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Full Length Research Paper

Removal of basic dye methylene blue by using bioabsorbents *Ulva lactuca* and *Sargassum*

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In the present study, the removal of textile dye methylene blue was studied by adsorption technique using adsorbents such as, alumina, *Ulva lactuca* and *Sargassum* (Maine algae). The batch technique was adopted under the optimize condition of amount of adsorbent, stay time, concentration, temperature and pH. By using uv spectrophotometer, concentration of dye was measured before and after adsorption. The removal data were fitted into the Langmuir and Freundlich adsorption isotherm equations. The values of their corresponding constants were determined. Thermodynamic parameters like free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of the systems were calculated by using Langmuir constant (K). The values of % removal and K_D for dye systems were calculated at different temperatures ranging (303 - 318 K) with the intervals of 5 ± 2°C. The present study shows that about 96% removal of dye was obtained by using biosorbents.

Key words: Methylene blue, adsorption, *Ulva, Sargassum*, alumina, biosorbents.

INTRODUCTION

Dyes are widely use in textile, paper, plastic, food and cosmetic industries. The wastes coming from these industries can effect on our atmosphere causing pollution. The level of pollutants even in very low concentration is highly visible and will affect aquatic life as well as food web. Many dyes are difficult to degrade. They are generally stable to light, oxidizing agents and are resistant to aerobic digestion (McKay and Sweeney, 1980). Hence, contaminations due to dyes pose not only a severe public health concern, but also many serious environmental problems because of their persistence in nature and non biodegradable characteristics.

The numbers of conventional methods are available for color removals from industrial effluents including ion exchange, adsorption, membrane technology and coagulation (Nigam, 2000). Among all the sorption process the activated carbon has been shown to be one of the most efficient adsorbent for the removal of dyes from effluents (Malik, 2002). For the removal of textile dyes from wastewater, a number of adsorbents like agricultural by-products such as date pith, sawdust, corn corb, barley husk, rice hull and bagasse pith have a potential to be used as an alternative sorbent (Banat et al., 2003; Garg et al., 2003; Robinson et al., 2002; Low et al., 2000; Mahejabeen and Hajira, 2007). Chemical modifications of these materials enhance their sorption capacities and thus improve the treatment processes. The textile industries use a mixture of different types of dyes for different applications. Hence there is a need to have sorbents capable of removing different types of dyes (Ong et al., 2007; Janos et al., 2003).

Among the biological materials, marine algae known as seaweeds, have been reported to have high metal binding capacities due to the presence of polysaccharides, proteins or lipid on the cell wall surface containing functional groups such as amino, hydroxyl, carboxyl and sulphate, which can act as binding sites for metals (Ramelow et al., 1992; Ho, 1990) The green algae, *Ulva lactuca* and *Sargassum* are particularly useful in these respects because of its wide distribution and relatively simple structure. *U. lactuca* and *Saragassum* has sheet-like thallus structures which have two cells thickness, resulting relatively in large surface area having uniform and physiologically active cells (Turner et al., 2007). *U. lactuca* is a widespread algae along the shores of Turkey. It grows well along the Black Sea coasts (Tüzen, 2002). In the present study the removal of methy-

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lene Blue dye from aqueous solution was studied using biosorbent Ulva lactuca and Saragassum as a natural, renewable bioasorbents Ulva Lactuca and Sargassum (Turner et al., 2007, El-Sikaily et al., 2007 and Sari et al, 2007).

The experimental parameters affecting the biosorption process such as pH, contact time, biomass dosage and temperature were studied. The equilibrium biosorption data were fitted in Langmuir and Freundlich adsorption isotherm equation. Thermodynamics parameters were also estimated in order to study the nature of the system.

MATERIALS AND METHODS

Reagents

Reagents include methylene blue C.I. 52015 (Merck), hydrochloric Acid (Merck), sodium hydroxide (Merck), activated alumina (Al_2O_3) (Merck). All chemicals used in the present investigation were spectroscopic grade. They were of ultra high purity (guaranteed 99.9%).

Biosorbents

U. Lactuca and *Sagrassum* were collected from the sand spit sea side near Karachi coast, Pakistan. They were washed thoroughly with tap water, then distilled water and dried in oven at 60 ± 2°C for over night in order to remove moisture and physiosorbed species. The dry constant was grind to obtain 100 micron mesh size and then it was use for adsorption studies.

Experimental

Stock solution of 1×10^{-3} M of methylene blue dye was prepared in double distilled water in 250 ml volumetric flask then it was diluted to 1×10^{-4} M to 1×10^{-6}.

Optimization of stay time

The stay time for Methylene blue-alumina system was determined by preparing a bed of 0.2 g of alumina in the column and then adds 50 ml of 3×10^{-6} M methylene blue dye for different time intervals. The absorbance was measured by using UV visible Spectrophotometer (CE 7400) at different time intervals ranging from (5 to 100 min) at 665 nm wave length.

Optimization of concentration

In order to find out the optimum concentration, 0.2 g of alumina was taken in a number of columns. A solution of different concentrations (1×10^{-6} to 1×10^{-4}) was prepared and passes through the columns, under optimized stay time and amount of adsorbent. The absorbance of filtrate was measured by using uv spectrophotometer (CE 7400).

Optimization of pH

7×10^{-6} M solution of methylene blue was prepared for the determination of optimum pH of methyene blue-alumina system. Solutions of different pH's solutions were prepared by using of 0.1 M HCl and 0.1 M NaOH. 50 ml of dye solution was added using the optimum amount of adsorbent (0.2 g) and then keep for 25 min. The absorbance of filtrate was measured and optimum pH was selected for further studies.

Study of adsorption isotherms

For the study of adsorption Isotherms different concentrations of methylene blue dye having concentrations 1×10^{-6}, 1×10^{-5}, 3×10^{-5} M was prepared. 50 ml of each dye content was taken into volumetric flasks using optimum amount of alumina, *Ulva*, and *Saragassum*. These flasks were placed in Thermostat bath (WBM 301) at desired temperature and then shaken for optimum time using 120 rpm.

RESULTS AND DISCUSSION

Calibration curve

Standard calibration methods were adopted for all the adsorption systems. The Beer's law generally holds over a wide range of concentrations. The state of colored ions in the dissolved state does not change with concentration. Discrepancies are usually found when solute molecules were ionized, dissociated or associated.

Effect of amount of adsorbent

The effect of amount of adsorbent (alumina) on the adsorption of methylene blue dye system was studied. The amount of adsorbent was varied from 0.1 to 1.0 g using concentration of dye 3×10^{-6} M. The 0.2 g adsorbent system show optimum adsorption. The results are shown in Figure 1.

Effect of stay time on adsorption

The effect of stay time for the adsorption of dye was studied for all the adsorption systems. The time was varied from (5 to 100 min). At 25 min the adsorption systems show best adsorption capacity compared to other time intervals. The results are shown in Figure 2.

Effect of concentration

The effect of dye concentration methylene blue on the adsorption of alumina was studied under the optimized conditions of time and amount of alumina. The concentration of dye was varied from 1×10^{-6} to 1×10^{-4} M. The results are shown in Figure 3.

Effect of pH

Take 50 ml of 7×10^{-6} M methylene blue dye for the adsorption studies. Under the optimized conditions of amount, stay time and concentration samples were run at room temperature (25 ± 2°C). The pH of dye solutions

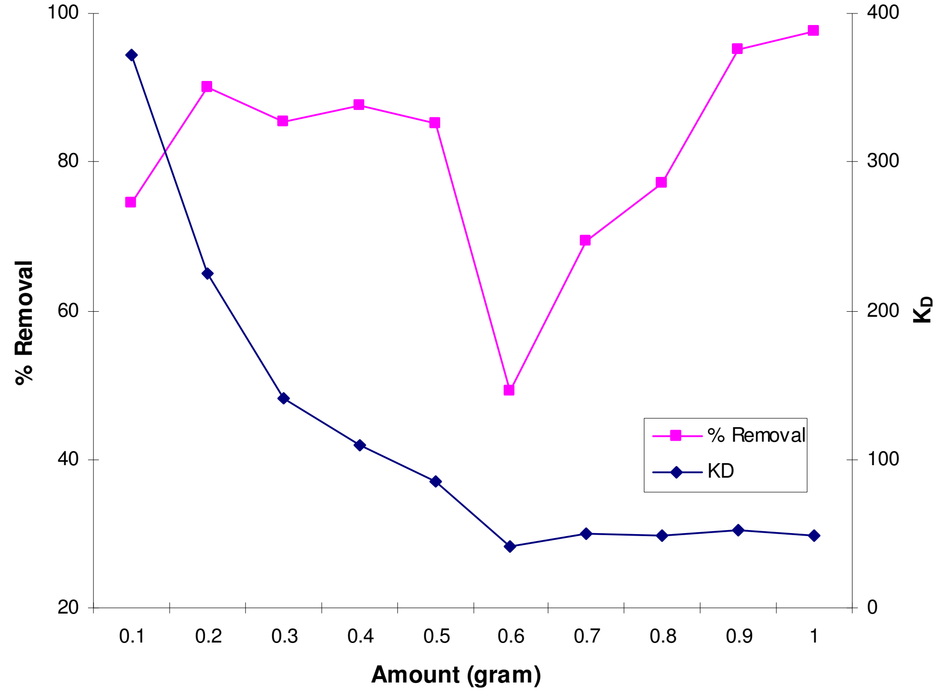

Figure 1. Optimization of amount of alumina for methylene blue.

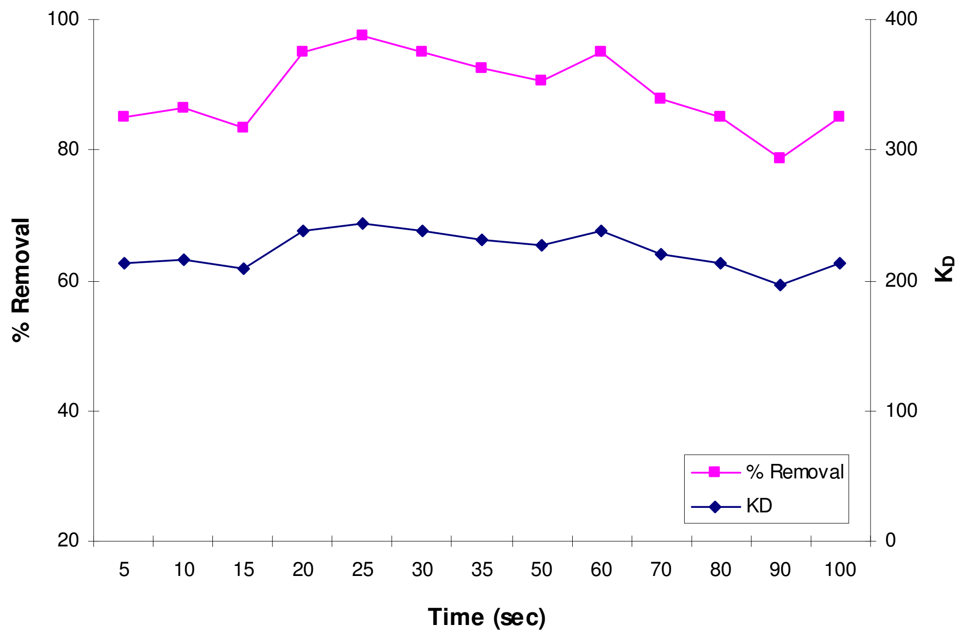

Figure 2. Optimization of time for methylene blue alumina system.

was varied from 2 -9 by using acid – base combination NaOH (0.1 M) and HCl (0.1 M). pH 7.0 was selected for further studies. The results are shown in Figure 4.

Adsorption isotherms

An adsorption isotherm is a graphical representation ad-

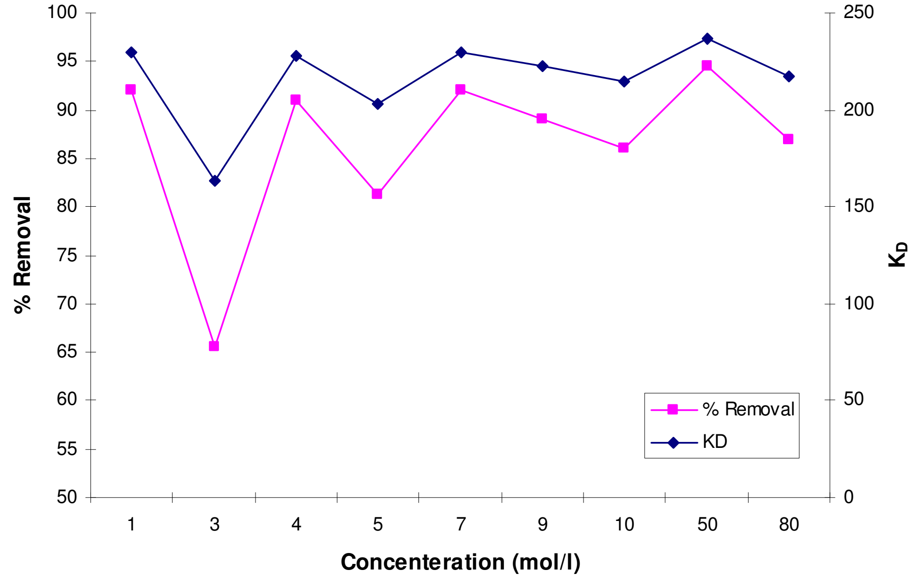

Figure 3. Optimization of concentration for methylene blue.

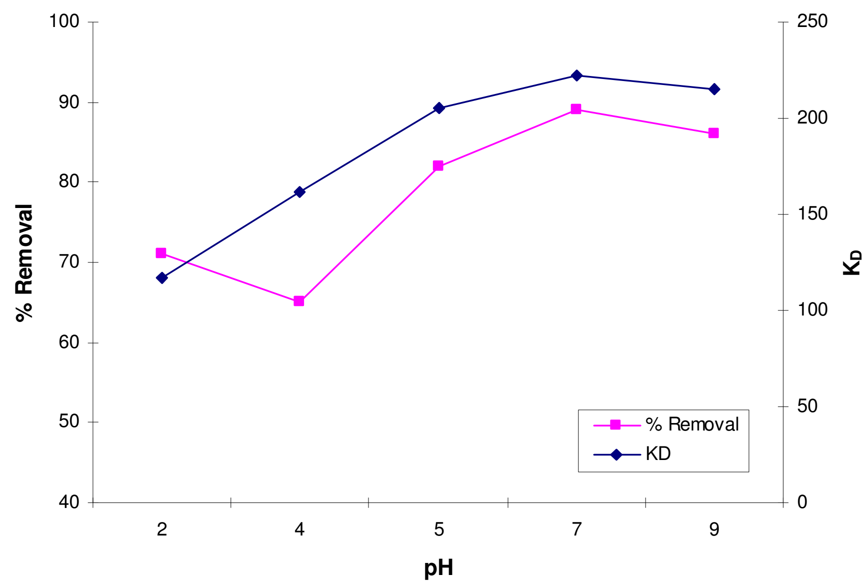

Figure 4. Optimization of pH for blue alumina system.

showing the relationship between the amount adsorbed by a unit weight of adsorbent and the concentration of sorbent remaining in the medium at equilibrium. It maps the distribution of adsorbed solute between the liquid and solid phases at various equilibrium concentrations. The adsorption isotherms were based on the data that are specific for each system. Adsorption isotherm for methylene blue dye on alumina system was obtained under the optimized conditions of amount of adsorbent, stay time, concentration and pH. The adsorption isotherms were determined at different temperatures are given in Table 1. These isotherms are classified as L, S and C type according to Giles classification (Afzal et al., 1992). The adsorption mechanism will be clear if we discuss the surface of adsorbent. At 60℃ for all the adsorbents, will remove the physisorbed species but chemisorbed species will remain on the surface. The methylene blue dye was adsorbed on the surface of alumina and biosorbents making it is easy to purify textile waste water bearing dye contents.

Table 1. Adsorption isotherm of methylene blue dye adsorption on *Ulva*, *Sargassum* and alumina systems.

S/N	Adsorption system	Concentration (mole/L)	%Removal			
			303 K	308 K	313 K	318 K
1.	Methylene blue-*Ulva*	3×10^{-6}	88.4	83.0	84.0	46.7
		5×10^{-6}	88.0	96.0	84.8	84.8
		7×10^{-6}	77.7	97.0	80.5	94.3
		1×10^{-5}	88.3	98.0	85.8	82.1
		3×10^{-5}	80.4	96.3	96.9	83.0
2.	Methylene blue–*Sargassum*	3×10^{-6}	65.0	51.0	70.1	78.8
		5×10^{-6}	70.3	80.0	90.0	83.4
		7×10^{-6}	80.6	78.5	99.9	82.7
		1×10^{-5}	97.7	86.4	76.4	86.1
		3×10^{-5}	82.3	89.2	97.4	95.5
3.	Methylene blue–alumina system	3×10^{-6}	81.2	68.0	51.7	82.0
		5×10^{-6}	86.6	67.9	83.4	21.4
		7×10^{-6}	74.4	60.1	66.8	70.5
		1×10^{-5}	87.5	83.2	72.1	78.9
		3×10^{-5}	85.4	83.0	72.4	80.6

Effect of temperature on adsorption

The dependence of dye adsorption on temperature was studied within the range of temperatures 303 – 318 K at the step of ± 5°C. The monitoring of isotherms shows that there is a decrease in the value of adsorption with the rise in temperature. It shows that the process of adsorption of dye on adsorbents (alumina, *Ulva* and *Sargassum*) was exothermic in nature.

Application of theories of adsorption

Langmuir theory

The Langmuir adsorption isotherm is the best known linear model for monolayer adsorption and most frequently utilized to determine the adsorption parameters. The well known Langmuir equation is given below:

$$(Cs / X/m) = (1 / KVm) + (Cs / Vm) \quad (1)$$

Where, K is the adsorption coefficient or Langmuir constant, V_m is the monolayer capacity, X/m is the amount of dye required to form monolayer over the surface of adsorbent and C_S is the equilibrium concentration. Langmuir sorption isotherm was applied on the adsorption data. The values of constants K and Vm were calculated by Langmuir plots are given in the Table 2. The values of K gives the measure of adsorbing capacity of adsorbent and shows the nature of binding so it is called "binding constant". The values of K for methylene blue–*Sargassum* system were decreased with the rise in temperature indicating weakening of adsorbate-adsorbent interaction at high temperatures. The values of K for methylene blue–alumina system were increased with the rise in temperature except at 318 K. The methylene blue–*Ulv*a system shows non linear behavior.

Freundlich theory

The Freundlich isotherm equation is expressed as

$$\text{Log } X/m = \log K + 1/n \log Cs \quad (2)$$

Where, X/m is the amount adsorbed per unit mass of the adsorbent, C_s is the equilibrium concentration, and 1/n and K are constants. The values of Freundlich constants 1/n and K are given in Table 3. These parameters give a measure of adsorbing capacity of the adsorbent and intensity of adsorption respectively.

Thermodynamic parameters

The values of thermodynamic parameters like free energy (Δ°G), enthalpy (ΔH°) and entropy (ΔS°) of adsorption were calculated from the Langmuir constant K using the following equations.

$$\Delta G = -RT\ln K_D \quad (3)$$

$$\text{Ln}k = \Delta S/R - \Delta H/RT \quad (4)$$

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

The values of ΔH° and ΔS° were calculated from the slope and intercept of the linear variation of ln K with the reciprocal of temperature (1/T) are given in Table 4. The

Table 2. Langmuir parameters of of methylene blue dye adsorption on *Ulva*, *Sargassum* and Alumina systems.

S/N	Adsorption system	Temperature (K)	Slope (1/Vm)	Intercept (1/KVm)	Vm (mol/g)	K
1.	Methylene blue-*Ulva*	303	5.019	0.072	0.199	69.231
		308	4.118	0.024	0.242	171.59
		313	4.009	0.179	0.294	22.361
		318	4.703	0.063	0.212	74.072
2.	Methylene blue-*Sargassum*	303	4.759	0.032	0.210	145.55
		308	4.287	0.193	0.233	22.130
		313	3.974	0.181	0.251	21.881
		318	4.052	0.191	0.246	21.123
3.	Methylene Blue-alumina	303	4.508	0.217	0.221	20.721
		308	4.584	0.217	0.218	21.114
		313	5.448	0.056	0.183	95.910
		318	4.493	0.394	0.222	11.380

Table 3. Freundlich parameters of methylene blue dye adsorption on *Ulva*, *Sargassum* and alumina systems.

S/N	Adsorption System	Temperature (K)	Slope (1/n)	Intercept (log k)	n	K
1.	Methylene blue-*Ulva*	303	0.043	2.306	23.201	202.341
		308	0.213	2.386	4.690	243.720
		313	0.124	2.389	8.019	244.961
		318	0.044	2.342	22.624	220.193
2.	Methylene blue-*Sargassum*	303	0.043	2.306	23.201	202.342
		308	0.213	2.386	4.690	243.721
		313	0.124	2.389	8.019	244.960
		318	0.044	2.342	22.626	220.193
3.	Methylene blue-alumina	303	0.078	2.318	12.755	208.114
		308	0.120	2.323	8.291	210.812
		313	0.118	2.298	8.474	198.970
		318	0.372	2.407	2.685	255.500

Table 4. Thermodynamic parameters of methylene blue adsorption on *Ulva*, *Sargassum*, and Alumina systems.

S/N	Adsorption System	Temperature (K)	$\Delta H°$ (KJ/mole)	$\Delta G°$ (KJ/mole)	$\Delta S°$ (J/K)
1.	Methylene blue-*Ulva*	303	14.620	-16.210	-11.64
		308	14.620	-13.175	-11.64
		313	14.620	-8.086	-11.64
		318	14.620	-11.38	-11.64
2.	Methylene blue-*Sargassum*	303	109.55	-12.54	-0.321
		308	109.55	-7.931	-0.321
		313	109.55	-8.030	-0.321
		318	109.55	-8.066	-0.321
3.	Methylene blue-alumina	303	8.298	-7.636	0.564
		308	8.298	-7.810	0.564
		313	8.298	-11.87	0.564
		318	8.298	6.431	0.564

values of Δ°G at different temperatures are negative for all systems, which show that the adsorption process is spontaneous. The values of enthalpy were positive for all systems it reveals the endothermic behavior of the system. Whereas entropy values were negative except for methylene blue–alumina system.

Conclusions

Natural biosorbents *U. lactuca* and *Sargassum* which were collected from Clifton beach Karachi (Pakistan) shows good adsorption capacity compared to commercial adsorbent alumina. About 96% removal was obtained by using the biosorbents. By applying adsorption isotherm equations, most of the systems follow adsorption models and also show spontaneous behavior.

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