Thermodynamics of Basic Dyes (Methylene blue and Basic blue 3) Adsorption on Activated Charcoal Prepared from the Wood of *Ailanthus Altisima*

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Summary: In this study, various thermodynamics parameters for the removal of two basic dyes Methylene blue (MB) and Basic blue3 (BB 3) from aqueous solution by the activated charcoal (M75) prepared from the wood of *Ailanthus altisima* were investigated. Most of the adsorption took place during the first 80 minutes. Equilibrium was however achieved in 2 hrs duration for the sample activated at 105 ^{0}C. In case of the sample activated at 800 ^{0}C, the equilibrium was established in one-hour. The color removal efficiency of the powdered activated charcoal prepared by the physical activation and solvent extraction, was determined by the adsorption isotherms. It was concluded that the wood of *Ailanthus altisima* can be used for making activated carbon for the wastewater treatment. This would thus help to manage solid wastes and reduce materials cost for water pollution control.

Introduction

The discharge of dyes in to watercourses is a serious pollution problem threatening the water supply and quality. Increasing concentration of these dyes in the water constitute a severe health hazard due to their non-degradability, toxicity, accumulation and magnification through out the food chain. Color removal from textile effluents has been the subject of great attention in the last few years, not only because of its toxicity but also mainly due to its visibility [1]. Through hundreds of years, the scale of production and the nature of dyes have changed widely and consequently the negative impact of dyes on the environment has increased. Adsorption treatment processes, which lowers the concentration of dissolved organic compounds [2-3] in water effluents, are rapidly gaining importance.

Synthetic dyes are used extensively in textile dying, printing industries color photography and as additives in petroleum products. Approximately 10, 000 different types of dyes and pigments are produced worldwide annually and it is estimated that 10 to 15 % of the dyes used is lost in the effluent during the dying process [4-5]. Effluents discharged from dyeing industries are highly colored and they can be toxic to aquatic life in the receiving waters [6-7]. Increasing stress of the environmental protection agencies on the decontamination of wastewaters has created an interest in the use of activated carbons for the purpose [8-9].

The economical removal of dyes from effluents still remains an important problem. A number of adsorbent such as chitin [10], silica gel [11], sawdust [12], natural clay [13], bagasse pith fibers [14 and polymeric adsorbents [15] have been used recently, but activated carbon technology and its potential for waste water treatment has been appreciated. This method is widely used due to its simplicity, effectiveness and low space requirements. Activated carbon can be produced from a variety of materials such as wood, coal, peat and lignin etc. Although the raw material are cheap but its activation at high temperatures make it expensive and skillful. Adsorption is a unit operation in which surface active materials in true solution are removed from the solvent by interphase transfer to the surfaces of an adsorbent particle. This process is used in environ-mental engineering practice for removal of various pollutants such as soluble organics, dyes, [16] pesticides etc., from wastewaters and for removal of taste and odour-producing substances from natural waters that are to be used as potable water supplies [17-18].

The objective of this work was to study the effectiveness of activated charcoal prepared from the low cost wood of *Ailanthus altisima* for the treatment of wastewaters.

Results and Discussion

In the studies of adsorption, surface area is the most important parameter to be considered. Surface area of the charcoal activated at 105 ^{0}C and 800 ^{0}C as given in Table-1, indicate an increase with the rise in activation temperature. The low surface area at lower

Table-1 Surface area of M75 activated at various temperatures.

Serial No.	Activation temperatures (^{0}C)	Surface area (m^2/ g)
1	105	150.00
2	300	200.00
3	600	293.13
4	800	294.37
5	1000	143.75

temperature may be due to the presence of surface complexes such as phenolic, hydroxyl group, anhydride, carboxylic acids, lactones, heterolytic ether structures and cyclicperoxides. The presence of these functional groups reduce the active sites for adsorption. At high temperatures the surface complexes start to decompose and leave the surface porous, which allow greater adsorption of the dyes as is indicated in Figures 1-4. It was found that above 800 °C, decrease in the surface area occurs as shown in Figure 5, which may be due to the decomposition of the surface at high temperature.

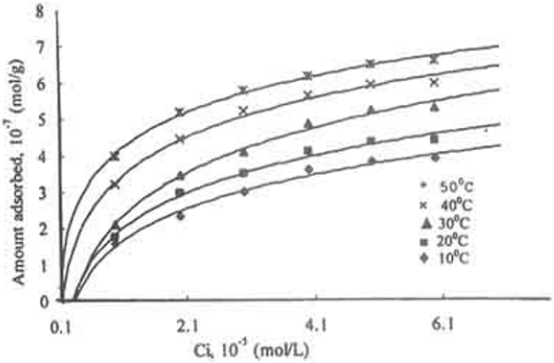

Fig. 1: Adsorption isotherm of BB 3 on M75 activated at 105 °C.

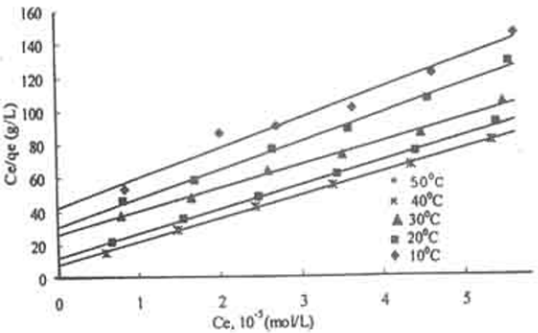

Fig. 2: Adsorption isotherm of BB 3 on M75 activated at 800 °C.

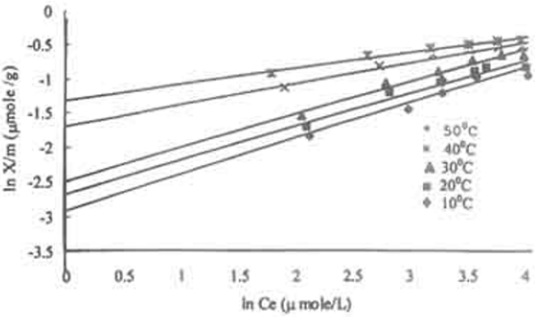

Fig. 3: Adsorption isotherm of MB on M75 activated at 105 °C.

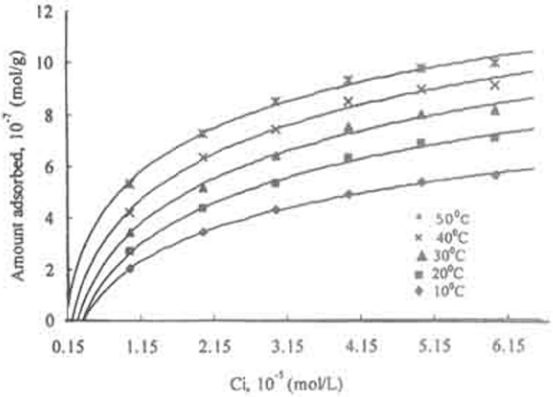

Fig. 4: Adsorption isotherm of MB on M75 activated at 800 °C.

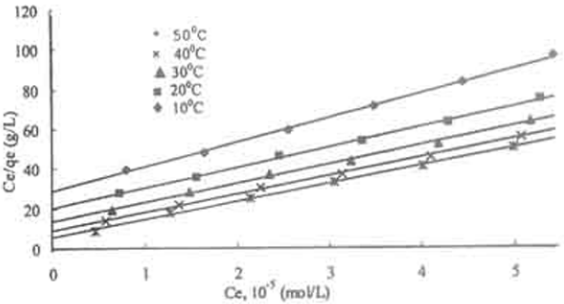

Fig. 5: Variation of surface area with temperature.

The effect of time for the optimum uptake of both the dyes are shown in Figures 6 and 9. These show that equilibrium reaches with in 2 hours for the sample activated at 105 °C, and for the sample activated at 800 °C it reaches in 1 hr. The equilibrium time predict diffusion mechanism of the dye from solution in to the micro pores of the adsorbent, while

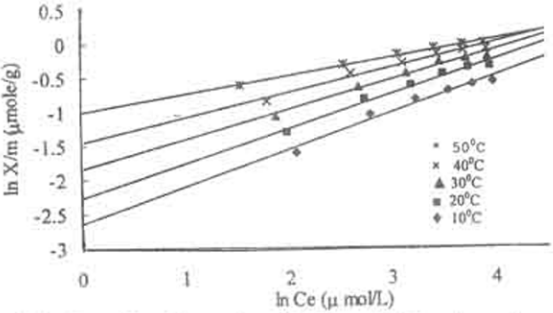

Fig. 6: Up take study of BB3 on M75 activated at 105 °C as a function of time at two different concentrations.

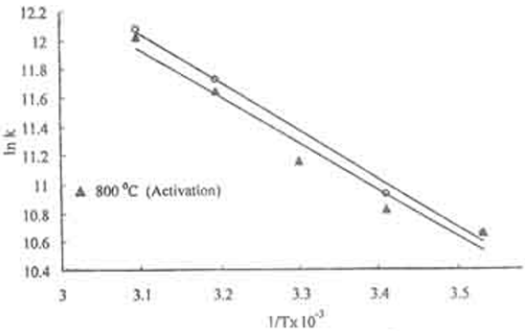

Fig. 7: Up take study of BB3 on M75 activated at 800 °C as a function of time at two different concentrations.

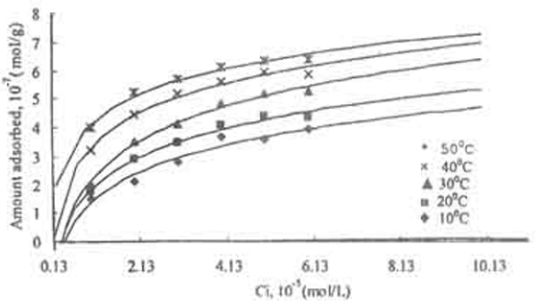

Fig. 8: Up take study of MB on M75 activated at 105 °C as a function of time, at two different concentrations.

some is adsorbed on the outer surface of the sample so both physical and chemisor-ptions mechanisms are possible [19]. The uptake study conducted at the same constant temperature for both the dyes indicate that the sample activated at lower temperature show lower adsorption as compa-red to the sample

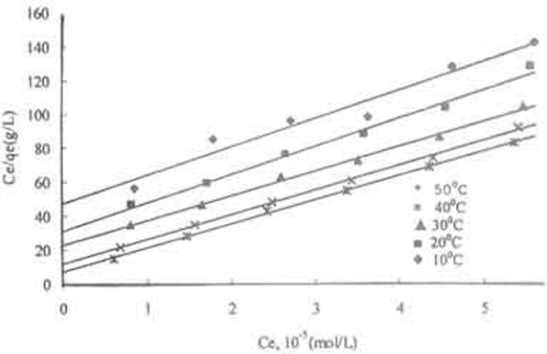

Fig. 9: Up take study of MB on M75 activated at 800 °C as a function of time, at two different concentrations.

activated at high temperature. The high adsorption on the sample activated at 800 °C is thus due to the increased surface area and porosity. It is also evident (Figures 1-4) that the amount adsorbed increases with increase in concen-tration of dyes. Further it is observed that BB 3 adsorption is greater than MB on both the activated carbon samples, which may be due to the fact that with the increase in molecular weight, the solubility of these dyes decrease in water. Lower interfacial energy is thus needed for the removal of dye at the solid-liquid interface, resulting in higher adsorption [20].

The linear form of Langmuir adsorption isotherm, ($Ce/qe = 1/KXm + Ce/Xm$, where Ce is the equilibrium concentration (mol/L), qe is the amount of dye adsorbed (mol/g), Xm is the monolayer capacity (mol/g) and K is the binding energy constant), was found to fit the data (Fig. 10-13) of both BB 3 and MB. The values of K and Xm were calculated from the slopes and intercepts of the plots and are reported in Tables-2 and 3. It can be seen that the values of Xm i.e. the monolayer adsorption capacity increases with the increase in activation

Table-2: Langmuir adsorption constants of Basic blue 3 and Methylene blue at different temperatures on M75 Activated at 105 °C.

Temperature	Basic blue 3		Methylene blue	
T (K)	$Xm, 10^{-3}$ (mol/g)	$K, 10^{3}$ (L/mol)	$Xm, 10^{-3}$ (mol/g)	$K, 10^{3}$ (L/mol)
283	5.619	42.74	5.93	35.834
293	5.919	55.979	5.99	53.602
303	7.241	53.607	6.87	63.403
313	6.925	122.991	6.88	125.502
323	7.269	176.424	7.04	220.783

Table-3: Langmuir adsorption constants of Basic blue 3 and Methylene blue different temperatures on M75 Activated at 800 °C.

Temp.	Basic blue 3		Methylene blue	
T (K)	$Xm, 10^{-7}$ (mol/g)	$K, 10^{3}$ (L/mol)	$Xm, 10^{-7}$ (mol/g)	$K, 10^{3}$ (L/mol)
283	8.165	42.850	8.55	38.585
293	9.882	50.235	9.79	47.821
303	10.53	70.340	10.77	63.744
313	10.091	113.711	10.97	101.196
323	11.16	166.219	11.55	162.561

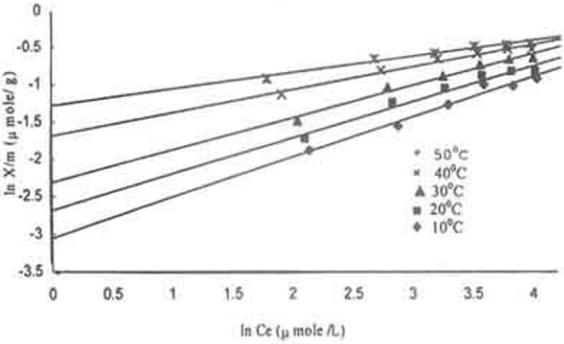

Fig. 10: Laungmuir adsorption isotherm of BB 3 on M75 activated at 105 °C.

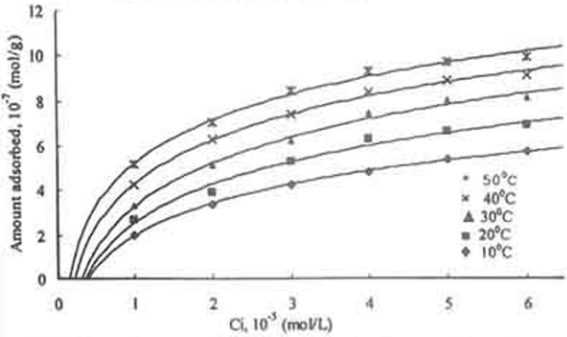

Fig. 11: Langmuir adsorption isotherm of B B3 on M75 activated at 800 °C.

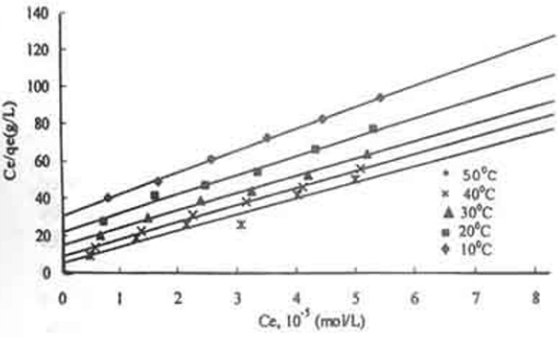

Fig. 12: Langmuir isotherm of MB on M75 activated at 105 °C.

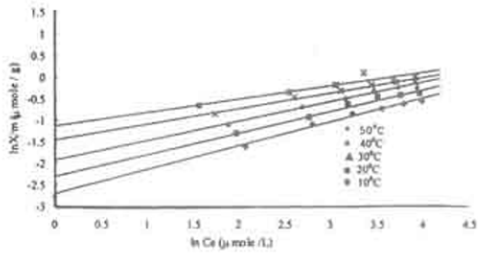

Fig. 13 Laungmuir adsorption isotherm of MB on M75 activated at 800 °C.

temperature. The data plotted according to the linear form of Freundlich isotherm (ln x/m =lnk + 1/n lnCe) are shown in Figures 14 and 17. The values of Freundlich constants "n" and "k" are given in Tables 4 and 5. It can be seen from the plots that the data is better represented by the Langmuir isotherm as compared to that of Freundlich.

Table-4: Freundlich adsorption constants for Basic blue 3 and Methylene blue at different temperatures on M75 Activated at 105 °C .

Temp.	Basic blue 3		Methylene blue	
T (K)	1/n	k	1/n	k
283	1.92	0.001	1.85	0.001
293	2.05	0.002	2.05	0.002
303	2.07	0.003	2.31	0.005
313	3.23	0.020	3.27	0.020
323	4.31	0.050	4.53	0.050

Table-5: Freundlich constants of Basic blue 3 and Methylene blue on M75 Activated at 800 °C.

Temp.	Basic blue 3		Methylene blue	
T (K)	1/n	k	1/n	k
283	1.86	0.002	1.76	0.001
293	1.98	0.005	1.98	0.004
303	2.31	0.014	2.21	0.010
313	2.74	0.030	2.78	0.030
323	3.74	0.100	3.23	0.070

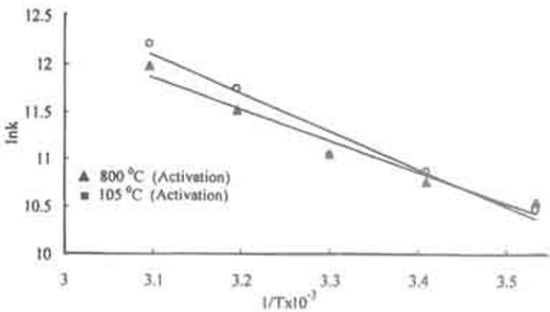

Fig. 14: Freundlich adsorption isotherm of BB3 on M 75 activated at 105 °C.

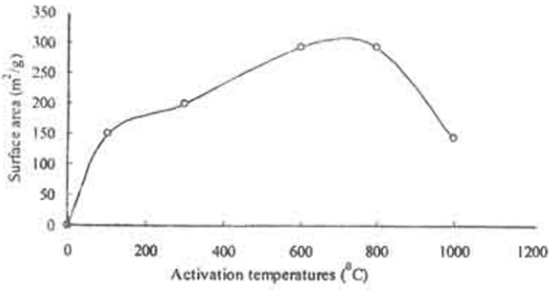

Fig. 15: Freundlich adsorption isotherm of BB3 on M 75 activated at 800 °C.

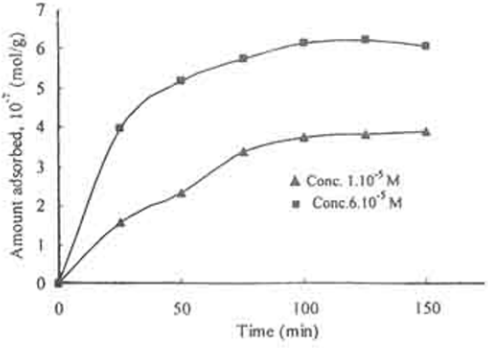

Fig. 16: Freundlich adsorption isotherm of MB on M 75 activated at 105 °C.

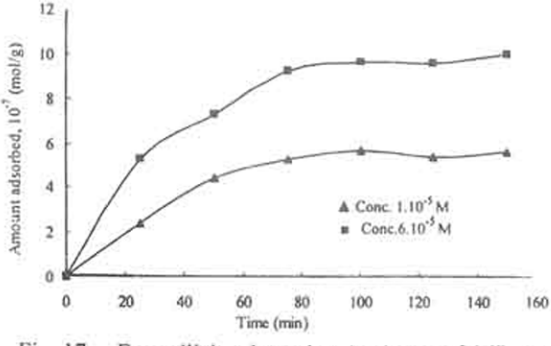

Fig. 17: Freundlich adsorption isotherm of MB on M 75 activated at 800 °C.

Thermodynamic parameters such as ΔH^0, ΔS^0 and ΔG^0 were calculated from the slope of the plots of ln$K$ vs. I/T (Fig. 18 and 19) using the equation·

$$\ln K = -\Delta H^0/RT + \Delta S^0/R.$$

Where R is the gas constant and T is the absolute temperature. The free energy change was calculated from the relation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

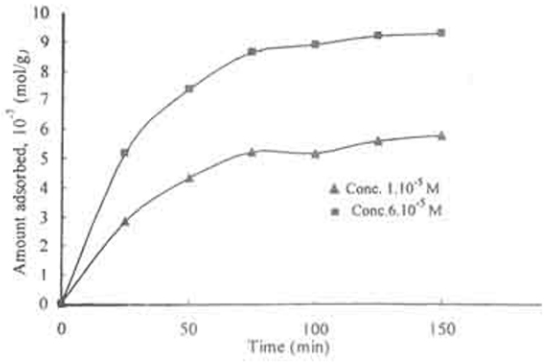

Fig. 18: Plot ln k vs 1/T of BB3 and M75 activated at 105 °C and 800 °C

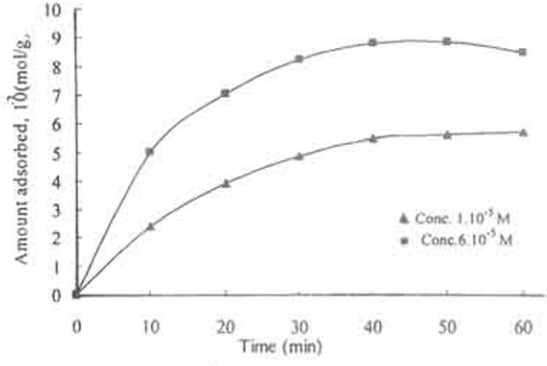

Fig. 19: Plot ln k vs 1/T of MB and M75 activated at 105 °C and 800 °C.

The values of ΔH^0, ΔS^0 and ΔG^0 are given in Tables-6 and 7. The positive values of ΔH^0 indicate that the adsorption is endothermic for both the dyes. The negative values of ΔG^0 show spontaneous nature of adsorption of both BB 3 and MB on activated charcoal and the decrease in ΔG^0 values with rise in temperatures for both dyes indicates that the adsorption process becomes more spontaneous at high temperatures. The spontaneous process of adsorption is also evident from the positive ΔS^0 values.

Experimental

Powdered activated charcoal was prepared from debarked wood of *Ailanthus altisima* by subjecting three kilograms of wood pieces for destructive carbonization at 450 °C - 600 °C in a specially designed closed steel container with a narrow out let for the escape of gaseous carbonization products. The charcoal prepared was ground in to fine powder and leached with molar solutions of

Table-6: Thermodynamics parameters for the adsorption of Basic blue 3 and Methylene blue at different temperatures on M75 Activated at 105 ^{0}C .

Temperature	Basic blue 3			Methylene blue		
T (K)	ΔH^0 (kJ mol^{-1})	ΔS^0 (kJ mol^{-1}K^{-1})	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (kJ mol^{-1}K^{-1})	ΔG^0 (kJ mol^{-1})
283			-24.71			-24.41
293			-26.55			-26.41
303	27.560	0.185	-28.40	32.76	0.202	-28.44
313			-30.25			-30.46
323			-32.09			-32.48

Table-7 Thermodynamics parameters of Basic blue 3 and Methylene blue on M75 Activated at 800 ^{0}C.

Temperature	Basic blue 3			Methylene blue		
T (K)	ΔH^0 (kJ mol^{-1})	ΔS^0 (kJ mol^{-1}K^{1})	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJmol^{-1})	ΔS^0 (kJ mol^{-1}K^{-1})	ΔG^0 (kJ mol^{-1})
283			-24.69			-39.24
293			-26.52			-41.08
303	26.81	0.182	-28.34	12.54	0.183	-42.91
313			-30.16			-44.74
323			-31.97			-46.57

HCl and HNO_3 in 1: 1 ratio for the removal of inorganic substances. It was then extracted with n-hexane and dried at 90 ^{0}C in a vacuum oven for 50 minutes. The samples having mesh size 180-212μ were activated under vacuum in a tube furnace at temperatures of 105 ^{0}C and 800 ^{0}C. Surface area of the samples was found by Snow's iodine adsorption method [21].

Concentrations of BB3 and MB were determined at wave lengths of 653 nm (λ_{max}) and 660 nm (λ_{max}) respectively, using Spectronic 20D. Standard solutions of 1.10^{-5} to 6.10^{-5} M of both Basic blue 3 (Analytical grade Aldrich No. 37801-1) and Methylene blue (Analytical grade Aldrich No.31 911-2) were prepared in doubly distilled water. Duplicate samples containing 20 ml portions of Basic blue 3 solutions at pH 7.02 were taken in reagent bottles that contained 0.2 g of the activated charcoal. The reagent bottles were shaken on a water bath electric shaker at a constant speed at different temperatures. After each interval of time the solutions were filtered, using filter paper sheets, by discarding first 4-5 ml portion of the filtrate. Same was done for Methylene blue with initial pH of 7.04. The amount adsorbed (mol/ g) was then calculated using the formula,

$$\frac{(Ci - Ce)V}{W}$$

Where *Ci* is the initial concentration (mol/ L), *Ce* is the equilibrium concentration (mol/ L), *V* is the volume of solution in liters and *W* is the amount of adsorbent in grams.

Conclusions

Results of the present study show that activated charcoal prepared from the wood of *Ailanthus altisima* by heating in the absence of air at 800 ^{0}C, produces an adsorbent that can be used for dyes removal from wastewaters. The Gibbs free energy of adsorption (ΔG^0) of the dyes decrease with increase in the adsorption maximum *Xm*. As the wood of *Ailanthus altisima* has no commercial value, it can therefore be used as a cheap precursor for activated carbon preparations that can be used in water treatment systems.

Acknowledgement

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