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EQUILIBRIUM AND THERMODYNAMIC STUDIES FOR DYE REMOVAL USING BIOSORPTION

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ABSTRACT

The efficiency of green adsorbent prepared from natural source for removal of a basic dye Methylene Blue (MB) from aqueous solution is examined in this study. Batch experiments were conducted at different temperatures to study the adsorption characteristics of MB removal on AAS powder. 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 AAS powder has good adsorption capacity towards MB dye removal. Thermodynamic parameters, such as free energy change (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o) were calculated. The analysis of experimental results revealed that MB adsorption on AAS powder was exothermic. Gibbs free energy change values from the experiments indicates that the adsorption process was spontaneous. Changes in values of entropy suggests that the adsorption process was favorable.

KEYWORDS: Adsorption, Methylene Blue, Isotherm, Thermodynamic Studies

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, Acacia Arabica Seed (AAS) powder was tested for removal of Methylene Blue (MB) dye from aqueous solutions. The equilibrium and thermodynamic data of the adsorption process was investigated.

MATERIALS AND METHODS

Materials

All the chemicals (i.e., Methylene blue, HCl and NaOH) used in this study were supplied by coastal enterprises, visakhapatnam, India. Methylene blue dye was used directly wtih out any further purification. All solutions used in this study were prepared by using deionized water. All the glassware was washed thoroughly with tap water first and then again washed with deionized water before their use in the experiment.

Preparation of Biosorbent

The AAS material was collected from nearby forest area in steel plant, Visakhapatnam, Andhra Pradesh, India. The AAS were separated from the waste material and washed with tap water till no color was obtained in effluent water. Then it was dried in sunlight for one week, chopped into small peices of less than 1cm and grounded in a commercial mixie. The grounded material was washed several times with de-ionized water till no color is seen in the effluent. Finally this wet solid material is dried in sunlight for three weeks. After that resulted AAS powder was placed in a rotap sieve shaker consist of various sizes of meshes and shaken for 30 minutes. At the end of 30 minutes, different sized particle mixtures were collected separately and stored in a dessicator for further use.

Preparation of Dye Solutions

The desired concentration of dye stock solution was prepared by dissolving accurately weighed amount of MB dye in deionized water in 500 ml volumetric flask. It was then diluted to the required concentrations of dye (0 ppm – 150 ppm) by mixing with appropriate volumes of deionized water.

Experimental Procedure for Equilibrium Studies

Different concentrated dye solutions of 50 ml were taken in a 250 ml Erlenmeyer flasks provided with lids and required pH’s were maintained by adding 0.1N HCl or 0.1N NaOH in dropwise. These dye solutions were contacted with the 0.2 g of biosorbent and kept at 30^0C and 150 rpm in a temperature & speed controlled shaker for equilibrium time. At the end of predefined time, the samples were centrifuged at 4000 rpm for 15 minutes and supernatant dye solutions were separated carefully from the adsorbent and were analyzed for dye concentrations. Dye concentrations were determined by using UV-Vis Spectrophotometer at a wavelength corresponding to the maximum absorbance of dye. Optimum parameters such as contact time, adsorbent dosage etc., were determined from the initial studies (not shown here). All the experiments used in this were conducted in triplicate and average values were used in the analysis.

Experimental Procedure for Thermodynamic Studies

Dye solution of concentration 100 ppm was taken in a stoppered 250 ml Erlenmeyer flask. This dye solution at known pH was kept at 20^0C and 150 rpm in a temperature & speed controlled shaker for equilibrium time. After the solution reaches desired temperature it was contacted with 0.2 g of AAS powder. At the end of optimum time of contact, carefully decanted solution was centrifuged at 4000 rpm for 15 minutes and supernatant dye solution was separated carefully from the adsorbent residues and was then analyzed for dye concentration in a UV-Spectrophotometer. This procedure was repeated similarly at different temperatures from 20–40^{0}C by keeping all other parameters kept constant.

RESULTS AND DISCUSSIONS

Adsorption Isotherms

Adsorption isotherms describe the interactive behaviour of adsorbate and adsorbent. Adsorption isotherms data is very important to predict the adsorption capacities of the adsorbent at various operating conditions. Analysis of this isotherms provide the data required for the efficient design of adsorption process. In this experiments, two commonly used isotherms were evaluated. Langmuir isotherm is based on assumption that the adsorption occurs at specific homogenous sites. This model is valid for monolayer sorption onto surface and finite number of identical sites and is given by

$$Q_e = \frac{K_L C_e}{(1+a_L C_e)} \quad (1)$$

where C_e is the equilibrium concentration of adsorbate in the solution (mg/l), Q_e is the equilibrium adsorbate concentration (mg/g) on the adsorbent, a_L(L/mg) and K_L (L/g) are Langmuir constants. The maximum adsorption capacity, Q_{max} (mg/g), represents a practical limiting adsorption capacity when the surface is fully covered with dye ions and assists in the comparison of adsorption performance, particularly in cases where the adsorbent does not reach its full saturation in experiments. The characteristics of Langmuir isotherm are determined from the separation factor, R_L. It is expressed as

$$R_L = \frac{1}{(1+K_L C_o)} \quad (2)$$

where K_L (l/mg) is the Langmuir constant and C_o (mg/l) is the initial dye concentration. Adsorption process is considered to be unfavorable, linear, favorable or irreversible based on $R_L>1$, $R_L=1$, $0<R_L<1$, and $R_L=0$ respectively (Francois Renault et al. 2008; Pradeep Sekhar et al. 2009; Yuyi Yang et al. 2010). Adsorption capacities of AAS powder at various conditions, were determined by Langmuir adsorption isotherm. A linear plots of C_e/q_e versus C_e were drawn to determine Q_{max} and K_L values (Figure 1). From the Figures 1 &2 it was confirmed that the adsorption obeys both the Langmuir and Freundlich models. The Langmuir constants, Q_{max}, a_L, and K_L at different temperatures were determined from the slope and intercept of these plots and these parameter values were shown in Table-1. The adsorption isotherms of MB adsorption on AAS powder found to be linear over the whole concentration range studied and high values of R^2 strongly support the fact that dye removal data closely followed the Langmuir adsorption model. The coefficients of determination, R^2, values indicate that the Langmuir isotherm provides a good fit to the isotherm data.The values of separation factor, $R_{L,}$ for all the temperatures were in the range of 0.10 to 0.15, which shows that the MB dye removal by AAS powder was favorable. These results were in conformity with adsorption of MB on pine apple stem (Sudipta Chatterjee et al. 2010).

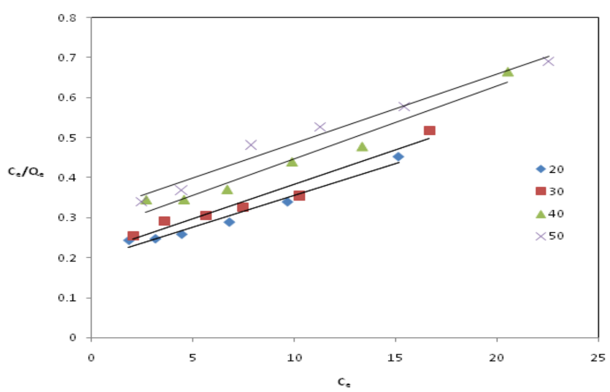

Figure 1: Langmuir Adsorption Isotherms at Various Temperatures

The empirical Freundlich isotherm model describe the non-ideal adsorption processes where adsorption takes place on heterogeneous surface. This isotherm is expressed by the following equation:

$$Q_e = K_f C_e^{1/n} \quad (3)$$

Where K_f and n are Freundlich constants characteristic of the system and they are indicators of adsorption capacity and heterogeneity of site energies, respectively (Sudipta Chatterjee et al. 2010; Li Wang, and Aiqin Wang. 2007). The values of K_f and n at different experimental temperatures were evaluated from the intercepts and slopes of the plots of ln Q_e versus ln C_e respectively. High values of K_f obtained from Figure-2 implies that the ready uptake of the dye from the solution with high adsorption capacity. n values greater than 1 indicates that the adsorption process is favorable (Yuyi Yang et al. 2010). R^2 values of Langmuir isotherm is slightly lower than R^2 of Freundlich isotherm which signals that adsorption data obeys Freundlich isotherm in better than Langmuir isotherm, which in turn indicates that adsorption process is heterogeneou in nature. (1/n) values lower than 1 implies that the process of MB adsorption on AAS power was may be due to chemical interactions between adsorbate and adsorbent (Francois Renault et al. 2008).

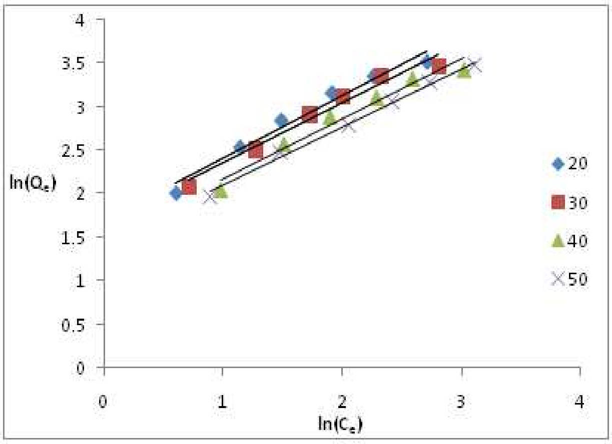

Figure 2: Freundlich Adsorption Isotherms at Various Temperatures

Table 1: Summary of Langmuir and Freundlich Isotherm Constants

Temperature, K	Langmuir Constants				Freundlich Constants		
	K_L	a_L	Q_{max}	R^2	K_f	1/n	R^2
323	3.212335	0.055895	57.47126	0.9737	4.14126	0.673	0.994
313	3.769318	0.068602	54.94505	0.9621	4.437096	0.687	0.963
303	4.746084	0.081633	58.13953	0.9533	5.212189	0.696	0.969
293	5.122951	0.082480	62.11180	0.9700	5.452095	0.714	0.970

Thermodynamic Studies

Thermodynamic parameters such as enthalpy change ΔH^o, free energy change ΔG^o and entropy change ΔS^o can be estimated using equilibrium constants changing with temperature. The free energy change of the sorption reaction is given by the following equation

$$\Delta G^o = -RT \ln(K_C) \quad (4)$$

$$\Delta G^o = \Delta H^o - T\,\Delta S^o \quad (5)$$

$$\ln K_C = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \quad (6)$$

Where ΔG^o is standard free energy change, J; R is universal gas constant, 8.314 $Jmol^{-1}K^{-1}$; T is absolute temperature. K_C is called adsorption affinity which is defined as the ratio of dye uptake and dye concentration in the aqueous solution at equilibrium (Q_e/C_e). Q_e is the amount of dye adsorbed per unit mass of adsorbent at equilibrium and C_e, the equilibrium concentration of the adsorbate in the solution.

The free energy change indicates the degree of spontaneity of the adsorption process and the negative values reflects a more energetically favorable adsorption. Positive values of ΔH^o indicates that the adsorption is endothermic, and an increase in T results in an increase in K_C. Conversely, when ΔH^o is negative, the adsorption is exothermic, and an increase in T causes a decrease in K_C (Francois Renault et al. 2008; Xubiao Yu et al. 2010).

The thermodynamic characteristics for the adsorption process were evaluated through computation of Gibb's free energy(ΔG^o), enthalpy of adsorption (ΔH^o) and entropy of adsorption (ΔS^0) from the experiments carried at four different temperatures. The free energy changes for MB dye adsorption onto AAS powder were determined by using the equilibrium concentration values obtained from Langmuir isotherm model. ΔG^o and ΔS^o values of MB dye at different temperatures (293, 303, 313, 323K) were given in Table-2. The negative values of ΔG^o confirmed the spontaneous nature of the process. The ΔG^o values obtained were in the range of -17.47 to – 31.11 kJ/mol, which were in the middle of physisorption and chemisorption, indicate that the adsorption process was a physical adsorption enhanced by a chemical effect (Francois Renault et al. 2008). The values of ΔG^o became more negative as temperature decreases which suggests that decrease in temperature was favorable for MB adsorption on AAS powder (Xubiao Yu et al. 2010). From the Figure-3, the standard enthalpy change, ΔH^o, and the standard entropy change , ΔS^o, were determined using the slope and intercept of the plot between ln K_a versus 1/T. The values of ΔH^o and ΔS^o were - 16.4387 kJ/mol and – 0.0454842 kJ/mol. K, respectively. The negative values of ΔH^o indicates that the adsorption of MB on AAS powder was physical in nature involving weak forces of attraction. On the other hand negative values of enthalpy change further indicate that adsorption was exothermic and lower temperature favours the adsorption process. Negative values of ΔS^o indicates the MB molecules were orderly adsorbed on the surface of the AAS powder (Lara Abramian, and Houssam El-Rassy, 2009).

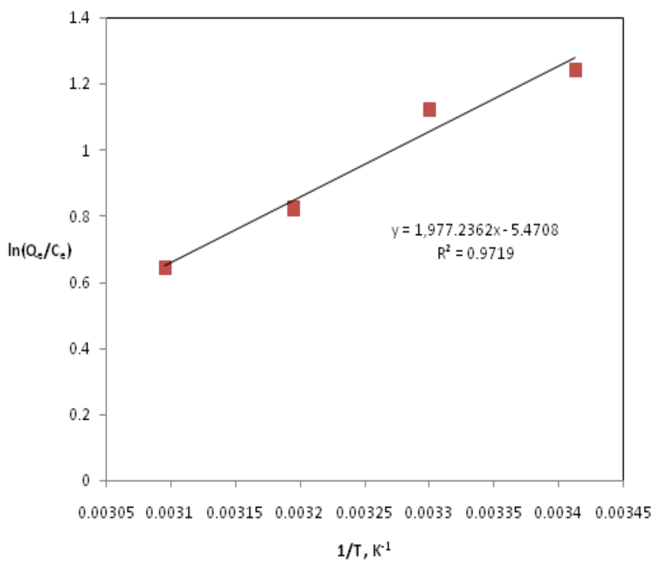

Figure 3: Calculation of Thermodynamic Parameters

Table 2: Summary of Thermodynamic Parameter

Temperature (K)	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	- ΔS^o (J/K.mol)
293	-31.1186	-16.4387	45.4842
303	-26.5702		
313	-22.0218		
323	-17.4734		

CONCLUSIONS

Adsorption studies of Methylene Blue dye from aqueous solutions onto AAS powder adsorbent were conducted. Equilibrium and thermodynamic studies were carried out by changing the initial dye concentration and temperature of solution. The influence of initial dye concentration, and Temperature on the dye removal were tested. The results indicate that MB dye adsorption on the AAS powder adsorbent was strong and it also reveals that adsorption capacities of AAS powder were affected significantly by the initial dye concentration, and temperature. Both Freundlich isotherm and Langmuir isotherm agrees well with the exprimental data, but Freundlich isotherm shows slight superiority over Langmuir isotherm in fitting the experimental data. Separation factor values indicate that adsorption process was favorable. Thermodynamic studies revealed that MB adsorption on AAS powder is exothermic in nature. Gibb's free energy values indicated the feasibility and spontaneous nature of the adsorption of MB on AAS powder adsorbent. Changes in entropy confirmed the changes in randomness at solid-liquid interface during adsorption process. Based on the results obtained, AAS powder can be considered as appropriate alternative for activated carbon for removal of dyes from aqueous solution.

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