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# THERMODYNAMICS OF ADSORPTION OF DYES FROM AQUEOUS MEDIA ON ACTIVATED CHARCOAL

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## Abstract

Adsorption of industrially important dyes namely bromophenol blue, alizarin 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 and temperature on the adsorption behavior of these dyes has been studied. It was noted that adsorption of all the dyes on activated charcoal decrease with an increase in temperature. The adsorption isotherms at different temperatures were found to be of L-type. The thermodynamic parameters such as ΔG, ΔH and ΔS were calculated from the slopes and intercepts of the linear variation of lnK against 1/T, where K is the adsorption coefficient obtained from Langmuir equations was used. The calculated values for the heat of adsorption and the free energy indicate that adsorption process is favored at low temperatures.

**Keywords:** Adsorption, dyes, thermodynamics of adsorption.

## INTRODUCTION

Industrial, agricultural and domestic wastes, due to the rapid development in the technology are discharged in the several receivers. Generally, this discharge is done 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 x $10^5$ tons and approximately 10000 different types of dyes and pigments are produced world wide annually [Pala *et al.* 2003]. It is estimated that 10–15% of the dye is lost in the effluents during 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 [Moreira *et al.* 1998, Albanis *et al.* 2000, Safarik *et al.* 2002]. Consequently, it is important to remove these pollutants from wastewater before their final disposal.

The method of color removal from industrial effluents includes 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 [Mckay *et al.* 1999, Khan *et al.* 2002]. Different adsorbents have been used for the removal of various materials from aqueous solutions, such as dyes, metal ions and other organic materials. These includes perlite [Dogan *et al.* 2000, Alkan and Dogan 2001, Demirbas and Dogan 2002, Dogan and Alkan 2003a,b,c], bentonite [Bereket *et al.* 1997], silica gels [Mohamed 1996], fly ash [Gupta *et al.* 2000, Mohan *et al*. 2002], lignite [Allen *et al.* 1989], peat [Ho and Mckay 1998], silica [Mckay and Otterburn 1981] etc. Activated carbon is structurally homogeneous material of high surface area, microporous structure and radiation stability, which is important in its use as adsorbent [Leyva-Ramos 1989, Tsai *et al.* 2001, Pendleton and Wu 2003], catalyst and catalyst support [Gerald and Russel 1991], so it widely used for industrial process. The adsorption properties of activated carbon depend mainly on its particle size, porosity, ash contents, and degree of carbonization and method of activation.

In order to fully understand the nature of adsorption, the thermodynamic studies play an important role. This paper presents the thermodynamics parameters such as free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS), which have been calculated using following equations [Afzal, *et al* 1992, Saleem *et al.* 1992, Qadeer *et al.* 1993, Konstantinou and Albanis 2000]:

$$\Delta G = -R\,T\,\ln K \tag{1}$$

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{2}$$

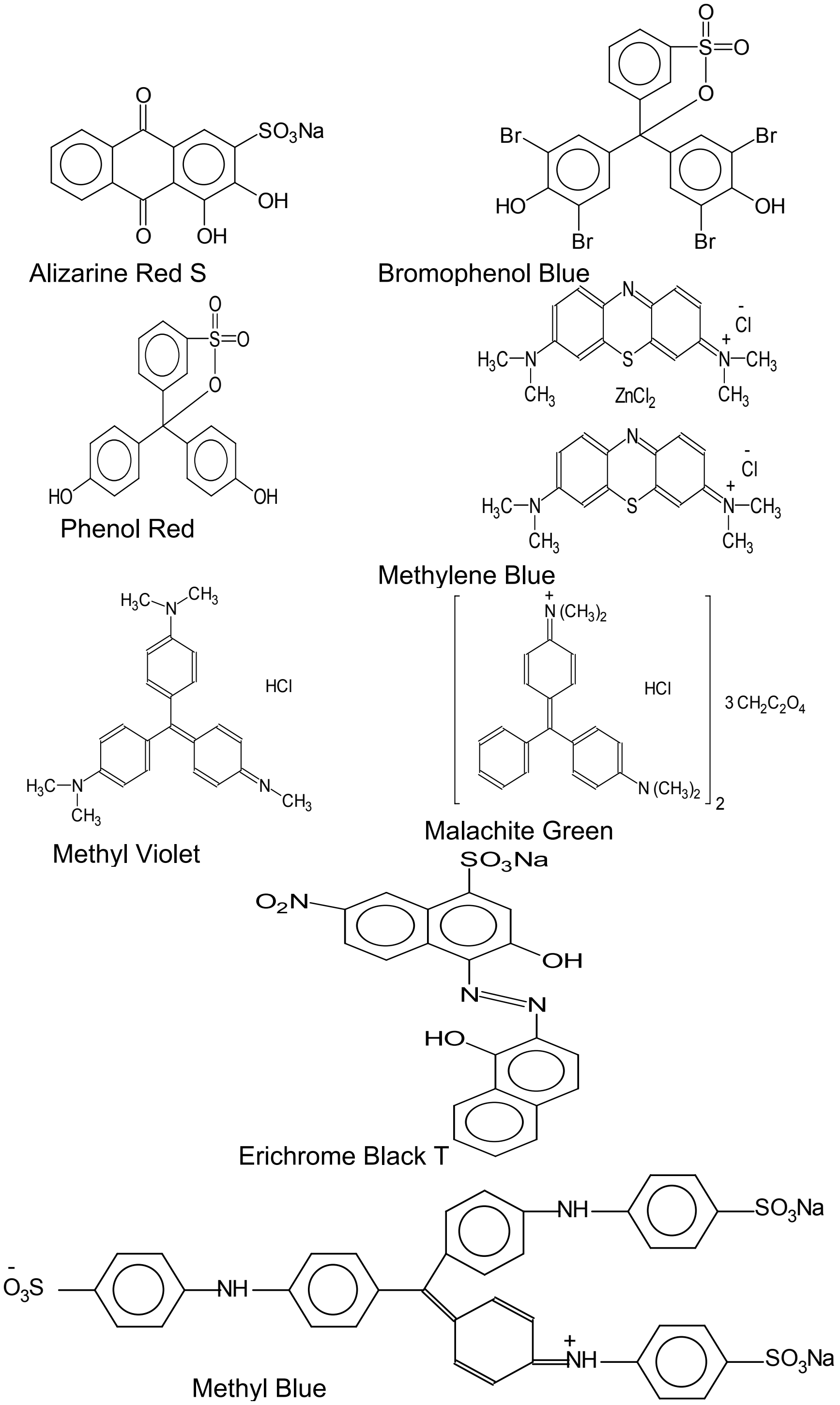
$$\Delta G = \Delta H - T\,\Delta S \tag{3}$$

## 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%, Merck), 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 5 times with distilled water and drying at 473 K followed by its storage in a desiccator. The structures of the dyes are shown in Fig. 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. Weighed amount (0.01g) 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 $\lambda_{max}$ of each dye and the values of $\lambda_{max}$ for each dye are tabulated in Table 1. The amount adsorbed, x/m (mg $g^{-1}$) is plotted against the equilibrium concentration, $C_s$ (ppm) to obtain the adsorption isotherms.



Alizarine Red S

Bromophenol Blue

Phenol Red

Methylene Blue

Methyl Violet

Malachite Green

Erichrome Black T

Methyl Blue

**Fig. 1:** Structure of dyes.

**Table 1:** Molar Mass and the $\lambda_{max}$ for Each Dye.

| S. No. | Dye | molar mass (g mol$^{-1}$) | $\lambda_{max}$ (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 |

# RESULTS AND DISCUSSION

## EFFECT OF SHAKING TIME

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 0.01g of activated charcoal for different intervals of time ranging from 5 to 60 minutes. The absorbance of the filtrate was noted by the spectrophotometer at the $\lambda_{max}$ of each dye. Fig. 2 shows that adsorption of dyes increased with increasing the shaking time and then attain constant value when equilibrium was established. The optimum shaking time was found to be 30 minutes, which was used for all further adsorption studies.

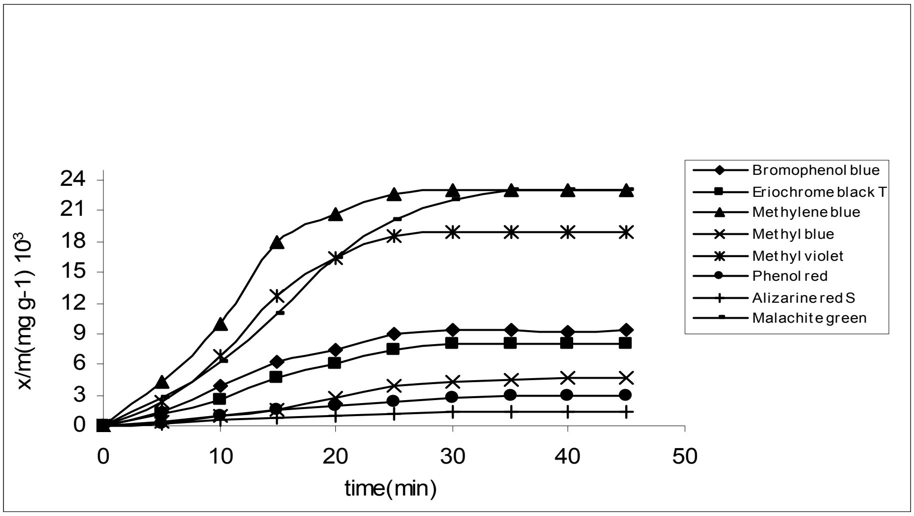


**Fig. 2:** Plots of Shaking Time versus Amount Adsorbed on Activated Charcoal for Various Dye Solutions.

## ADSORPTION ISOTHERMS

Adsorption isotherms obtained at 298, 303, 308, 313 and 318K for bromophenol blue, alizarine red-S, malachite green, methylene blue, methyl blue, methyl violet, eriochrome black-T and phenol red and only the adsorption isotherm for methyl violet at various temperatures is shown in Fig. 3. 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. It is clear from Fig. 3 that adsorption decreased with increase in temperature because the adsorption is an exothermic process. This 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 behavior. This also indicated that desorption steps increase at higher temperature than the adsorption. This type of adsorption is likely classified as reversible adsorption. A behavior similar to this has also been observed by Longhinotti *et al*. [1998] on the studies of adsorption of orange (IV) and orange G on biopolymer chitin.

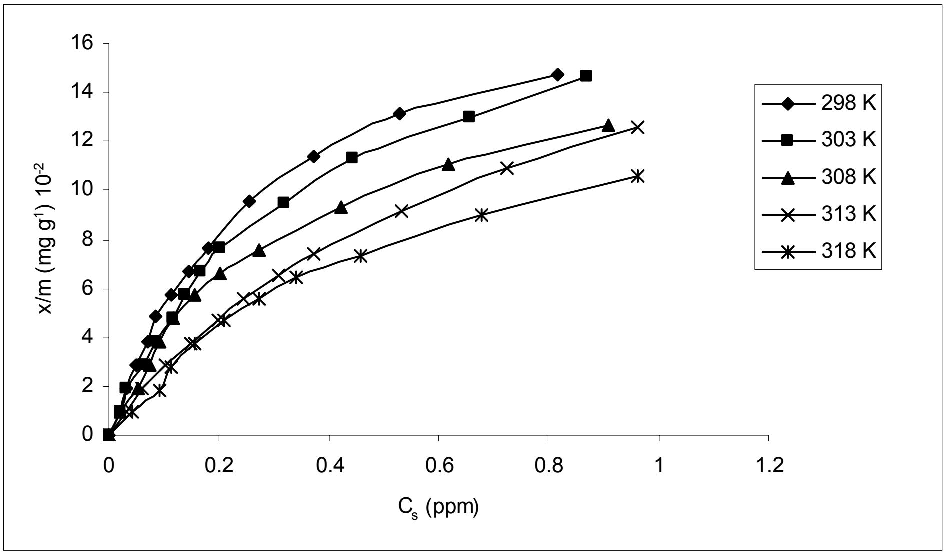


**Fig. 3:** Adsorption Isotherms of Methyl Violet on Activated Charcoal at Various Temperatures.

## THERMODYNAMIC PARAMETERS

The free energy of the adsorption was calculated by equation (1) where "K" is the adsorption coefficient obtained from the Langmuir equation [Mittal Et al. 2005]. The values of free energy are negative for all the system as shown in Table 2, indicating that the process is spontaneous. The ∆G values for all the case more or less approximatly remains constant, indicating that there is no effect of temperature on free energy of adsorption.

The heat of adsorption was calculated by using equation (2) by plotting a graph lnK versus reciprocal of temperature as shown in Fig. 4. The slope gave the value of heat of adsorption shown in Table 2. The values of ∆H for all the systems are negative, indicating that the processes are exothermic. The similar results for the adsorption of ethyl orange, mentanil yellow and acid blue from aqueous solutions on industrial waste were obtained by Jain *et al.* [2003].

**Table 2:** Thermodynamic Parameters for the Adsorption of Various Dyes on Activated Charcoal.

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

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 the chemisorption of these dyes. The ΔH values for alizarine red S, bromophenol blue and eriochrome black T are less than 40 KJ mol$^{-1}$ but BET isotherm confirm the chemisorption of these dyes on the activated charcoal. The entropy was calculated by equation (3). The entropy of adsorption of molecules from the solution on the surface was a decreased shown in Table 2. Molecules before adsorption can move in three dimensions but as they get adsorbed on the surface, the motion of molecules restricted towards the surface and their disorderness decreased resulting in the decrease in entropy. But in case of bromophenol blue the entropy increased. The behavior similar to this was also observed by Amina *et al.* [2004] 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 unfavorable 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.

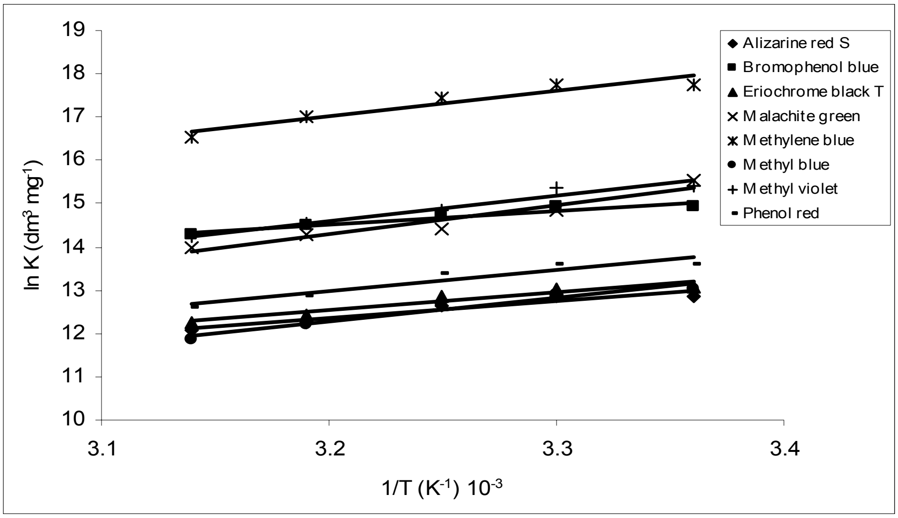


**Fig. 4:** Plots of lnK vs 1/T for the Adsorption of Various Dyes on Activated Charcoal.

## CONCLUSIONS

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. The adsorption of all the dyes was found to decrease with the increase in temperature. The B.E.T isotherm was not obeyed by all the dyes, suggesting that the adsorption on activated charcoal is chemisorption and the value of – ΔH between 26-55 kJ mol$^{-1}$ also confirm this. The negative ΔG and ΔH values show that the adsorption of dyes on activated charcoal is spontaneous and exothermic.

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