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UPTAKE OF DYES FROM AQUEOUS SOLUTION BY USING *OPERCULINA TURPETHUM-A BIOMATERIAL*

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ABSTRACT

A carbonaceous sorbent prepared from an indigenous agricultural waste *Opercuuna turpethum* (Convolvulaceae), by acid treatment was tested for its efficiency in removing basic dyes (Auramine-O, Methylene Blue and Rhodamine B) from aqueous solution . Preliminary studies have shown that the removal was faster with less time and less adsorbent dose required for maximum removal. Thermodynamic parameters obtained from the temperatures studies revealed that uptake process is endothermic and spontaneous.

INTRODUCTION

Owing to the high cost of conventional adsorbents, in recent years numerous low cost alternative materials have been evaluated, as documented in the series of reviews (Pollard, *et al.* 1992 and Namasivayam, 1995), for the removal of heavy metals and dyes from water and wastewater (Mohammad, 1997 and Babel and Kumiawan, 2003).Waste agricultural materials have been used for many years as a source of carbon. Normally the feed material is heated to high temperature (700-1200 °C) to remove the volatile matter and the resulting carbon is then activated either physically or chemically. Carbonization of agricultural materials can also be performed by dehydration with sulphuric acid and phosphoric acid. Such carbons have been reported to have the capability of decolourising dyes and possess ion exchange properties related to the presence of surface functional groups on the carbon (Hanzawa and

Satonaka, 1995).

MATERIALS AND METHODS

Preparation of carbon

Operculina Turphethum root was collected from Thanjavur district, S.India and chopped into small pieces. Carbon was prepared as (Stephen Inbaraj and Sulochana, 2001) from root by treating the chopped pieces with concentrated sulphuric acid (sp. gr. 1.84) in a weight ratio of 1:1.8 (root : acid). The resulting black product was kept in an air-oven maintained at 160° ± 5°C for 6 h followed by washing with distilled water until free of excess acid and dried at 105°± 5°C. The carbon product obtained was ground designated as OTC, and the portion retained between 44 and 89 µm sieves was used for dye adsorption experiments.

Adsorbates

Auramine-O (Au-O), methylene blue(MB) dyes were supplied by Bayer and rhodamine-B (Rh-B) dye was supplied by Ciba-Geigy. From the stock solutions of each dye (1000 mg/L) desired dye concentration solutions were prepared by making suitable dilutions with distilled water to a known volume.

Adsorption experiments

Batch experiments were carried out by agitating 100 mL of adsorbate solution of desired concentration with a known weight of OTC , after adjusting the solution pH to 6.0 for dye adsorption taken in 200 mL polythene containers in an orbital shaker (250 rpm) equipped with incubation hood for regulating temperature (Scigenics - Orbitek LTH) . After equilibrium is achieved, samples were withdrawn from the shaker, centrifuged and the supernatant solution was analysed for residual adsorbate concentration. Initial dye solution of 40 mg/L was taken for time and pH studies, 100 mg /L for temperature studies and in the case of adsorbent dose studies, 60 mg/L was taken for dye OTC, system. The aforementioned conditions apply for all dye and metal adsorption systems, except Rh-B-PCC system for which 30 mg /L was taken for all the studies. A known carbon dose of 0.20, 0.40, 1.50, 0.30, 0.50 and 0.30 g/L was added for Au-O-OTC, MB-OTC, Rh-B-OTC systems respectively, in time, temperature and pH studies. The pH of the adsorbate solution was adjusted using small amounts of dilute hydrochloric acid or sodium hydroxide. Equilibrium time of 12 h was maintained for dose studies and 6 h for temperature studies.

Analytical methods

The residual dye concentrations were measured in the visible region at their respective maximum wavelengths (432 nm for Au-O, 665 nm for MB and 553.8 for Rh-B), spectrophotometrically using Jasco double beam Spectrophotometer (UVIDEC-430B). The results are shown in Table 1. and their thermodynamic parameters are in Table 2.

RESULTS AND DISCUSSION

The results indicate that the removal of dyes are dependent on time, adsorbent dose and temperature . The removal increased with increase in adsorbent dose in the case of both dyes and metals studied. This may be attributed to the availability of more binding sites for adsorption as the Au-O-OTC, MB-OTC and Rh-B-OTC dose was increased molecules, thus allowing prevalence of randomness in the system (Kadirvelu and Brasquet, 2000).

As the temperature of the system was increased, there was an increase in the percent removal and dyes and metals, indicating the endothermic nature of the process. The enhancement of adsorption capacity on increasing the temperature may be due to increase in the mobilit.y McKay *et al.* 1982) and diffusion of adsorbate species. Since diffusion is an endothermic process, it would be expected that an increased solution temperature would result in the enlargement of pore size due to "activated diffusion" causing the micropores to widen and deepen ("pore burrowing") and create more surface for adsorption (Giles *et al.* 1974).

Thermodynamic parameters like change in enthalpy (ΔH°) , change in entropy (ΔS^0) and change in free energy (ΔG°) were determined using the relations in Eqs. 1-3 (Namasivayam and Yamuna, 1995).

$$Kc = \frac{C_{Ac}}{Ce} \qquad (1)$$

$$\Delta G^0 = -RT\ln K_c \qquad (2)$$

$$\log K_c = \frac{\Delta S^0}{2.303\ R} - \frac{\Delta H^0}{2.303\ RT} \qquad (3)$$

Where Kc is the equilibrium constant, C_{Ac} and C_e are the solid phase and liquid phase concentration, respectively, at equilibrium (mg/L), t is the temperature in Kelvin (K) and the is me gas constant. The decrease in AG° values while increasing the temperature indicates the spontaneous nature of the process at higher temperatures. The ΔH° and ΔS° were obtained from the slope and intercept of the van't Hoff plot of logKc versus 1/T. The positive value of ΔH° confirms the endothermic adsorption of dyes on the adsorbents. The positive value of ΔS^0 show increased randomness at the solid solution interface during adsorption and reflects the affinity of OTC for adsorbate species studied (Kelleher, *et al.* 2002). The adsorbed water molecules, which are displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate.

There was no significant influence on dye adsorption while changing the pH, The absence of any influence of pH indicates the strong affinity of large

Table 1
Effect of time, adsorbent dose and temperature on the removal of dyes

Dye	% of Removal								
	Time			Dose(g/l)			Temperature (*C)		
	20	60	180	0.2	0.3	0.4	30	40	50
Au-O[b]	53.5	95.2	96.0	7.8	72.0	73.4	94.1	95.2	96.3
MB*	93.5	97.0	97.6	86.3	87.7	88.3	85.9	95.4	96.6
Rh-B[e]	63.2	64.1	66.1	72.4	82.3	83.4	87.3	92.1	93.4

Table 2
Effect of temperature on dye adsorption and thermodynamic parameters

Temperature	q_e	K_C	ΔG^O (KJ/ mol)	AH* (KJ/ mol)	ΔS^O (J/mol/K)
AU-O-OTC System					
303	470.5	15.9	-6.97		
313	476.0	19.8	-7.76	63.82	191.14
323	481.5	26.2	-8.77		
MB-OTC System					
303	429.5	6.09	-4.56		
313	477	20.7	-7.88	41.49	195.31
323	483	28.4	-8.99		
Rh.B-OTC System					
303	436.6	6.87	-4.86		
313	460.5	11.66	-6.39	41.78	132.12
323	467	14.15	-7.18		

dye molecules onto adsorbents at either H^+ or OH^- ions could not influence the dye adsorption (Stephen Inbaraj and Sulochana, 2002). The strong affinity of dyes onto OTC is corroborated with the positive values of ΔS^0 obtained.

CONCLUSION

The foregoing preliminary study has revealed that the carbonaceous adsorbent prepared from *Operculina Turpethum* can be effectively used in the treatment of dyes from wastewater. This methodology is economically feasible. The results of the study reveal that the above mentioned bio material are very useful in industrial application.

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