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Full Length Research Paper

Remediation of azo dyes by using household used black tea as an adsorbent

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In the present study used black tea and its impregnates were used as an adsorbents for the removal of textile dyes such as methylene blue and malachite green. The impregnation technique was adopted for the preparation of metal impregnates. The present study shows that used black tea and its impregnate exhibit adsorption tendency for the dyes. By applying batch method, the adsorption process were carried out at various temperatures ranging from 303 to 318 K ± 2 K under the optimized conditions of concentration, stay time and amount of adsorbent. Adsorption isotherm equations such as Freundlich, Langmuir and D-R were applied to calculate the values of respective constants. Thermodynamic parameters like free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were also calculated. The results show that used black tea show better adsorption tendency compared to its Impregnates.

Key words: Dyes, adsorption, black tea, removal, impregnates.

INTRODUCTION

Dyes are major ingredients of our everyday life. They are use in different industries like textile, paper, plastic, petroleum, food, paint, leather industry, drugs for photodynamic therapy against cancer and as a food colors. Many industries used these dyes during the manufacturing of their products and according to previously published reports a typical sized fabric industry consumes about 39.62 - 52.83 gallons of waters and generate about 39.62 gallons of effluent per kg of finished textile produced (Bhogle, 2007). The presence of dyes in industrial effluent is of particular concern to the environmental engineers because it can pose serious threat to the surroundings. Dyes in the waste water undergo chemical as well as biological changes. They consume dissolve oxygen from the water and destroy aquatic life. The chemicals used for the synthesis of dyes are hazardous to human life. These substances can also cause reproduction damage in human and cause cancer in the offspring of animal exposed during pregnancy. The aromatic amines are carcinogenic for humans and cause liver, bladder, intestine and skin cancer in human as well as in animals. Other chronic effects include skin allergy. It is therefore necessary to treat textile effluents prior to their discharge into the receiving water (Hameed, 2008). Discolorations are possible with one or more of the following methods; adsorption, precipitation chemical degradation, photo degradation and biodegradation. Adsorption has been found to be an efficient and economically cheap process to remove pollutants such as colors, dyes and metal impurities (Khan, 2002). Some of the adsorbent materials that have been used with varying success include rice husk (Malik, 2003; Mukhtat and Tahir, 2008), cornelian cherry, apricot stone, almond shell (Demirbas et al., 2004; Demirbas et al., 2002), cotton stalks (Attia et al., 2004), coir pith (Namasivayam and Kadirvelu, 1994), wood (Poots et al., 1978), sunflower stalks (Sun and Xu, 1997), charcoal (Khan, 1991 and Khan, 1994) and orange peel (Arami et al., 2005) were successfully employed for the removal of dyes from aqueous solutions.

In the present study a waste material, used black tea (UBT), was apply as an adsorbent. Used black tea is an abundant and low cost natural adsorbent. The basic constituents which have a considerable influence on taste and color characteristics of tea include polyphenolic bodies, caffeine, non-caffeine nitrogenous compounds, pectic substances and minerals (Abul et al., 2005). A new surface on the used balck tea was also prepared by adopting impregnation technique by impregnating with lead (Pb) metal at low concentration (Qadeer et al., 1993;

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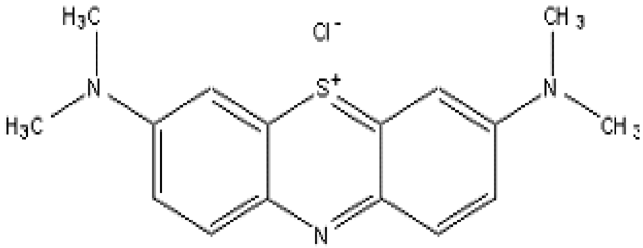

Figure 1. Structure of methylene blue.

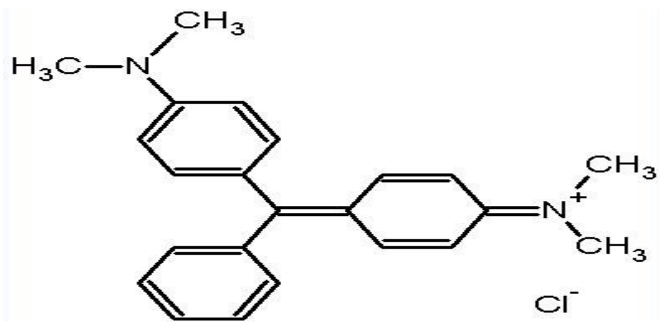

Figure 2. Structure of malachite green.

Tahir and Uddin, 2007). A specific advantage of this technique lies in the fact that minimal reagent loss occurs. The active phase is almost exclusively confined to the pores of the support. There are two ways of doing this; one is the incipient wetness method and other is the total adsorption technique (Saleem et al., 2002 and Khan et al., 2005). In our study, used black tea leaves (UBT) and its metal impregnated form "Impregnated used balck tea (IM-UBT)" were used for dye removal (Amarasinghe et al., 2007).

MATERIALS AND METHODS

Adsorbate

The basic dyes used in present study were malachite green (C.I. 52015) and methylene blue (C.I 42000). Dyes were purchased from Scharlau, Spain. The structures of methylene blue and malachite green are shown in Figures 1 and 2.

Preparation of adsorbents

Used inexpensive household black tea was collected from the University hostel tea shop. Then dry it in electric oven at 60C ± 2°C for 48 h and then placed in electric muffle furnace (J-FM 3, JISICO) at 105°C for 3 h in order to get its surface activated. Two type of adsorbents were prepared, one of them is used black tea (UBT) and its impregnated form (IM-UBT) by using 0.6 M $Pb(NO_3)_2$. Impregnations was done by shaking with 0.6 M $Pb(NO_3)_2$ solution for 1 h at 130 rpm using JISICO shaking incubator (J-NSIL-R/J-NSIL). Then the whole content was filtered and the residue dried in oven at 60 ± 2 °C for 1 h.

Optimization of amount of adsorbent

In order to find out the effects of amount of adsorbent at which maximum adsorption occurs, a test experiment was performed. For this purpose, first of all 50 ml of 9 x 10^{-6} M solution of malachite green was taken in a conical flask with different amount of adsorbent ranging from 0.1 to 1.2 g and shaken for 30 min at 130 rpm. Similarly, the same procedure was repeated for methylene blue dye by using 1.2 x 10^{-5} M dye solution.

Optimization of stay time

For each dye system, effect of time of adsorption was also determined. For this purpose 50 ml of 9 x 10^{-6} M malachite green dye was taken in number of conical flasks and placed on shaking incubator. The time period was varied from 5 min to 1 h; after each 5 min, 1 flask was removed from the shaking incubator. The same procedure was repeated for methylene blue dye by using 1.2 x 10^{-5} M dye solution.

Study of adsorption isotherms

50 ml of dye solution having different concentrations were placed in flasks. Optimum amount of adsorbents UBT and IM-UBT were added in each shaking flask containing different concentration of dye solutions. These flasks were placed in the shaking incubator at desired temperature under the optimized conditions. After the specific time period, the solutions were filtered using Whatman no. 42 filter paper and analyzed by using UV-visible spectrophotometer (UV- 1601, Shimadzu, Japan) for concentration of dye remaining in solution. These experiments were repeated at various temperatures in the range of 30 to 45 ± 5°C.

RESULTS AND DISCUSSION

Adsorption of dye, methylene blue and malachite green, which are cationic in nature, were studied on UBT and IM-UBT as a functional of amount of adsorbent and temperature. The surface of UBT is homogenous and in its normal state, it is covered with adsorbed film which contains oxygen and other impurities both of which are physically and chemically adsorbed (Sabrina and Hasmah, 2008). Because the methylene blue and malachite are cationic, it can form a stable bond with the surface of adsorbent. Lead was used as a new system to vary the surface of the adsorbent in IM-UBT.

Effect of the amount of the adsorbent

The effect of amount of adsorbent on the adsorption of malachite green dye and methylene blue dye were studied. The adsorption of dye increases as the amount of adsorbent increased up to 0.7 g for malachite green and 1.0 g for methylene blue, and then decreases. The K_D values follow the same behavior by using 9 x 10^{-6} M concentration of malachite green and 1.2 x 10^{-5} M of concentration methylene blue. The results are shown in Figure 3.

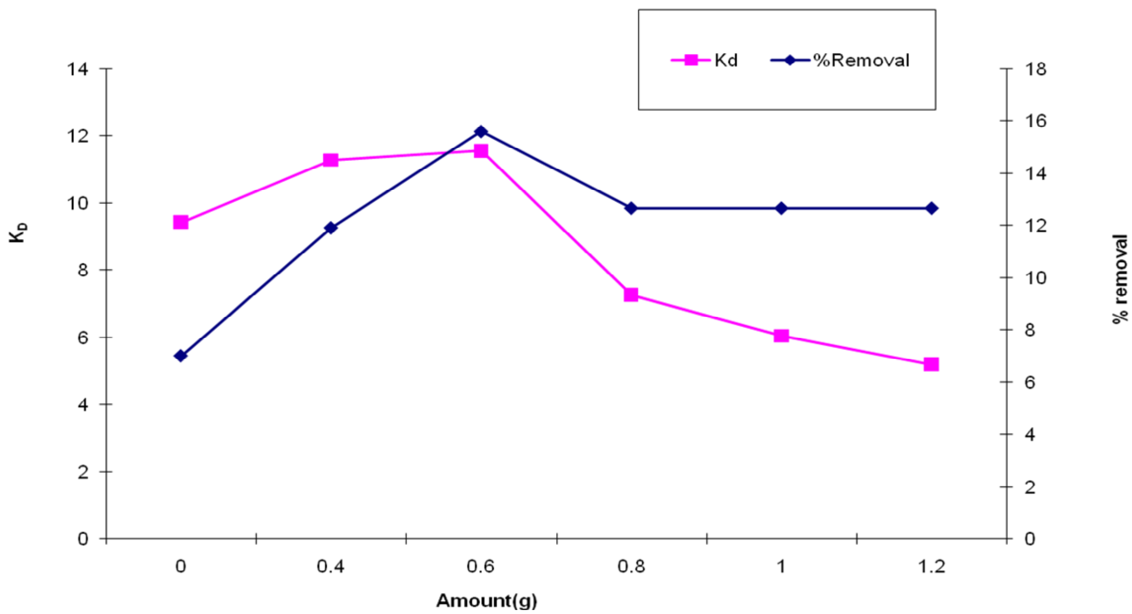

Figure 3. Optimization of amount of UBT for malachite green adsorption.

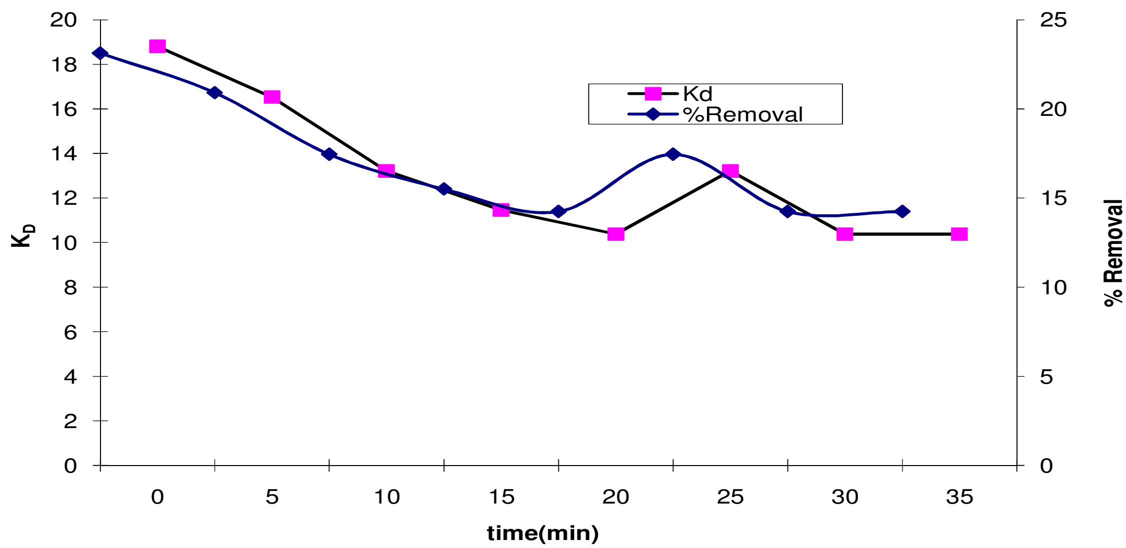

Figure 4. Optimization of stay time for UBT-malachite green system.

Effect of the stay time on adsorption

The effect of stay time on the adsorption was studied for all the systems. The values of adsorption % removal were increased with increase in time and reaches maximum value, then the values slightly decreases and attains a constant value when adsorption equilibrium is reached. The optimum stay time for malachite green dye and methylene blue dye systems on the UBT was 10 and 25 min, respectively. The results are shown in Figure 4.

Effect of temperature on adsorption

The temperature and concentration of dye was also studied in the range of temperatures 303 to 318 K. The inspection of adsorption isotherm shows a decrease in the amount of adsorption of dye with the rise in temperature. It shows that adsorption of dye on UBT is exothermic in nature. Freundlich, Langmuir and D-R Isotherm equations were applied using the adsorption data as shown in Table 1.

Table 1. Comparative study of removal (%) for malachite green and methylene blue dyes using using UBT and IM-UBT.

Dye	Conc. (mol/l)10^6	UBT % Removal				IM-UBT % Removal			
		303K	308K	313K	318K	303K	308K	313K	318K
Malachite green	6.5	11.811	90.909	10.188	10.797	45.500	13.600	64.470	56.660
	5.5	13.095	13.186	17.432	10.683	79.954	22.721	76.628	81.124
	4.5	19.125	66.606	11.295	11.320	85.595	10.339	38.873	12.820
	3.5	19.287	21.406	23.636	14.545	91.166	27.203	39.944	16.372
	2.5	24.017	31.088	15.568	21.556	93.347	21.637	65.563	14.134
Methylene blue	12	10.040	11.981	13.395	56.140	55.546	67.736	75.577	52.190
	9.2	49.630	94.487	89.220	69.040	13.438	17.487	15.044	52.232
	8.2	57.360	18.534	57.360	20.890	49.851	11.875	33.951	12.398
	7.2	28.550	54.163	32.870	12.620	50.045	55.670	89.802	52.693
	6.2	44.530	15.568	17.384	81.710	77.060	90.977	28.793	79.165

Table 2. Freundlich parameters for the removal of malachite green and mehtylene blue dye using UBT and IM-UBT.

Temperature (K)	Malachite green dye				Methylene blue dye			
	UBT		IM-UBT		UBT		IM-UBT	
	K (10^3)	n	K (10^3)	n	K (10^3)	N	K (10^3)	n
303	0.0028	0.23234	0.0670	0.21399	0.0964	0.41237	0.3373	1.2159
308	0.0003	0.58004	0.0787	0.28860	4.8383	1.9098	0.0434	1.8723
313	0.4840	0.15350	6.9598	0.9180	0.8834	1.3831	1476.7	0.5479
318	0.0455	0.25169	0.0021	0.34129	6.9839	1.1880	9×10^{-14}	0.3798

Freundlich adsorption isotherms

The Freundlich isotherm equation is expressed as

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

Where X/m is the amount adsorbed per unit mass of the adsorbent, Cs is the equilibrium concentration and 1/n and K are constants. These parameters give a measure of adsorbing capacity of the adsorbent and intensity of adsorption, respectively (Tahir et al., 2008). The decreasing value of K with the rise in temperature indicates that adsorption affinity of dye decreases with the rise in temperature. It reveals that the process of adsorption is less favorable at high temperatures. Results are shown in Table 2.

Langmuir adsorption isotherm

All the adsorption systems follow Langmuir adsorption isotherm equation. The values of K and V_m were calculated by Langmuir equation.

$$(Cs / X/m) = (1 / KV_m) + (Cs / V_m) \qquad (2)$$

The value of K gives a measure of adsorbing capacity of adsorbent and shows the nature of binding; so called binding constant. Whereas "V_m" is the monolayer capacity. The value of K was decreases with the increase in temperature except for UBT-malachite green system. The decrease in the values of K indicates the weakening of adsorbate - adsorbent interaction at high temperatures. The values of V_m (monolayer capacity) are given in Table 3.

D-R adsorption isotherm

The adsorption data were applied on Dubinin-Radushkevich (D-R) isotherm equation, which is represented in the linearized form as:

$$\ln X/m = \ln X_m - K\, \acute{\varepsilon}^2 \qquad (3)$$

$$\acute{\varepsilon} = RT\ln (1+1/ C_S) \qquad (4)$$

Where, X_m is the monolayer capacity of adsorbent, K is a constant related to adsorption energy, έ is adsorption potential, R is a gas constant, T is absolute temperature, X/m and C_S have usual meaning as described in equation(1). The D-R plots of ln (X_m) Vs $€_2$ were obtained at va-rious temperatures and the values of K and X_m are given in Table 4. It reveals that the value of K decreases

Table 3. Langmuir parameters for the removal of malachite green and methylene blue dye using UBT and IM-UBT.

Temperature K	Malachite Green Dye				Methylene Blue			
	UBT		IM-UBT		UBT		IM-UBT	
	K 10^3	Vm (10^3)	K (10^3)	Vm (10^3)	K (10^3)	Vm (10^3)	K (10^3)	Vm (10^3)
303	179211	0.0018	9210.6	0.0021	0.0555	0.5448	1.1345	1.9049
308	37202.0	0.0016	6483.8	0.0053	1.0599	2.9700	0.3000	1.0511
313	3846.00	0.0042	576.94	0.0046	0.2145	0.7719	0.5736	0.4035
318	6039.00	0.0029	36458	0.0014	12.031	21.381	0.0424	0.4187

Table 4. D-R Parameters for the removal of malachite green and methylene blue dye using UBT and IM-UBT.

Dye	Temperature K	UBT			IM-UBT		
		X_m	K (mol^2/kJ^2)	E_s (KJ/mol)	X_m	K (mol^2/kJ^2)	E_s (KJ/mol)
Malachite green	303	0.1248	-0.8907	0.7492	0.0104	-0.0046	10.425
	308	0.1286	-0.9529	0.7243	0.0412	-0.0053	9.7128
	313	0.0764	-0.7918	0.7946	0.0716	-0.0095	7.2547
	318	0.0847	-0.8572	0.7637	0.0016	-0.0003	40.824
Methylene blue	303	124.44	-0.0078	8.0064	12.021	-0.0080	7.9056
	308	5.2036	-0.0047	10.314	5.0944	-0.0051	9.9014
	313	0.6664	-0.0007	26.726	902.30	-0.0166	5.5901
	318	21.156	-0.0072	8.3333	0.2534	0.0099	4.6578

Table 5. Thermodynamics parameters (ΔH° and ΔS°) for malachite green and methylene blue dye system using UBT and IM-UBT.

Dye	Conc. mol/L (10^6)	UBT		IM-UBT	
		ΔH (KJ mol^{-1})	ΔS KJ $deg^{-1}mol^{-1}$ (10^3)	ΔH (KJ mol^{-1})	ΔS KJ $deg^{-1}mol^{-1}$ (10^3)
Malachite green	6.5	21.071	-43.759	0.8501	10.043
	5.5	13.224	-22.147	18.639	-1.9629
	4.5	2.0950	-50.154	-4.0850	27.477
	3.5	5.3999	1.4915	3.6394	5.8164
	2.5	3.0250	6.7567	-0.5979	19.643
Methylene blue	12	-15.595	0.0656	-18.493	72.223
	9.2	18.980	-0.0447	51.878	-124.53
	8.2	-40.546	0.1517	-25.870	99.593
	7.2	48.830	-0.1402	-25.983	47.068
	6.2	52.404	-0.1528	18.648	-48.059

with the rise in temperature due to strengthening of the adsorbate-adsorbent interaction for all systems (Tahir et al., 2008).

Thermodynamic parameter

The values of thermodynamic parameters ΔG°, ΔH° and ΔS° were calculated from the Langmuir constant K. They were calculated from the plot of ln K with the reciprocal of temperature (1/T) by using the following equations

$$\Delta G° = -RT\ln K_D \quad (5)$$

$$Lnk = \Delta S°/R – \Delta H°/RT \quad (6)$$

$$\Delta G° = \Delta H° - T\,\Delta S° \quad (7)$$

Table 6. Comparative study of ∆G° for malachite green and methylene blue dye using UBT and IM-UBT.

Dye	Conc. mol/L (10^6)	UBT ∆G° $KJmol^{-1}$ (10^3)				IM-UBT ∆G° $KJmol^{-1}$ (10^3)			
		303K	308K	313K	318K	303K	308K	313K	318K
Malachite Green	6.5	34.329	34.548	34.767	34.986	-2.1929	-2.2431	-2.2933	-2.3435
	5.5	19.934	20.045	20.156	20.266	19.233	19.243	19.253	19.263
	4.5	17.291	17.542	17.793	18.043	-12.410	-12.547	-12.685	-12.822
	3.5	4.9479	4.9405	4.9330	4.9256	1.8693	1.8401	1.8109	1.7817
	2.5	0.9777	0.9439	0.9101	0.8763	-6.5497	-6.6479	-6.7461	-6.8443
Methylene Blue	12	-15.614	-15.615	-15.615	-15.615	-40.376	-40.373	-41.098	-41.459
	9.2	18.993	18.993	18.993	18.994	89.610	90.232	90.855	91.478
	8.2	-40.591	-40.592	-40.546	-40.594	-56.046	-56.345	-57.042	-57.540
	7.2	48.872	48.873	48.873	48.874	-40.244	-40.479	-40.715	-40.950
	6.2	52.450	52.451	52.451	52.452	33.209	33.450	33.690	33.930

The values of ∆G° at different temperatures are negative except for malachite green- UBT system. The positive value of ∆G° shows non-spontaneous behavior. While negative values show the spontaneous process. The values of ∆H° and ∆S° are positive in case of malachite green-UBT system, while other systems show both endothermic and exothermic behaviors. The results are shown in Tables 5 and 6.

Conclusion

From the present study we can conclude that the waste material, black tea and its impregnates, can be used as an adsorbent. The result show that used black tea leaves shows better adsorption capacity as compared to its impregnates. About 94.487% removal was obtained for methylene blue-used black tea system at 308 K temperature compare to other systems.

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