Original Research Paper

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EQUILIBRIUM AND THERMODYNAMIC STUDIES FOR DYE REMOVAL USING BIOSORPTION.

Engineering

KEYWORDS: : Adsorption, Congo red, Isotherm, Thermodynamic Studies

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ABSTRACT

The efficiency of green adsorbent prepared from natural source for removal of a basic dye Congo red from aqueous solution is examined in this study. Batch experiments were conducted at different temperatures to study the adsorption characteristics of Congo red removal on Valoria bryopsis. The equilibrium data were analyzed using Freundlich and Langmuir, adsorption isotherms. Freundlich adsorption isotherm model gave a good fit to the experimental data. The results proved that Valoria bryopsis has good adsorption capacity towards Congo red dye removal. Thermodynamic parameters, such as free energy change (G^o), enthalpy change (H^o) and entropy change (S^o) were calculated. The analysis of experimental results revealed that Congo red adsorption on Valoria bryopsis was exothermic. Gibbs free energy change values from the experiments indicate that the adsorption process was spontaneous. Changes in values of entropy suggest that the adsorption process was favorable.

INTRODUCTION

Dyes are extensively used in textile, dyeing, paper, leather, food processing, cosmetics, and dye manufacturing industries to make their products attractable and valuable. There are more than 100,000 kinds of commercially available dyes with over 7×10^5 tons of dyes produced annually (U˘gurlu, 2009; Bulut and Aydin, 2006). In literature it is reported that annually 2% of dyes produced are discharged into effluent from manufacturing operations, while 10% is discharged from textile and associated industries (Amin, 2009, mahmoodi et al, 2011). The effluents from these industries are characterized by high alkalinity, biological oxidation demand, and chemical oxidation demand and require proper treatment before they are discharged into water streams (Kaushik and Malik, 2009). Presence of color in water inhibits the sunlight penetration into water streams and reduces photosynthetic action. Some dyes are reported to cause carcinogenic and mutagenic problems. Presence of very small concentrations of dye in water makes them unaesthetic and affects human as well as aquatic life and hence, need to be treated (K. Kadirvelu,2005; McKay, 1982; McKay et al., 1985). Dye wastewater is very difficult to treat, because of its synthetic origin and complex aromatic structure (Asha Srinivasan et al, 2010). Conventional methods such as coagulation, flocculation, activated sludge, biodegradation, oxidation, membrane separation, adsorption, and photo degradation, have been extensively used to treat effluents containing dyes. However, these methods are generally expensive, ineffective, less adaptable to a wide range of dye wastewaters, require high energy and creats high disposal problems (Banat et al., 1996, Pagga & Brown, 1986, Xu & Lebrun, 1999, Jiraratananon, Sungpet, & Luangsowan, 2000). Among the available physical and chemical processes, the adsorption process is one of the suitable, effective and economic processes in dye removal.

Recently, color removal has become a major scientific interest, and hence significant attention has been directed toward the exploration of various biosorbent materials. Numerous attempts have been made to develop an effective and

low-cost adsorbent but they have not been highly successful because of limitations of low adsorption capacity, low regeneration problem and high costs (R. Shrivastava, Chia-Yun Chen et al, suman dutta et al; Gupta et al., 2004; Srivastava, 1987; Özer et al., 2007; Hameed et al., 2007; Saeedeh Hashemian , 2011). Therefore, there is a need to find new, economical, easily available and highly effective adsorbents. In the present work, Valoria bryopsis was tested for removal of Congo red removal dye from aqueous solutions. The equilibrium and thermodynamic data of the adsorption process was investigated.

EXPERIMENTAL SECTION

Adsorption Experiments

Batch equilibration method

The adsorption experiments were carried out in batch process at 30, 40, 50 and 60 ˚C temperatures. A known weight of adsorbent material was added to 50 mL of the dye solutions with an initial concentration of 5 mg/L to 25 mg/L. The contents were shaken thoroughly using a mechanical shaker rotating with a speed of 120 rpm for three hours The solution was then filtered at preset time intervals and the residual dye concentration was measured.

Table. 1. Effect of adsorbent dosage on removal of CR dye

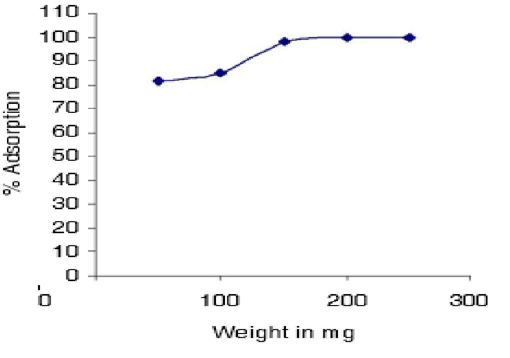
S. No	Adsorbent dosage (mg)	CR % of adsorption
1.	50	81.48
3.	150	97.77
4.	200	100.0
5.	250	100.0

Effect of variable parameters:

Dosage of adsorbent

The adsorption capacities for different doses of the adsorbent (namely 50,100,150,200 and 250mg) were determined at definite time intervals for the concentration range 50– 250 mg/L by keeping all other factors constant. The results are shown in Table1 and Figure1. It is apparent that the percentage removal of dye increases rapidly with increase in adsorbent dose, probably due to the greater availability of the exchangeable sites or the increased surface area.

Figure.1. Effect of adsorbent dosage on removal of CR dye



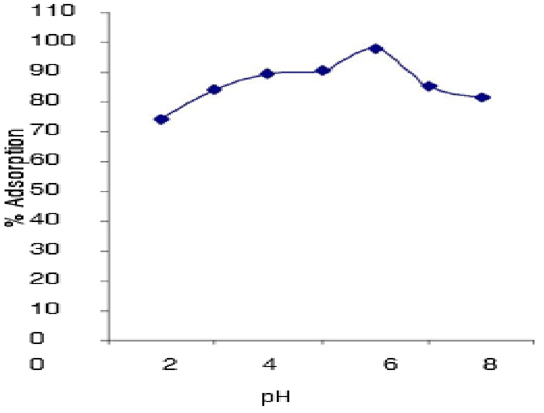
Initial concentration of dye

Experiments were conducted with different initial concentrations of dyes ranging from 5 to 25 mg/L. All other factors were kept constant.

Contact time

The effect of contact time on the removal of the dye in a single cycle was determined by keeping particle size, initial concentration, dosage, temperature, pH and concentration of other ions constant. For varying initial dye concentrations ranging from 5 to 25 mg/L. As much as 97.77% of the dye was found to be removed with a contact time of 3 hours.

Figure.2.Effect of pH on removal of Congo red using Valoria bryopsis



pH

Adsorption experiments were carried out at pH 1,2,3,4,5,6,and 7. The acidic and alkaline pH of the media was maintained by adding the required amounts ofdilute hydrochloric acid and sodium hydroxide solutions. The parameters like particle size of the adsorbents, dye concentration, dosage of the adsorbent, temperature and concentration of other ions were kept constant while carrying out the experiments. The pH of the samples were maintained using a portable pH meter, Systronics make. The pH meter was calibrated with 4.0 and 9.2 buffers. . Figure 2 shows the effect of pH on dye removal efficiencies of Valoria bryopsis. It can be observed that the removal of dye by Valoria bryopsis was maximum at pH 5.

Temperature

The adsorption experiments were performed at four different temperatures namely, 30, 40, 50 and 60˚C in a thermostat attached with a shaker, Hasthas make. The constancy of the temperature was maintained with an accuracy of ± 0.5 ºC.

Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dye. The effect of various reagents used for desorption were studied. The results with water, acetic acid , 0.1M Hydrochloric acid are presented in the Table-2.

Desorption increases with increase in theacidly of the desorbing medium. It is higher in hydrochloric acid than in acetic acid. This could be due to the increased solubility of congo red in acidic medium.

Table.2.Desportion of Valoria bryopsis

Adsorbate	% Desorption		
	H2O	ACOH	HC1
Valoria bryopsis	30.72	65.78	82.42

Table.3. First order parameters for the adsorption of Congo red using Valoria bryopsis at 30oC

Adsorbate	Mg/l	Equilibrium uptake mg/g		k 1	r 2
		$q_{e(I)}$	$q_{e(exp)}$		
Valoria bryopsis	10	3.3333	2.4424	0.02108	0.9847
	20	6.6666	8.9186	0.02799	0.9828
	30	9.9999	9.9991	0.01594	0.9094

Table.4. Pseudo second order parameters for the adsorption of Congo red using Valoria bryopsis at 30oC

Adsorbate	Mg/l	Equilibrium uptake mg/g	k 2	r 2
		q e		
Valoria bryopsis	10	3.4674	0.01550	0.9670
	20	4.5335	0.08977	0.9302
	30	10.5203	0.01773	0.5256

Adsorption Kinetics

Kinetics of the adsorption process was studied by measuring the percentage adsorption at different time intervals namely 10,20,30,40,50 and 60 min and the data fed into four kinetic models – first order, pseudo – second order, Elovic h and the intraparticle diffusion(Tables 3,4,5 & 6). The values of rate constants and adsorption capacities were measured.

Table.5. Elovic parameters for the adsorption of Congo red using Valoria bryopsis at 30oC

Adsorbate	Mg/l	A	α βE	β1	r 2
Valoria bryopsis	10	0.6699	1.1258	1.6804	0.5667
	20	0.1169	0.04164	0.3558	0.9671
	30	0.4544	0.2174	0.4785	0.7406

Table.6. Intraparticle diffusion for the adsorption of Congo red using Valoria bryopsis at 30oC

Adsorbate	Mg/l	A	k_{id}	r 2
Valoria bryopsis	10	0.4086	2.7346	0.9748
	20	1.0859	1.5907	0.9285
	30	1.7099	2.5375	0.8499

Table.7. Isotherm parameters for the adsorption of Congo red using Valoria bryopsis at 30oC

Adsorbate	Model	Model parameters			
		KL	bL	qo	r^2
Valoria bryopsis	Langmuir plot- I	20.2015	3.5454	5.6977	0.9956
	Langmuir plot- II	10.0994	1.0847	9.3135	0.9152

Freundlich plot

Adsorbate	Model	Model parameters			
		KF	1/n	n	r^2
Valoria bryopsis	Freundlich plot - I	4.9430	0.5224	1.9142	0.8460
	Freundlich plot -II	11.0773	0.8007	1.2488	0.6992

DKR plot

Adsorbate	Model	Model parameters			
		ε^2	β	qo	r^2
Valoria bryopsis	DKR plot-I	9.5113	0.04916	5.0470	0.9437
	DKR plot-II	9.2830	0.01454	2.3858	0.9992

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Adsorption Isotherms :

The results of adsorption experiments from Table . 7 were fed into three different isotherm equations- Freundlich, Langmuir and Dubinin-Kaganer-Radushkevich. Various parameters involved were calculated.

Thermodynamic Parameters:

Van't Hoff equation in the following form, was parameters such as Gibb's free energy change (change (S) were listed in Table. 8 : used to calculate the thermodynamic G), enthalpy change (H) and entropy

Table.8. Thermodynamic parameters for the adsorption of Congo red using Valoria bryopsis

Adsorbate		- G KJ / mol					
	Mg/l	30°c	40°c	50°c	60°c	H KJ / mol	S J/mol
Valoria bryopsis	25	6.7786	8.0696	9.0377	11.2059	30.1877	67.9890
	50	4.7217	6.8044	7.3967	10.2660	47.2116	170.2338
	100	4.4523	5.6028	6.9021	8.8586	36.8785	135.7409

$$\log K_c = \left(\frac{\Delta S}{2.303\,R}\right) \quad \left(\frac{\Delta H}{2.303\,R T}\right)$$

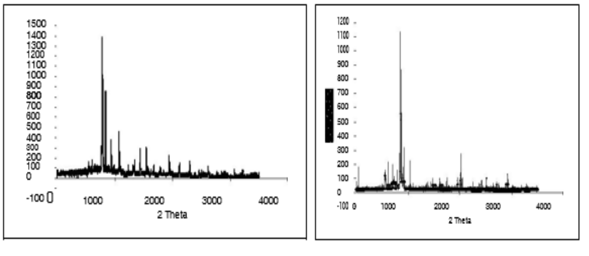
Where K_c isthe equilibrium constant for the adsorption process, TisabsoluteTemperature and R, thegasconstant,Vant Hoff plot were constructed for eachsystem andH and S were calculated from the slope and intercept of the plots respectively .

XRD Study:

Xray Diffraction Studies of the carbon prepared from the marine algaewere carried out using Rigaku corporation, JapanX-ray Diffractometer 40KV / 30mA, Model D/Max ULTIMA III .

The XRD pictures takenbefore and after adsorption are shown in fig .3 It is evident from the figure that there is no appreciable change in the spectra. This may be due to the fact that adsorption did not alter the chemical nature of the surface of the adsorbent i.e. the adsorption is physical in nature.

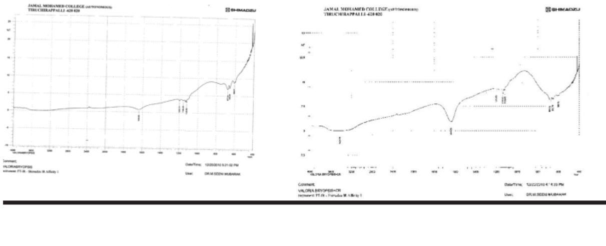
Figure 3. XRD Pattern of Valoria bryopsis before and after adsorption of congored dye



IR Study:

Fourier transform infrared spectroscopy (FTIR) was used to determine the functional groups on the carbon surface. The spectra were measured within the range of 400 -4000 cm-1 in a Shimadzu spectrophotometer. Some fundamental FTIR frequencies of the adsorbent, before and after adsorption, are presented in table 10 As can be inferred from Figure 4 the absorption frequencies are shifted to higher wave numbers with the adsorption of congo red. From th findings it is presumed that the dye was incorporated onto the adsorbent through interaction with the active functional groups.

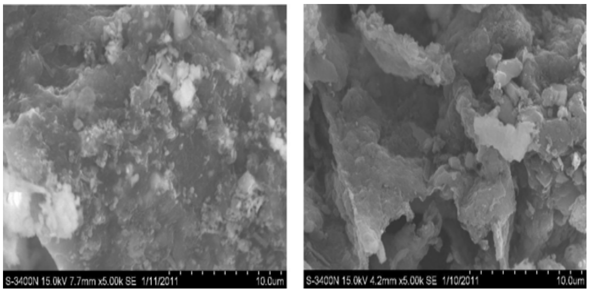
Figure 4. FTIR Spectrum of Valoriya bryopsis before and after congored dye adsorption



SEM analysis:

The surface morphology of the activated carbon was examined using scanning electron microscopy (SEM), the corresponding SEM micrographs being obtained using at an accelerating voltage of 15 kV (Hitachi SE 900) at 5000× magnification (Figure 5). At such magnification, the activated carbon particles showed rough areas of surface on which micro pores were clearly identifiable.

Figure 5. SEM micrograph of Valoria bryopsis before and after congored dye adsorption



CONCLUSION

The experimental data correlated reasonably well with the Langmuir, Freundlich and DKR adsorption isotherms. Adsorption of the dye is not favoured at around neutral pH. The amount of congo red dye adsorbed decreased with increasing ionic strength and increased with increase in temperature. The values of ΔH°, ΔS° and ΔG° show that the carbon employed has a considerable potential as an adsorbent for the removal of congo red dye.

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