsorbate [28].

Fig. 6 shows effects of different temperatures for conged adsorption on both the adsorbents. The rate of uptake of dye with both the adsorbents was found to increase with increase in temperature, thereby indicating the process to be endothermic in nature.

3.7. Adsorption isotherms

The adsorption studies were conducted at a fixed initial concentration of conged with varying adsorbent dose. The equilibrium data were analyzed by Langmuir and Freundlich isotherms. These isotherms are useful for estimating the total amount of adsorbent needed to adsorb a required amount of adsorbate from solution.

3.7.1. Langmuir isotherm

Adsorption isotherm data have been described by the Langmuir adsorption isotherm [29]. The Langmuir isotherm has been used by many workers to study the sorption of a variety of compounds. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The linear form of the isotherm was analyzed in the

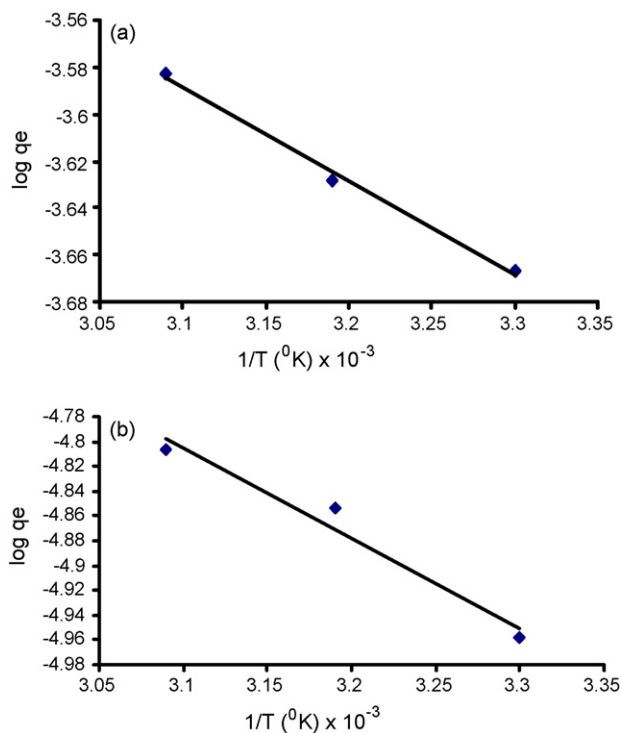


Fig. 6. Effect of temperature on the adsorption of conged (6×10^{-5} M) by (a) AC and (b) ASD at pH 6.5.

light of the model.

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \quad (1)$$

where q_e is the amount adsorbed (mol/g) and C_e is the equilibrium concentration of the adsorbate (mol L^{-1}). Q_0 and b are the Langmuir constants related to maximum adsorption capacity and energy adsorption, respectively. When $1/q_e$ is plotted against $1/C_e$, a straight line with slope $1/bQ_0$ is obtained, which shows that the adsorption of conged over AC and ASD follows the Langmuir isotherms in Fig. 7, for both the adsorbents. Langmuir constants are calculated and the values of these constants at 30 , 40 , and 50°C are given in Table 1.

3.7.2. Freundlich isotherms

The adsorption data for adsorption over activated carbon and activated sawdust were also found to be fitted to the linear form of the Freundlich equation [30]

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (2)$$

where q_e is the amount adsorbed (mol/g) and K_f and n are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. When $\log q_e$ was plotted against $\log C_e$, straight line with slope $1/n$ was obtained, which shows that the adsorption of dye over AC and ASD follows the Freundlich isotherms. Fig. 8 was used to calculate the Freundlich constants K_f and n for activated carbon and activated sawdust, respectively, and their values are given in Table 2.

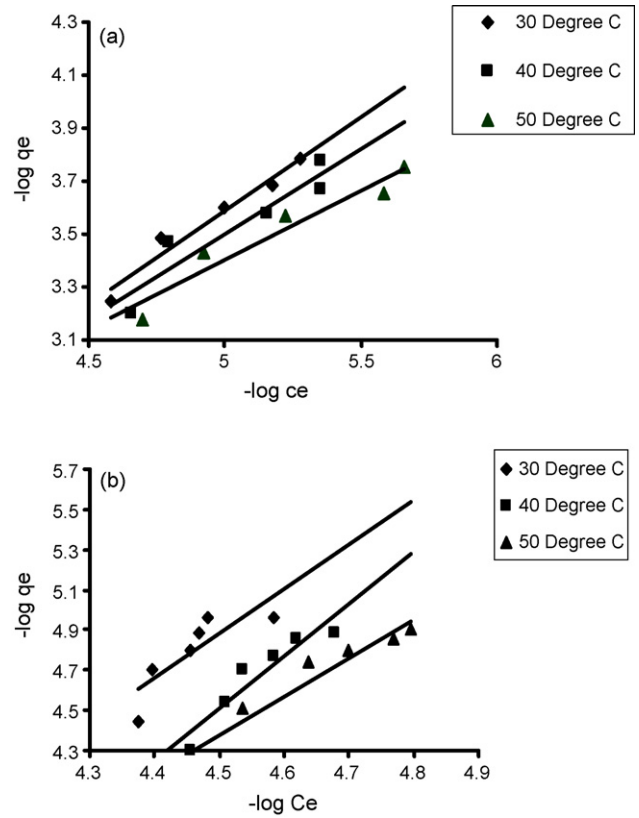
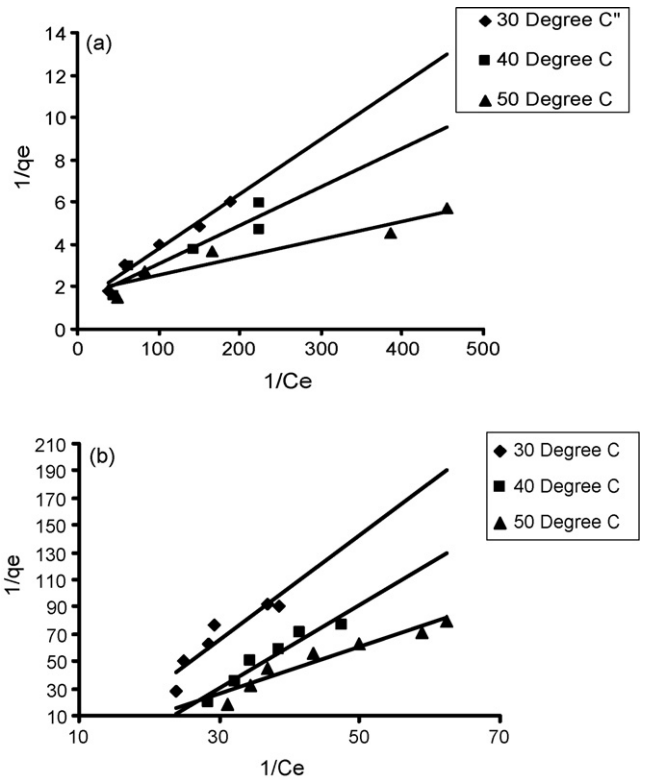


Fig. 7. Langmuir adsorption isotherms of congored by (a) AC and (b) ASD at different temperatures.

Fig. 8. Freundlich adsorption isotherms of congored by (a) AC and (b) ASD at different temperatures.

3.8. Thermodynamic parameters

Thermodynamic parameters for the adsorption of congored on AC and ASD were calculated using the following equations and the values are given in Table 3.

$$\Delta G^\circ = -RT \ln b \tag{3}$$

$$\Delta H^\circ = -R \left[\frac{T_2 T_1}{(T_2 - T_1)} \right] \ln \left(\frac{b_2}{b_1} \right) \tag{4}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \tag{5}$$

The negative values of ΔG° indicate that adsorption of congored with both the adsorbents was spontaneous, while positive ΔH° values indicative of endothermic nature of the adsorption [31]. The negative ΔS° values for the adsorbents show decreased randomness at the solid solution interface during the adsorption of dye.

Table 1
Langmuir constants for the adsorption of congored over activated carbon (0.2 g/L) and activated sawdust (2.5 g/L) at pH 6.5 and different temperatures

Temperature (°C)	Activated carbon			Activated sawdust		
	b (mol g ⁻¹)	Q^0 (L mol ⁻¹)	R^2	b (mol g ⁻¹)	Q^0 (L mol ⁻¹)	R^2
30	44.369	0.8668	0.9659	12.959	0.02009	0.859
40	67.77	0.8107	0.8763	20.159	0.01624	0.931
50	199.917	0.5884	0.9025	15.183	0.03810	0.9212

Table 2
Freundlich constants for the adsorption of congored over activated carbon (0.2 g/L) and activated sawdust (2.5 g/L) at pH 6.5 and different temperatures

Temperature (°C)	Activated carbon			Activated sawdust		
	K_f	n	R^2	K_f	n	R^2
30	1.0493	1.4017	0.9636	7.62×10^{-6}	0.4501	0.6799
40	1.8369	1.5460	0.8818	57.78×10^{-9}	0.3830	0.8913
50	6.1602	1.9120	0.926	47.51×10^{-6}	0.5173	0.8976

Table 3

Thermodynamic parameters and values of rate constant (K_{ad}) for the uptake of congored over activated carbon (0.2 g/L) and activated sawdust (2.5 g/L) at pH 6.5

Adsorbents	$-\Delta G^\circ$ (kJ mol $^{-1}$)	ΔH° (kJ mol $^{-1}$)	$-\Delta S^\circ$ (J K $^{-1}$ mol $^{-1}$)	K_{ad}		
				30 °C	40 °C	50 °C
Activated carbon	9.55×10^3	90.94×10^3	331.67×10^3	100.64×10^{-3}	74.15×10^{-3}	331.67×10^{-3}
Activated sawdust	6.45×10^3	23.83×10^3	57.37×10^{-3}	6.45×10^3	23.83×10^3	57.37×10^{-3}

3.9. Adsorption rate constant study

To determine the specific rate constant of adsorption process of activated carbon and activated sawdust, Lagergren's first order rate expression was applied [32] by using following equation:

$$\log(q_e - q_t) = \log q_e - \frac{K_{ad}}{2.303} \times t \quad (6)$$

where q_e and q_t signify the amount adsorbed at equilibrium and time t , respectively. The plots between $\log(q_e - q_t)$ and t were found to be linear for both the systems (Fig. 9). The correlation coefficients for AC at 30, 40 and 50 °C are 0.9042, 0.9816, and 0.90. Whereas for ASD correlation coefficients are 0.90, 0.92, and 0.9673 at 30, 40 and 50 °C, which clearly confirm the first order nature of the processes in each case. The K_{ad} values evaluated, for each system, from the respective Lagergren plot are listed in Table 3. For Pseudo second order model, the correlation coefficients for both the adsorbents are <0.82 which shows that the adsorption of congored over both adsorbents is not a pseudo second order reaction.

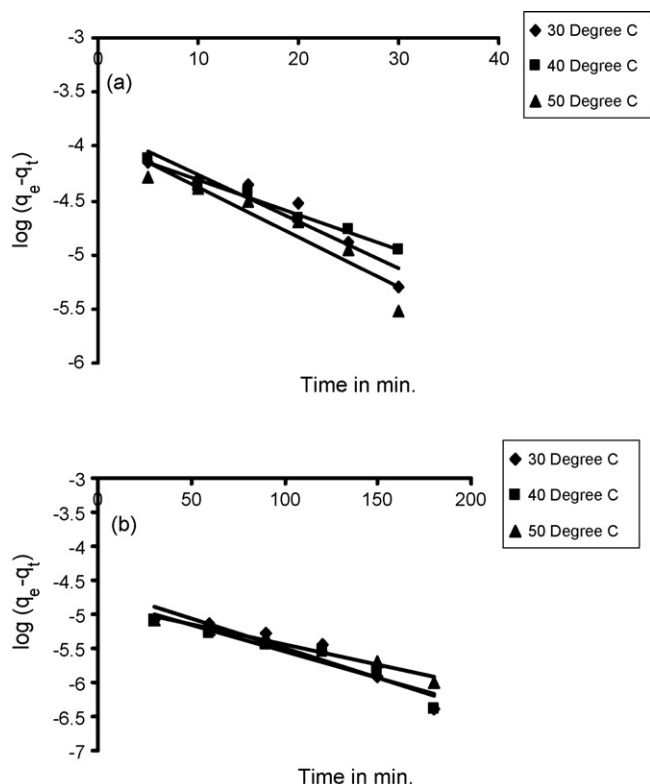


Fig. 9. Lagergren plots of congored by (a) AC and (b) ASD at different temperatures.

4. Chemical oxygen demand

COD test is widely employed as means of measuring the pollution strength of domestic and industrial wastes. COD of initial colored, and treated filtrate of AC and ASD solutions was determined. Usual 2 h open reflux method [33] was applied for the COD determination and the treated solution showed a significant decrease in COD value of the initial color solution (6×10^{-5} M) from initial 900 mg/L to final 198 and 242 mg/L of the treated solution with 89.9 and 73.5% COD removal efficiency, indicating good potential of employing adsorption.

5. Conclusions

On the basis of results obtained, it can be safely concluded that both activated carbon and activated sawdust act as potential adsorbents for the removal of congored from wastewater. Activated sawdust is a cheap and easily available material that thus can act as a better replacement for activated carbon. Being a waste product, the use of activated sawdust as adsorbent would also solve their disposal problem. In view of all these findings, it may be concluded that the developed adsorbent is very useful, economic, and reproducible for the removal of congored. This system can be used for the successful removal of congored from wastewater and any other effluent.

References

- [1] A. Bhatnagar, A.K. Jain, A comparative adsorption study with different industrial wastes as adsorbents for removal of cationic dyes from water, *J. Colloid Interface Sci.* 281 (2005) 49–55.
- [2] N. Kannan, M.M. Sundaram, Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—A comparative study, *Dyes Pigments* 51 (2001) 25–40.
- [3] M. Isik, D.T. Sponza, A batch study for assessing the inhibition effect of direct yellow 12 in a mixed methanogenic culture, *Process Biochem.* 40 (2005) 1053–1062.
- [4] F. Kargi, S.S. Ozmihci, Biosorption performance of powdered activated sludge for removal of different dyestuffs, *Enzyme Microb. Technol.* 35 (2004) 267–271.
- [5] F.L. Slejko, *Adsorption Technology: A Step by Step Approach to Process Evaluation Application*, Marcel Dekker, New York, 1985.
- [6] I.H. Suffet, M.J. McGurie, *Activated Carbon Adsorption of Organics from Aqueous Phase*, Ann. Arbor, Michigan, 1985, pp. 1–2.
- [7] J.P. Chen, M. Lin, Equilibrium and kinetics of metal ion adsorption on to commercial H-type granular activated carbon experimental and modeling studies, *Water Res.* 35 (2001) 2385–2394.
- [8] Y.S. Ho, C.C. Chiang, Sorption studies of acid dye by mixed sorbents, *Adsorption* 7 (2001) 139–147.
- [9] V. Meshko, L. Markovska, M. Mincheva, A.E. Rodrigues, Adsorption of basic dyes on granular activated carbon and natural zeolite, *Water Res.* 35 (2001) 3357–3366.

- [10] F.C. Wu, R.L. Tseng, R.S. Juang, Kinetic modeling of liquid phase adsorption of reactive dyes, metal ions on chitosan, *Water Res.* 35 (2001) 613–618.
- [11] X.Y. Yang, B. Al-Duri, Application of branched pore diffusion model in the adsorption of reactive dyes on activated carbon, *J. Chem. Eng.* 83 (2001) 15–23.
- [12] V.K. Gupta, A. Ali, Adsorbents for water treatment: low-cost alternatives to carbon, in: H. Arthur (Ed.), *Encyclopedia of Surface and Colloid Science*, vol. 1, Marcel Dekker, USA, 2002, pp. 136–166.
- [13] F.C. Wu, R.L. Tseng, R.S. Juang, Adsorption of dyes, humic acid from water using chitosan-encapsulated activated carbon, *J. Chem. Technol. Biotechnol.* 77 (2002) 1269–1279.
- [14] R.L. Tseng, F.C. Wu, R.S. Juang, Liquid-phase adsorption of dyes, phenols using pinewood-based activated carbons, *Carbon* 41 (2003) 487–495.
- [15] C. Namasivayam, N. Muniasamy, K. Gayatri, M. Rani, K. Ranganathan, Removal of dyes from aqueous solution by cellulosic waste orange peel, *Bioresour. Technol.* 57 (1996) 37–43.
- [16] C. Namasivayam, D. Prabha, M. Kumutha, Removal of direct red and acid brilliant blue by adsorption onto banana pith, *Bioresour. Technol.* 64 (1998) 77–79.
- [17] G. McKay, G. Ramprasad, P.P. Mowli, Equilibrium studies for the adsorption of dye stuffs from aqueous solution by low cost materials, *Water, Air, Soil Pollut.* 29 (1986) 273–283.
- [18] K.R. Ramkrishna, T. Viaraghavan, Dye removal using low cost adsorbents, *Water Sci. Technol.* 36 (1997) 189–196.
- [19] K.G. Bhattacharya, A. Sharma, Kinetics and thermodynamics of methylene blue adsorption on neem (*Azadirachta indica*) leaf powder, *Dyes Pigments* 65 (2005) 51–59.
- [20] M. Dogan, M. Alkan, A. Turkyilmaz, Y. Ozdemir, Kinetics and mechanisms of removal of methylene blue by adsorption on perlite, *J. Hazard. Mater.* 109 (2004) 141–148.
- [21] P. Waranusantigul, P. Pokethitiyook, M. Kruatrachue, E.S. Upatham, Kinetics of basic dye (methylene blue) biosorption by gyan duckweed (*spirodela polyrrhiza*), *Environ. Pollut.* 125 (2003) 385–392.
- [22] M. Otero, F. Rozada, L.F. Calvo, A.I. Garcia, A. Moran, Kinetic and equilibrium modeling of methylene blue removal from solution by adsorbent materials produced from sewage sludges, *Biochem. Eng. J.* 15 (2003) 59–68.
- [23] D.N. Jadhav, A.K. Vanjara, Removal of phenol from wastewater using sawdust, polymerized sawdust and sawdust carbon, *Ind. J. Chem. Technol.* 11 (2004) 35–41.
- [24] R. Jain, S. Sikarwar, Photocatalytic and adsorption studies on the removal of dye conged from wastewater, *Int. J. Environ. Pollut.* 27 (2006) 158–178.
- [25] G. McKay, M.S. Otterburn, J.A. Aga, Filters earth and fire clay as adsorbents for dyestuffs-equilibrium and rate studies, *Water, Air, Soil Pollut.* 24 (1985) 307–322.
- [26] S. Preethi, A. Sivasamy, S. Sivanesan, V. Ramamurthi, G. Swaminathan, Removal of safranin basic dye from aqueous solutions by adsorption onto corncob activated carbon, *J. Ind. Eng. Chem. Res.* 45 (2006) 7627–7632.
- [27] G. Karthikeyan, K. Anbalagan, N. Muthulakshmi, Adsorption dynamics and equilibrium studies of Zn (II) onto chitosan, *J. Chem. Sci.* 116 (2004) 119–127.
- [28] Z. Al-Qodah, Adsorption of dyes using shale oil ash, *Water Res.* 34 (2000) 4295–4303.
- [29] I. Langmuir, The constitution and fundamental properties of solids and liquids, Part 1. Solids, *J. Am. Chem. Soc.* 38 (1916) 2221–2295.
- [30] H. Freundlich, W. Heller, Rubber die adsorption in lusungen, *J. Am. Chem. Soc.* 61 (1939) 2228–2230.
- [31] V.K. Gupta, I. Ali, D. Mohan, Equilibrium uptake and sorption dynamics for the removal of a basic dye (basic red) using low cost adsorbents, *J. Colloid Interface Sci.* 265 (2003) 257–264.
- [32] Y.S. Ho, G. McKay, The sorption of lead (II) on peat, *Water Res.* 33 (1999) 578–584.
- [33] APHA, *Standard Methods for Water and Wastewater Examination*, 19th ed., Am. Public Health Assoc., Washington, DC, 1995.