Kinetics of Removal of Dye (Basic blue 3) from Aqueous Solution by Activated Charcoal Prepared from the Wood of *Brausonitia papyrifera* (Paper Mulberry)

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Summary: The use of activated charcoal (M-76) prepared from low cost wood of Brausonitia paypyrifera (Paper Mulberry), for the removal of dye Basic blue3 (BB3) from aqueous solution was investigated. The linear applicability of Langergren equation points towards pseudo-first order rate expression. Activation energy of adsorption were also determined. The results indicate that Brausonitia papyripera could be employed as low cost alternative to commercial activated carbon in wastewater treatment for the removal of basic dyes.

Introduction

Among the different pollutants of aquatic ecosystem, dyes are a large and important group of chemicals. Most of these dyes are used in the textile industries. These dyes include different compounds with unknown environmental behavior with possible toxicity and carcinogenicity [1]. For industrial liquid effluents, color is the first indication of water pollution [2]. The industrial dumping of effluents containing dyes not only affect the natural beauty of the rivers, but also is extremely toxic to aquatic life, interfering in the transmission of sunlight and thus reducing the photosynthesis.

One of the major problems faced by the textile industries is the removal of the dyes in the effluents. Some processes have been employed in order to solve this problem such as, adsorption, chemical flocculation, flotation, sedimentation [3], chemical oxidation [4] and biological techniques [5,6]. Adsorption appears to be effective and good alternative for the treatment of effluents.

Activated charcoal with large internal surfaces and pores has potential for dyes adsorption. Even though adsorption is only one to several molecules deep, moderate amount of activated carbon can effect the removal of significant amounts of pollutants from wastewater [7,8], soil and waste gas [9]. Due to their great adsorption capability, activated charcoal is also used for the removal of undesirable substances from edible oil, fats, sugar, alcoholic beverages, chemicals and pharmaceuticals as well as solvents. It is also used as catalyst support [10, 11]. Activated carbon is also a recommended and a strategic adsorbent for removal of organic volatile compounds [12], which are used in perfumes, paints, solvents, varnishes and chemical cleaners. The adsorption of these substances on activated charcoal is influenced by various factors such as contact time, solution concentration [13], temperature and pH etc. The effects of contact time and temperature on the different samples of the prepared charcoal were investigated in the present study.

Results and Discussion

Charcoal prepared from the wood of *Brausinititia papyripera* was found an effective adsorbent for the removal of dyes from aqueous solution. Kinetic plots of adsorption of Basic blue 3 on activated charcoal at different temperatures are shown in the figures, 1, 3, 5, 7 and 9. It is clear from the curves that initially the adsorption increases with time and then the process slows down and attains a constant value after about 50 minutes. The slow down of the process as indicated by the plateau of the curve, may be due to the surface coverage and the diffusion of the dye into the micro pores of the adsorbent. These figures also indicate enhanced adsorption at high temperatures.

Figure 12 shows that the surface area of the activated samples increases with the activation temperature from 105^0C-800^0C which may be due to escape of various surface functional groups on charcoal and then as the temperature approaches 1000^0C it decreases. This smaller surface area may be due to the decomposition of the surface at tempera-

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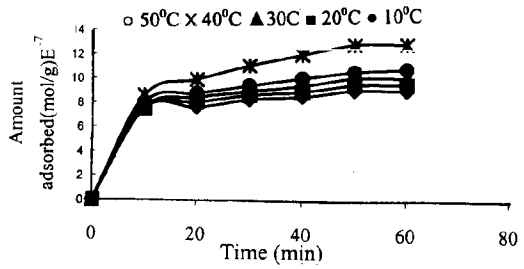

Fig.1: Adsorption on BB 3 on M-76 activated at 105°C at different temperatures.

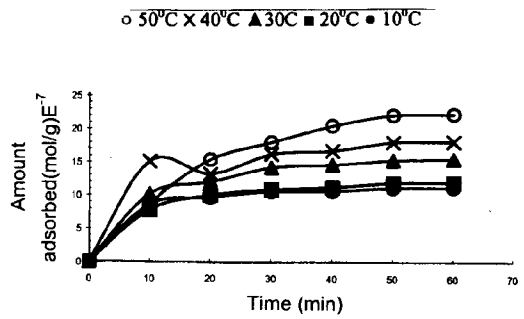

Fig.3: Adsorption on BB 3 on M-76 activated at 300°C at different temperatures.

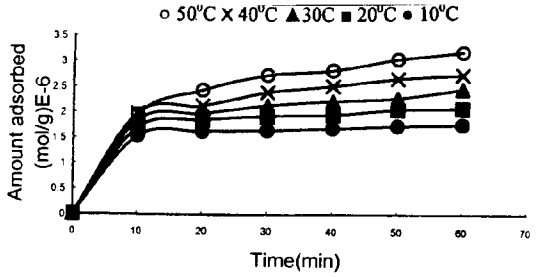

Fig. 5: Adsorption on BB 3 on M-76 activated at 600°C at different temperatures.

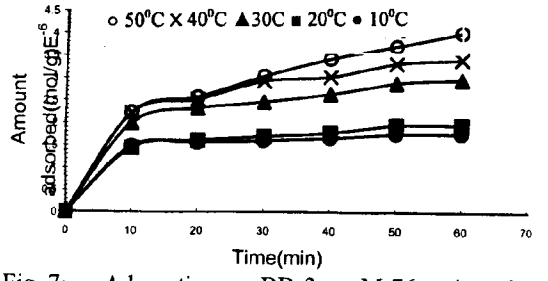

Fig. 7: Adsorption on BB 3 on M-76 activated at 800°C at different temperatures.

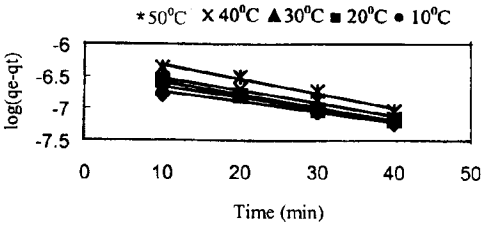

Fig.2: Lagergren plots of BB 3 on M-76 activated at 105°C at different temperatures.

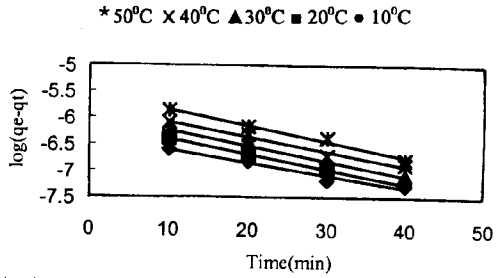

Fig.4: Lagergren plots of BB 3 on M-76 activated at 300°C at different temperatures.

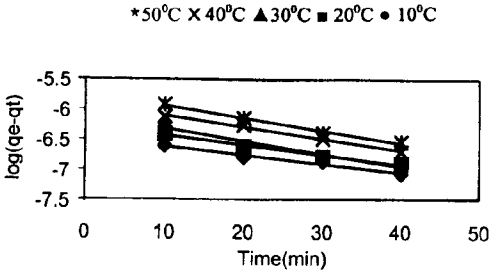

Fig.6: Lagergren plots of BB 3 on M-76 activated at 600°C at different temperatures.

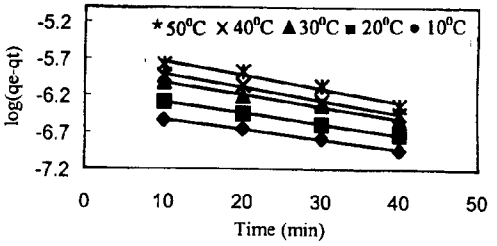

Fig.8: Lagergren plots of BB 3 on M-76 activated at 800°C at different temperatures.

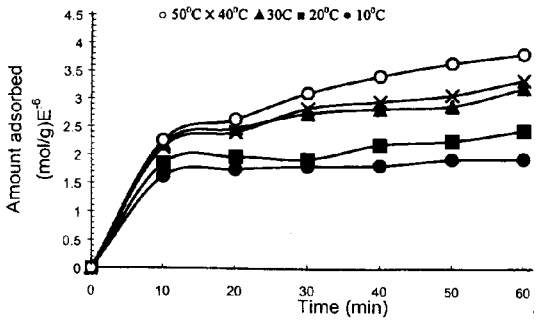

Fig. 9: Adsorption on BB 3 on M-76 activated at 1000°C at different temperatures.

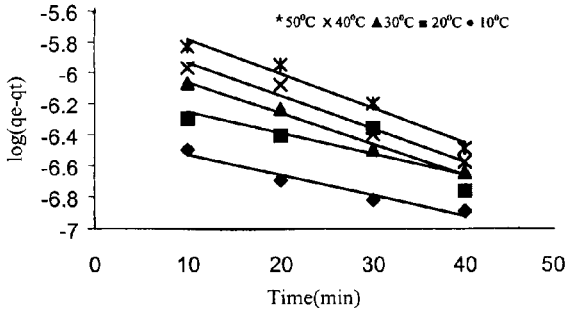

Fig.10: Lagergren plots of BB 3 on M-76 activated at 1000°C at different temperatures.

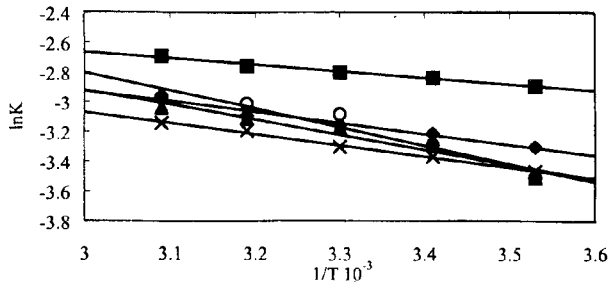

Fig.11: Arrhenius plots of BB 3 on M-76 activated at 105°C to1000°C at different tempera-tures.

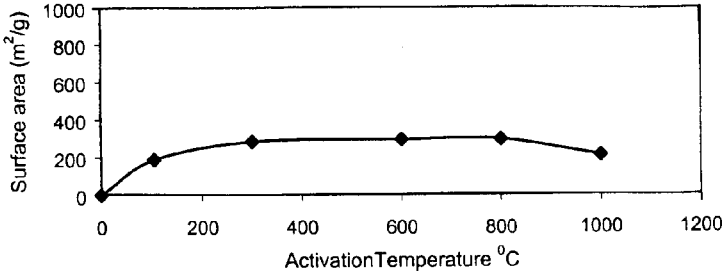

Fig. 12: Plot of surface area vs activation tempera-tures.

tures above 800°C. The results indicate that surface area is responsible for the adsorption of the dye on the activated charcoal, as is demonstrated by the high adsorption capacity of the samples activated at 800°C compared to that activated above this temperature.

For determining the kinetic rate constants, Lagergren equation[16] was used in the form,

$$\log(q_e - q_t) = \frac{-kt + \log q_e}{2.303}$$

Where q_e is the amount of dye adsorbed at equilibrium and q_t is the amount adsorbed at time t. Plot of log $(q_e - q_t)$ vs. time were found to be linear, indicating a pseudo first order kinetic mechanism. The kinetic parameter k was calculated from the slope of the graphs shown in figures 2, 4, 6, 8 and 10. The values of rate constant k given in the table 1, increase with the rise in temperature, which indicates the process of adsorption to be endothermic. The k values were used to compute activation energy

Table. 1. Values of rate constant (k) for the sample activated at 105°C to 1000°C.

Temp. (°C)	Rate Constants k (min^{-1}) Activation temperatures.				
	105 °C	300 °C	600 °C	800 °C	1000 °C
10	0.0368	0.0555	0.0300	0 .0313	0.0299
20	0.0403	0.0587	0.0375	0.0345	0.0373
30	0.0426	0.0607	0.0419	0.0368	0.0458
40	0.0451	0.0633	0.0444	0.0409	0.0490
50	0.0518	0.0677	0.0476	0.0430	0.051

Table.2. Activation energies (Ea) of the carbon particles of size 180-212 (μ) activated at different temperatures

Activation temperatures (°C)	Activation energy (KJ/mole)
105	6.05
300	3.60
600	6.77
800	6.22
1000	10.54

(E_a) using the Arhennius equation [17] by plotting ln k vs. 1/T.

$$\ln k = \ln a - \frac{E_a}{RT}$$

The plots of ln k vs. 1/T are shown in figure 11. The slopes of the curves give Ea values in KJ/mol (Tab. 2).

Experimental

Powdered activated charcoal was obtained from debarked wood of *Brausonitia papyrifera* by subjecting three kilogram 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 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°C in a vacuum oven for 50 minutes. The samples having mesh size 180-212μ were activated under vacuum [14] in a tube furnace at temperatures of 105°C, 300°C, 600°C, 800°C and 1000°C.

Surface areas were found by Snow's iodine method [15] by using the formula 12.5(24-V)m^2/gm, where V is the volume of sodium-thiosulphate used.

Concentration of the dye was determined spectrophotometrically at 653nm (λ_{max}), using spectronic 20D. Standard solutions of 1.10^{-5} to 6.10^{-5}M of the Basic blue 3 (Analytical grade Aldrich NO. 37801-1) were prepared in doubly distilled water.

Duplicate samples containing 20ml portion of 5.10^{-5}M Basic blue 3 at pH 7.02 were taken in reagent bottles that contained 0.200g of activated charcoal. The reagent bottles were shaken on a water bath electric shaker at a constant speed and at different temperatures, for different time intervals. After each interval of time the solutions were filtered, using filter paper sheets by discarding first 4-5ml portion of the filtrate. 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

The present study indicates that the *Brausonitia papyrifera* charcoal could be employed as low cost alternative to the commercial activated carbon, in waste water treatment for the removal of dyes. The enhanced adsorptions at higher temperatures indicate endothermic reaction. Thus the use of the charcoal for the removal of Basic dyes from industrial wastewater effluents at high temperatures would be more efficient than at lower ones. The use of the prepared activated carbon is cost effective and superior to the biological processes in the sense that the operation is simple and is not affected by toxic substances.

Acknowledgement

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References

1. T. A. Albanis, T. M.Sakellarrides and T. G. Danis, *Global Nest.*, **2**, 237 (2000).
2. E. Longhanotti and F. Pozza, *Braz. Chem. Soc.*, 9, 435 (1998).

3. M. M. Assadi and M. R. Jehangiri, *Desalination*, **141**, 1 (2000).
4. V. Meshko, L. Markovska, M. Mincheva and A.E. Rodridgues, *Water Research.*, **35***(14)*, 3357 (2001).
5. R. F. P. M. Moreira, J. L. Soares and A. E. Rodrigues, *Braz. J. Chem. Eng.*, **18**, 10 (2001).
6. Y. Guo, S. Yang, F. Wuyou, Q. Jurui, L. Renzhi, Z. Wang and X. Honding, *Dyes and pigments.*, **56**(3), 219 (2003).
7. R. Tseng, W. Feng-chen and R.S. Juang, *Carbon.*, **41**(3), 487 (2003).
8. F. K. Bangash, S. Alam and M. Iqbal, *Jour. Chem. Soc. Pak.*, **23**, 215 (2001).
9. S. H. Lin and A.L.Chen, *Water Research*, **31**, 868 (1997).
10. G. Marban and A. B. Fuertes, *Appl. Catal. Beh. Envi.*, **34**, 55 (2001).
11. G. Mishera and M.Tripathy, *Colourage.*, **37**, 35 (1993).
12. A. B. Fuertes, G. M. Marban and D. M. Nevskaia, *Carbon.*, **41**, 87 (2003).
13. P. K. Malik, *Dyes and pigments*, **56**(3), 239 (2003).
14. N. Z. Cao and C. Roy, *Energy and Fuel*, **15**, 1263 (2001).
15. M. L. Stubebaker, *Rubber Chem. and Technology*, **30**, 4101 (1957).
16. H. S. Altandogan, S. A. Dogar, *Waste Management.*, **22**, 357 (2002).
17. K. J. Laidlar, "*Chemical Kinetics*" 3rd ed., Harper and Row, Inc., New York, pp. 39, (1987).