Adsorption of dyes from aqueous solutions on activated charcoal

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Abstract

Adsorption of industrially important dyes namely bromophenol blue, alizarine red-S, methyl blue, methylene blue, eriochrome black-T, malachite green, phenol red and methyl violet from aqueous media on activated charcoal has been investigated. The effect of shaking time, pH and temperature on the adsorption behaviour of these dyes has been studied. It was noted that adsorption of all the dyes on activated charcoal decreases with an increase in the pH and the temperature. The adsorption isotherms at different temperatures were found to be of L-type. Adsorption data was fitted to Freundlich, BET and Langmuir isotherms and various adsorption parameters have been calculated. The thermodynamic parameters such as ΔG, ΔH and ΔS were calculated from the slopes and intercepts of the linear variation of $\ln K$ against $1/T$, where K is the adsorption coefficient obtained from Langmuir equation, was used. The calculated values for the heat of adsorption and the free energy indicate that adsorption of dyes is favored at low temperatures and the dyes are chemisorbed on activated charcoal.
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Keywords: Adsorption; Dyes; Activated charcoal; Adsorption isotherm; Thermodynamics of adsorption

1. Introduction

Industrial, agricultural and domestic wastes, due to the rapid development in the technology, are discharged in the several receivers. Generally, this discharge is directed to the nearest water sources such as rivers, lakes and seas. Textile dyeing process is an important source of contamination responsible for the continuous pollution of the environment. The volume of wastewater containing processed textile dyes is on steady increase. Over 7×10^5 tonnes and approximately 10,000 different types of dyes and pigments are produced world wide annually [1]. It is estimated that 10–15% of the dye is lost in the effluents during the dyeing process. Colour is a characteristic of wastewater, which is easily detected. Control of water pollution has importance for both organisms, which live in water and those who benefit from water. Many dyes reaching the water source are difficult to decompose and cause many problems due to their carcinogenicity [2–4]. Consequently, it is important to remove these pollutants from wastewater before their final disposal.

The methods of color removal from industrial effluents include biological treatment, coagulation, flotation, adsorption, oxidation and hyperfiltration. Among the treatment options, adsorption has become one of the most effective and comparable low cost method for the decolourization of textile wastewater [5,6]. Different adsorbents have been used for the removal from aqueous solutions of various materials, such as dyes, metal ions and other organic materials includes perlite [7–12], bentonite [13], silica gels [14], fly ash [15,16], lignite [17], peat [18], silica [19], etc. Activated carbon is a structurally homogeneous material of high surface area, has microporous structure and show radiation stability. It is therefore widely used in various industrial process as adsorbent [20–22], catalyst or catalyst support [23]. The adsorption properties of activated carbon depend mainly on its particle size, porosity, ash contents, degree of carbonization and method of activation.

This paper reports the results of the adsorption of alizarine red-S, bromophenol blue, malachite green, methyl violet, methylene blue, phenol red, methyl blue and erichrome black-T from aqueous solutions on activated charcoal. The adsorption behavior of the dyes as a function of temperature, pH and shaking time were also studied. Adsorption data was fitted to Freundlich (Eq. (1)), Langmuir (Eq. (2)) and BET (Eq. (3)) isotherms and their

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corresponding adsorption parameters such as K_F, n and K and V_m, respectively, have been calculated.

$$\log \frac{x}{m} = \log K_F + \frac{1}{n} \log C_s \qquad (1)$$

where x/m is the amount adsorbed per unit mass of the adsorbate, C_s the equilibrium concentration, and $1/n$ and K_F are constants. The constant K_F is related to the degree of adsorption, n provides the rough estimation of the intensity of the adsorption:

$$\frac{C_s}{x/m} = \frac{1}{K V_m} + \frac{C_s}{V_m} \qquad (2)$$

$$\frac{C_s/C_0}{x/m(1 - C_s/C_0)} = \frac{1}{x_m C} + \frac{C-1}{x_m C} \frac{C_s}{C_0} \qquad (3)$$

where K is the adsorption coefficient, V_m the monolayer capacity, x_m the amount of dye required to form the monolayer over the surface of adsorbent and C is the constant.

In order to fully understand the nature of adsorption, the thermodynamic studies play an important role. This paper also presents the thermodynamics parameters related to the adsorption of dyes such as free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS), which have been calculated using following equations [24–27]:

$$\Delta G = -RT \ln K \qquad (4)$$

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (5)$$

$$\Delta G = \Delta H - T \Delta S \qquad (6)$$

2. Materials and methods

Bromophenol blue (95%, Perking Chemical, China), methylene blue (82%, Fluka), methyl blue (60%, Fluka), methyl violet (85%, Fluka), alizarine red S (70%, Fluka), malachite green oxalate (90%, Merk), phenol red (95%, Polskie Odezynniki) and eriochrome black-T (65%, Riedel-de Haen). The % of dye content is given for each dye and were used as such. Charcoal supplied by Scientific and Technological Development Corporation of Pakistan (STEDEC) was further purified and activated by washing five times with distilled water and drying at 473 K followed by its storage in a desicator. The structures of the dyes are shown in Fig. 1.

2.1. Adsorption studies

Stock solutions of dyes were prepared by dissolving weighed amounts in distilled water and thereby necessary dilutions were prepared in the same solvent. Buffer solutions of various pH ranging 1–7 were used; buffers of pH 1, 2, 4 and 7 were supplied by Fluka and of pH 5 was made from the mixture of $0.1 \, mol \, dm^{-3}$ potassium hydrogen phthalate and NaOH. Buffer of pH 3 was made from the mixture of $0.1 \, mol \, dm^{-3}$ of potassium hydrogen phthalate and HCl. Buffer of pH 6 was made from the mixture of $0.1 \, mol \, dm^{-3}$ of potassium dihydrogen phosphate

Table 1
Molar mass and the λ_{max} for each dye

S. no.	Dye	Molar mass (g mol^{-1})	λ_{max} (nm)
1	Bromophenol blue	670.02	590
2	Alizarin red S	342.26	430
3	Malachite green oxalate	927.02	620
4	Eriochrome black-T	461.39	530
5	Methylene blue	775.98	665
6	Methyl blue	799.80	610
7	Phenol red	354.37	435
8	Methyl violet	393.96	585

and NaOH. The various solutions of pH 1–7 were prepared by addition of 2 ml of dye from stock solutions and diluted to 100 ml with buffer solutions of respective pH. The pH was monitored by pH meter (Model HM-7E). The absorbance of the dye solutions was measured at various wavelengths and values of λ_{max} were obtained. The λ_{max} for each dye is shown in Table 1. Weighed amount (0.01 g) of activated charcoal in a flask containing 25 ml dye solution was shaken in a water bath incubator (Hitachi BT-47) at 298, 303, 308, 313 and 318 K. The solutions were filtered. The absorption spectra were then recorded by a spectrophotometer (Shimadzu UV-120-01) at their respective λ_{max} of each dye. The amount adsorbed, x/m (mg g^{-1}) is plotted against the equilibrium concentration, C_s (ppm) to obtain the adsorption isotherms.

The adsorption of mixture of methyl blue, eriochrome black-T and phenol red was also studied on the activated charcoal in the concentration range 0.05–5 ppm. Weighed amount (0.01 g) of activated charcoal in a flask containing 25 ml mixed dye solution was shaken in a water bath incubator (Hitachi BT-47) at 298 K. The solutions were filtered. The concentration of the remaining amount of each dyes was determined by measuring the absorbance of the mixture of dyes at their respective λ_{max} and then applying Beer–Lambert law to calculate the concentration of each dye. The effect of interference between the colours of the dye was excluded because the mixture of dyes was scanned for λ_{max} and only three λ_{max} (eriochrome black-T = 530, phenol red = 435, methyl blue = 610 nm) were found corresponding to the individual dyes of the mixture.

2.2. Time optimization

For the purpose of finding out the optimum shaking time experiments were performed using a 25 ml aqueous solutions of bromophenol blue (6.7 ppm), methylene blue (7.7 ppm), phenol red (3.5 ppm), alizarine red S (6.8 ppm), malachite green (4.6 ppm), eriochrome black-T (2.3 ppm), methyl blue (4 ppm) and methyl violet (2 ppm) and were shaken together with 0.01 g of activated charcoal for different intervals of time ranging from 5 to 60 min. The absorbance of the filtrate was noted by the spectrophotometer at the λ_{max} of each dye. Fig. 2 shows that adsorption of dyes increased with increasing the shaking time and attained a constant value when equilibrium was established. The optimum shaking time was found to be 30 min, which was used for all further adsorption studies.
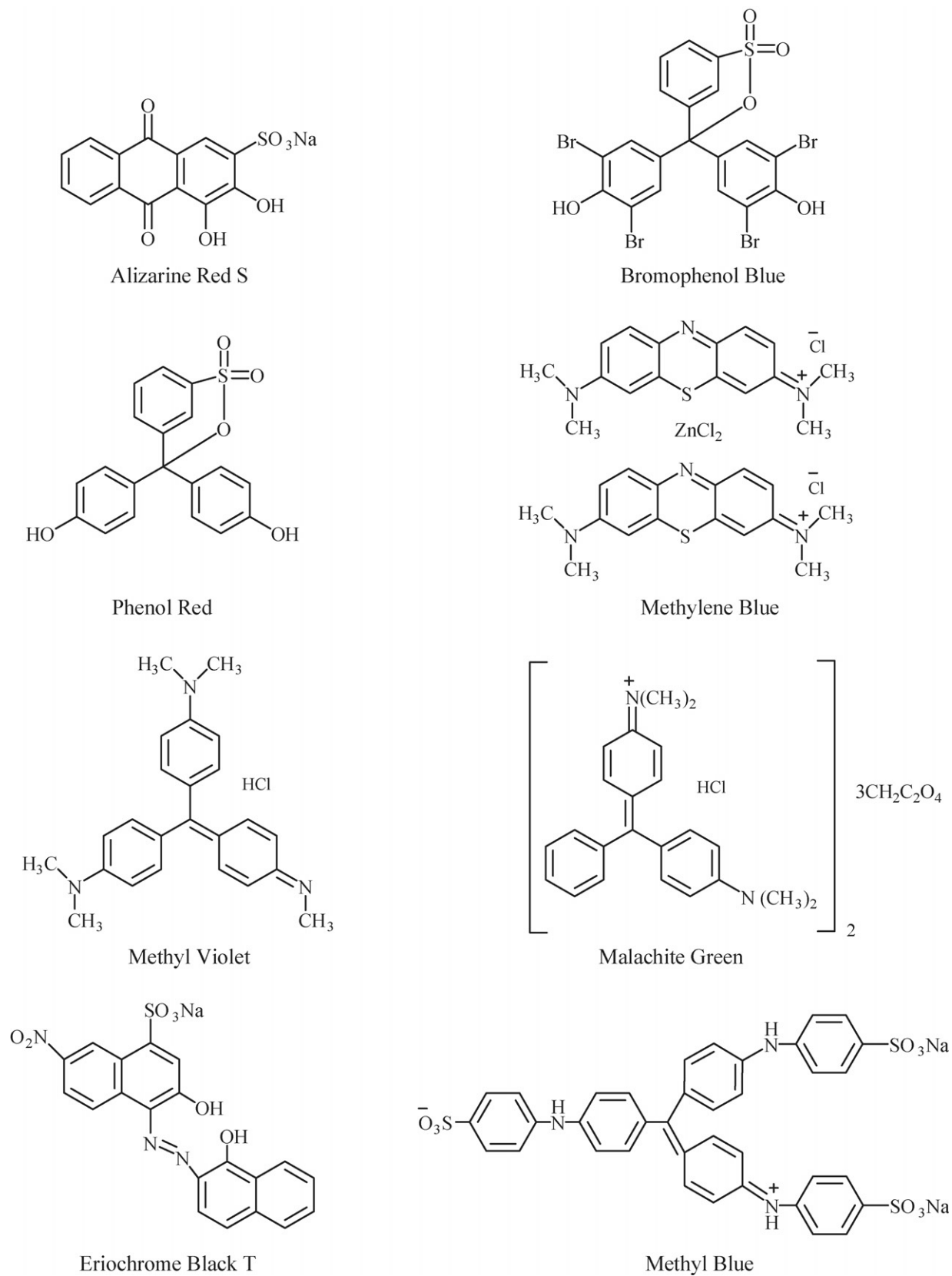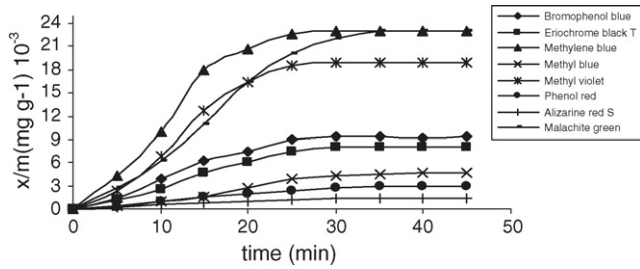
Fig. 1. Structures of dyes.

Fig. 2. Plots of shaking time vs. amount adsorbed on activated charcoal for various dye solutions.
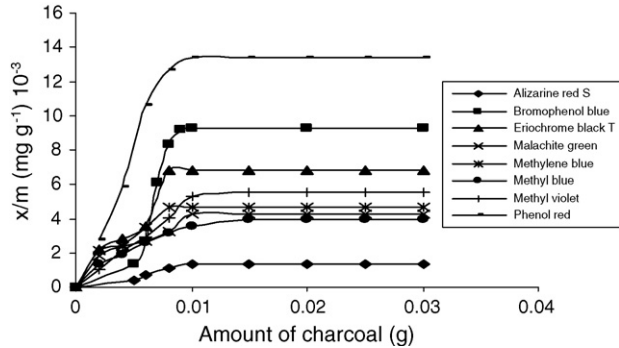

Fig. 3. Plots of amount of charcoal vs. amount adsorbed on activated charcoal for various dye solutions.

2.3. Optimization of amount of adsorbent

For the purpose of optimizing the amount of the adsorbent, experiments were performed using a 25 ml aqueous solutions of bromophenol blue (6.7 ppm), methylene blue (7.7 ppm), phenol red (3.5 ppm), alizarine red S (6.8 ppm), malachite green (4.6 ppm), eriochrome black-T (2.3 ppm), methyl blue (4 ppm) and methyl violet (2 ppm) and were shaken together for 30 min adding different amount of charcoal. The absorbance of the filtrate was noted by the spectrophotometer at the λ_{max} of each dye. Fig. 3 shows that adsorption of dyes increased with increasing the amount of charcoal and attained a constant value when equilibrium was established. The optimum amount was found to be 0.01 g, which was used for all further adsorption studies.

3. Results and discussion

3.1. Adsorption isotherms

Adsorption isotherms were obtained at 298, 303, 308, 313 and 318 K for bromophenol blue, alizarine red-S, malachite green, methylene blue, methyl blue, methyl violet, eriochrome black-T and phenol red however only the isotherms at 298K are shown in Figs. 4 and 5. The isotherms are of L-type, indicating that they have high affinity for activated charcoal. The initial sharp rise in the extent of adsorption with increasing dye concentration shows that the bombarding solute molecules find difficulty in accessing vacant sites on the adsorbent as more and more sites are filled up.

Adsorption data for the dyes on activated charcoal was fitted to the linear form of Freundlich isotherm (Eq. (1)) as shown
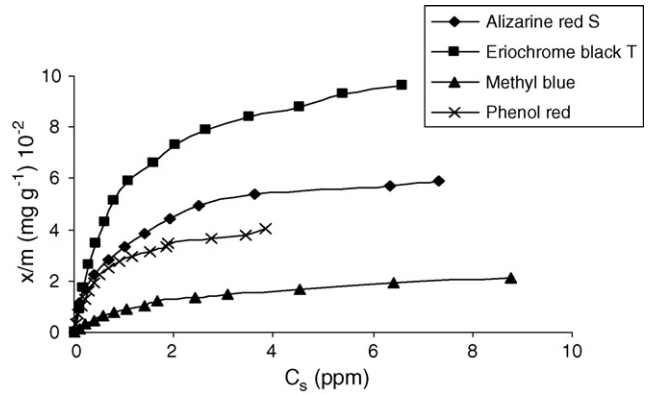

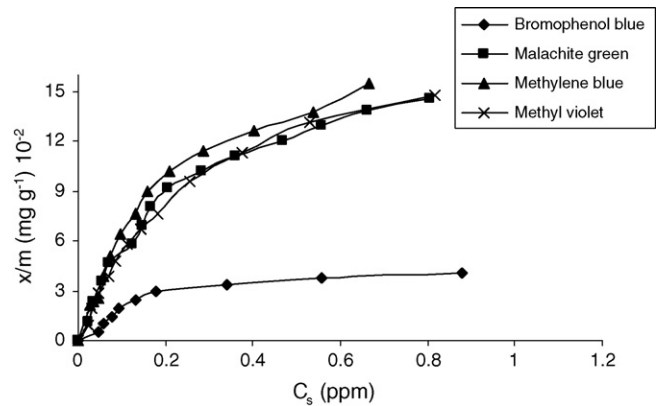Fig. 4. Adsorption isotherms of various dyes on activated charcoal at 298 K.

Fig. 5. Adsorption isotherms of various dyes on activated charcoal at 298 K.

in Fig. 6. The values of the constants, K_F and n, are given in Table 2. It may be noted that the value of K_F and *n* decrease with an increase in temperature for all the dyes on activated charcoal indicating that adsorption is favourable at low temperature. The values of K_F for alizarine red s are in the range of 3–7 but for methylene blue are 4018–41476. The value of K_F is related to the degree of adsorption. The dye having the greater value of K_F has high affinity toward the adsorbent as compared to other having low K_F value. In the present study, methylene blue has the highest value of K_F which mean that it has the highest affinity toward the adsorbent as compared to all the other dyes. The value
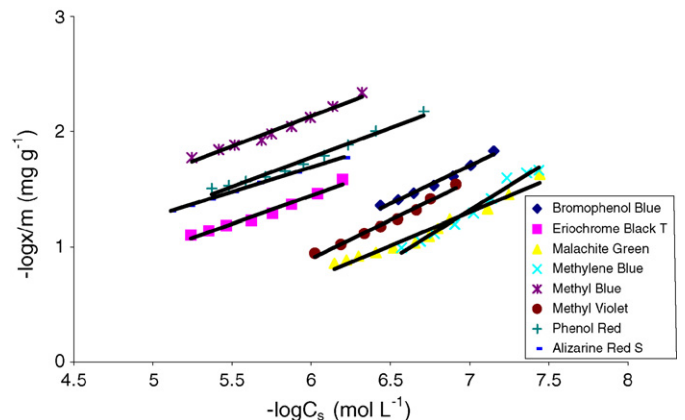

Fig. 6. Freundlich isotherms of various dyes on activated charcoal at 298 K.

of n in all the cases is greater than unity indicating that the amount adsorbed increases less rapidly than the concentration.

Langmuir isotherm (Eq. (2)) is found to be obeyed by all the dyes on activated charcoal as shown in Figs. 7 and 8. This indicates that the dyes are chemisorbed on the surface of the activated charcoal. These logarithmic equations for the adsorption studies of dyes on activated charcoal gave high linearity with a range of correlation coefficient between 0.9751 and 0.9991. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogeneous distribution of active sites on the activated carbon surface, since the Langmuir equation assumes that the surface is homogeneous. The values of the adsorption coefficient K and the monolayer capacity V_m calculated from Langmuir equation are given in Table 3. The values of K and
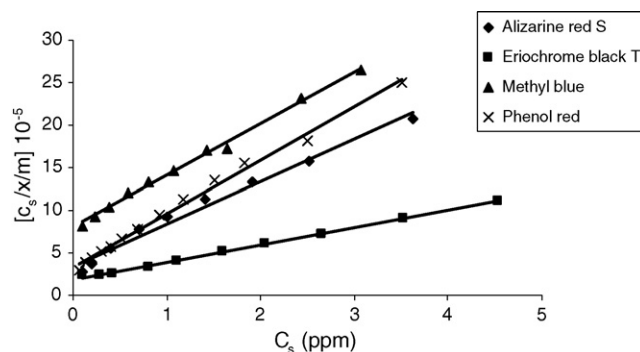

Fig. 7. Langmuir isotherms of various dyes on activated charcoal at 298 K.

Table 2
Freundlich parameters for various dyes on activated charcoal

| Dyes	Temperature (K)	n	K_F	Correlation coefficient (R^2)
Aalizarize red S	298	2.35	7.37	0.9991
	303	2.15	7.36	0.9981
	308	1.91	7.29	0.9834
	313	1.03	6.23	0.9792
	318	1.03	3.70	0.9671
Bromophenol blue	298	1.53	756.14	0.9850
	303	1.52	623.15	0.9769
	308	1.50	402.86	0.9618
	313	1.49	121.36	0.9679
	318	1.47	23.20	0.9869
Erichrome black-T	298	2.05	30.27	0.9739
	303	1.84	30.15	0.9952
	308	1.51	26.18	0.9876
	313	1.32	22.62	0.9784
	318	1.28	15.73	0.9675
Malachite green	298	1.74	522.28	0.9678
	303	1.53	423.16	0.9721
	308	1.53	293.49	0.9637
	313	1.54	112.06	0.9729
	318	1.54	82.84	0.9728
Methylene blue	298	1.18	41476.30	0.9758
	303	1.18	28436.16	0.9751
	308	1.17	4923.80	0.9894
	313	1.75	4677.35	0.9375
	318	1.70	4018.83	0.9435
Methyl blue	298	1.91	10.24	0.9781
	303	1.73	10.13	0.9796
	308	1.56	11.01	0.9851
	313	1.55	9.62	0.9508
	318	1.53	6.98	0.9589
Methyl violet	298	1.50	1231.96	0.9873
	303	1.46	1020.38	0.9464
	308	1.47	958.43	0.9481
	313	1.48	756.14	0.9747
	318	1.47	522.28	0.9455
Phenol red	298	1.93	19.51	0.9813
	303	1.91	19.16	0.9765
	308	1.89	18.28	0.9613
	313	1.84	15.97	0.9885
	318	1.79	9.95	0.9803
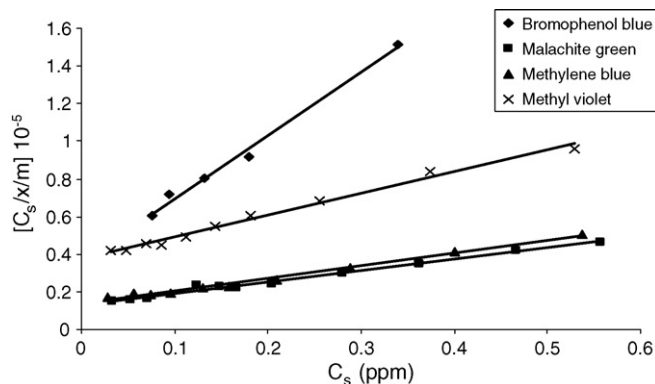
Fig. 8. Langmuir isotherms of various dyes on activated charcoal at 298 K.
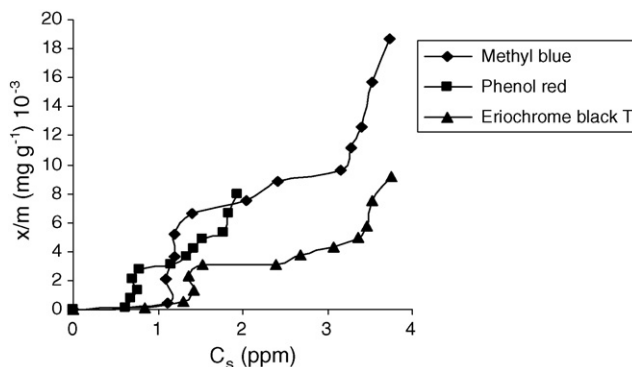
Fig. 11. Adsorption isotherms for the mixture of dyes at 298 K.

may also be explained on the basis that the solubility of the dyes is increased at higher temperature and adsorbate–adsorbent interactions decreased resulting into decreased adsorption. All the dyes studied here have shown this behaviour. This also indicated that desorption steps increase at higher temperature than the adsorption. This type of adsorption is likely to be classified as reversible adsorption. A behavior similar to this has also been observed by Longhinotti et al. [28] on studies of adsorption of orange (IV) and orange G on biopolymer chitin. The adsorption of malachite green also decreases with the temperature in our case. A similar bevaviour also showed by Tahir and Rauf [29].
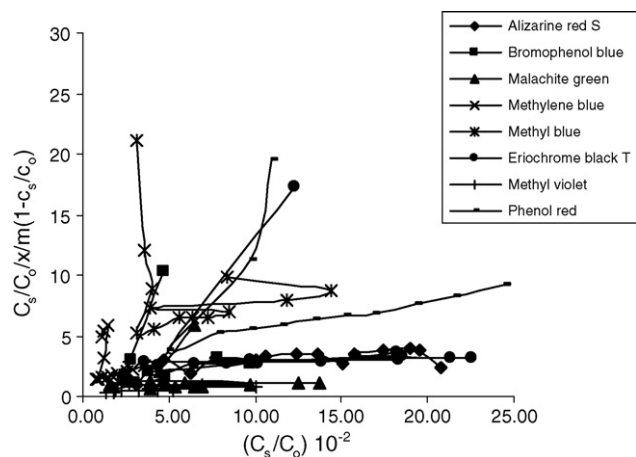

Fig. 9. BET isotherms of Eriochrome black-T at different temperatures.

V_m are found to decrease with increasing temperature. The BET isotherm is not obeyed by all the dyes, this suggests that the adsorption of all the dyes on activated charcoal is chemisorption as shown in Fig. 9.

3.2. Effect of temperature

Fig. 10 shows that adsorption decreases with increase in temperature because the adsorption is an exothermic process. This
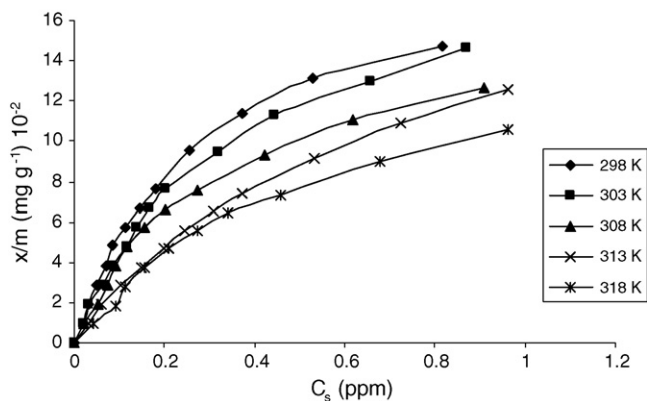
3.3. Adsorption of mixture of dyes

The adsorption of mixture of methyl blue, eriochrome black-T and phenol red was also studied on the activated charcoal in the concentration range 0.05–5 ppm. The adsorption isotherms are found to be of S-type as shown in Fig. 11, contrary to the individual studies where it was observed to be of L-type isotherms as shown in Figs. 3 and 4. This indicates that the dye–dye interaction increased and the attraction between the adsorbent and dyes decreased. Adsorption data was fitted to Freundlich isotherm Fig. 12. The values of Fruendlich constants K_F are 206.585, 1335.057 and 1282.921 and the values of n are 1.016, 1.067 and 0.988 for eriochrome black-T, methyl blue and phenol red, respectively. The value of K_F is related to the degree of adsorption. The adsorption isotherm and the value of K_F showed that

Fig. 10. Adsorption isotherms of methyl violet on activated charcoal at various temperatures.
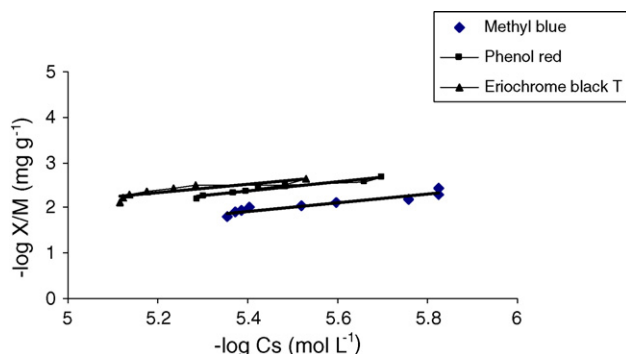

Fig. 12. Freundlich isotherms for the mixture of dyes at 298 K.

Table 3
Langmuir parameters for various dyes on activated charcoal

Dyes	Temperature (K)	K ($\times 10^5$) (dm^3 mg^{-1})	V_m (mg g^{-1})	Correlation coefficient (R^2)
Alizarine red S	298	3.89	0.064	0.9869
	303	3.87	0.062	0.9967
	308	3.09	0.061	0.9875
	313	2.11	0.060	0.9832
	318	1.74	0.052	0.9783
Bromophenol blue	298	30.95	0.081	0.9935
	303	30.14	0.050	0.9937
	308	25.85	0.050	0.9991
	313	20.09	0.050	0.9974
	318	15.97	0.050	0.9835
Eriochrome black-T	298	4.71	0.106	0.9981
	303	4.63	0.103	0.9984
	308	3.85	0.099	0.995
	313	2.52	0.092	0.9838
	318	2.08	0.091	0.9974
Malachite green	298	55.70	0.180	0.9942
	303	27.90	0.179	0.9935
	308	18.33	0.172	0.988
	313	15.88	0.171	0.9893
	318	11.75	0.170	0.9771
Methylene blue	298	519.75	0.192	0.9922
	303	502.11	0.191	0.9945
	308	374.64	0.186	0.9765
	313	247.62	0.172	0.9851
	318	151.68	0.170	0.9867
Methyl blue	298	4.50	0.024	0.9928
	303	4.05	0.025	0.9931
	308	3.20	0.025	0.9938
	313	2.02	0.025	0.9887
	318	1.39	0.024	0.9805
Methyl violet	298	49.51	0.202	0.9934
	303	47.33	0.172	0.9965
	308	28.58	0.173	0.9938
	313	20.30	0.172	0.9976
	318	15.24	0.171	0.9779
Phenol red	298	8.13	0.0409	0.9981
	303	8.03	0.0408	0.9899
	308	6.39	0.0406	0.9883
	313	3.86	0.0350	0.9816
	318	2.96	0.0310	0.9905

the adsorption of methyl blue is greater than phenol red and eriochrome black-T in the mixture.

3.4. Effect of pH

Adsorption is also affected by the pH change of the solution [30,31] as shown in Fig. 13. The concentration of each for this study was 2×10^{-5} mol dm^{-3} and the other procedure is the same as given in Section 2.1. The hydrogen ion concentration (pH) primarily affects the degree of ionization of the dyes and the surface properties of the adsorbents. Fig. 13 shows that the adsorption of the selected dyes decreased with pH except methylene blue and malachite green on activated charcoal. This can be explained on the basis of formation of positively charged surface on activated charcoal. Low pH value results in lowering
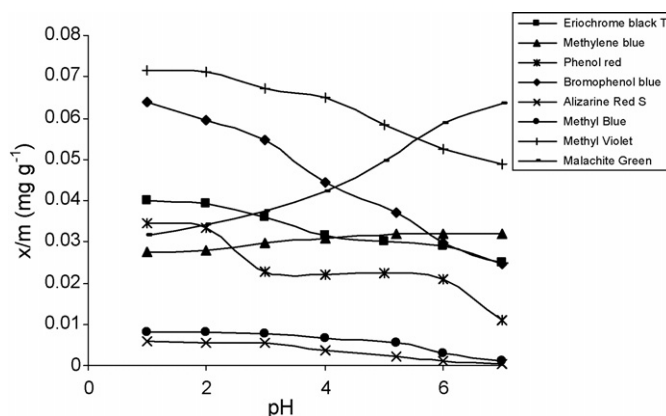

Fig. 13. Plots of pH vs. amount of dyes adsorbed at 298 K.

Table 4
Thermodynamic parameters for the adsorption of various dyes on activated charcoal

Dyes	Temperature (K)	$-\Delta G$ (kJ mol^{-1})	$-\Delta H$ (kJ mol^{-1})	$-\Delta S$ (kJ mol^{-1} K^{-1})
	298	31.89	33.36	0.00499
	303	32.41	33.36	0.00318
Alizarine red S	308	32.37	33.36	0.00325
	313	31.91	33.36	0.00469
	318	31.90	33.36	0.00464
	298	37.03	26.02	+0.0370
	303	37.59	26.02	+0.0382
Bromphenol blue	308	37.81	26.02	+0.0383
	313	37.77	26.02	+0.0375
	318	37.76	26.02	+0.0369
	298	32.36	33.77	0.00473
	303	32.86	33.77	0.00230
Erichrome black-T	308	32.93	33.77	0.00273
	313	32.36	33.77	0.00449
	318	32.38	33.77	0.00437
	298	38.48	55.65	0.0576
	303	37.39	55.65	0.0603
Malachite green	308	36.93	55.65	0.0608
	313	37.16	55.65	0.0591
	318	36.95	55.65	0.0588
	298	44.02	47.66	0.0122
	303	44.67	47.66	0.0099
Methylene blue	308	44.66	47.66	0.0096
	313	44.30	47.66	0.0107
	318	43.72	47.66	0.0124
	298	32.25	45.89	0.0458
	303	32.53	45.89	0.0441
Methyl blue	308	32.46	45.89	0.0436
	313	31.78	45.89	0.0451
	318	31.31	45.89	0.0458
	298	38.19	48.19	0.0336
	303	38.72	48.19	0.0313
Methyl violet	308	38.07	48.19	0.0329
	313	37.79	48.19	0.0332
	318	37.64	48.19	0.0332
	298	33.72	41.53	0.0262
	303	34.25	41.53	0.0240
Phenol red	308	34.23	41.53	0.0237
	313	33.47	41.53	0.0257
	318	33.31	41.53	0.0259

of the negative charge on the surface of the charcoal, increasing the positive charge on the surface thus enhancing the adsorption of the negatively charged adsorbate. With the increase in pH value the hydroxyl ion concentration increases and on the surface of the charcoal the negative charge increased so that the adsorption capacity of the adsorbent for the dyes having negative charge is also decreased. But the adsorption of methylene blue and malachite green increased with the pH on the surface of activated charcoal. This is due to the positive charge on these dyes as shown by their structure in Fig. 1. The optimum pH value for the adsorption of methylene blue was observed 13.40 by Ravikumar et al. [32]. We have studied the effect of pH on adsorption of dyes within pH range 1–7 because after pH 7 the λ_{max} of the dyes change.

3.5. Thermodynamic parameters

The free energy of adsorption was calculated by Eq. (4) where "K" is the adsorption coefficient obtained from the Langmuir equation [33]. The values of free energy are negative for all the system as shown in Table 4, indicating that the process is spontaneous. The ΔG values for all the cases more or less approximately remains constant, indicating that there is no effect of temperature on free energy of adsorption.

The heat of adsorption was calculated using Eq. (5) by plotting a graph of ln K versus reciprocal of temperature as shown in Fig. 14. The slope gave the value of heat of adsorption shown in Table 3. The values of ΔH for all the systems are negative, indicating that the processes are exothermic. The sim-
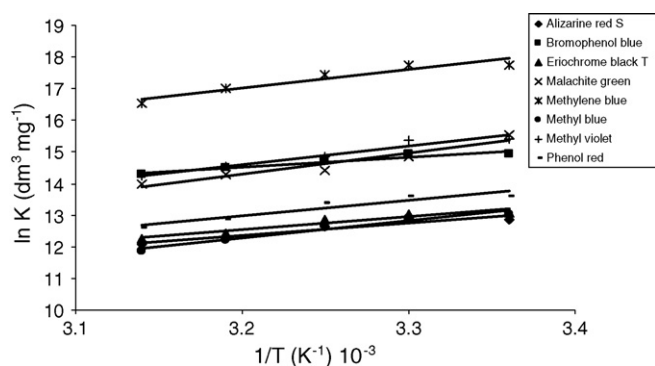
Fig. 14. Plots of ln K vs. $1/T$ for the adsorption of various dyes on activated charcoal.

ilar results for the adsorption of ethyl orange, mentanil yellow and acid blue from aqueous solutions on industrial waste were obtained by Jain et al. [34]. The values of ΔH for malachite green, methylene blue, methyl violet, phenol red and methyl blue are more than 40 kJ mol^{-1} as shown in Table 3, indicating chemisorption of these dyes [31]. The ΔH values for alizarine red S, bromophenol blue and eriochrome black-T are less than 40 kJ mol^{-1} but BET isotherms confirm the chemisorption of these dyes on the activated charcoal. The entropy was calculated by Eq. (6). The entropy of adsorption of molecules from the solution on the surface was decreased as shown in Table 3. Molecules before adsorption can move in three dimensions but as they get adsorbed on the surface, the motion of molecules is restricted towards the surface and their disorderness decreased resulting in the decrease in entropy. But in case of bromophenol blue the entropy increased. The behaviour similar to this was also observed by Amina et al [35] for the adsorption of methylene blue and congo red but our result for the methylene blue are different. The reorientation or restructuring of water around the nonpolar solute or surface is very unfavourable in term of entropy, since it disturbs the existing water structure and imposes a new and more ordered structure on the surrounding water molecules. As a result of adsorption of bromophenol blue onto activated carbon surface, the number of water molecule surrounding the bromophenol blue decreases and thus the degree of freedom of the water molecule increases. Therefore, the positive value of entropy suggested the increased randomness at the solid-solution interface during the adsorption of bromophenol blue.

4. Conclusion

Activated charcoal is efficiently utilized as an adsorbent for the removal of hazardous dyes from the aqueous solutions. The adsorption isotherms for all the dyes investigated here are of L-type however for tertiary mixture of dyes the isotherms are S-type. The adsorption of all the dyes was found to decrease with the increase in temperature. The BET isotherm was not obeyed by all the dyes, suggesting that the adsorption on activated charcoal is chemisorption and the value of $-\Delta H$ between 26 and 55 kJ mol^{-1} also confirm this. The adsorption also decreased with the pH except in case of methylene blue and malachite green. The negative ΔG and ΔH values show that the adsorption of dyes on activated charcoal is spontaneous and exothermic.

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