

Adsorption of Azo Dye on Activated Carbon Prepared from Waste Wood: 2. Equilibrium

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Summary: The present study was designed to investigate the effect of activation temperature on carbon prepared from the wood of *Salvadora oleoides*. The samples were characterized. Activation at 800 °C is higher due to the decrease in polarity of the carbon surface, resulted from the decomposition of some of the acidic oxygen surface functionalities. Increase in adsorption rate was observed for higher temperature activated sample due to the increase in the surface area and opening of the blind pores and the increase in pore volume. Lower rate of dye adsorption on sample activated at 400 °C may be due to the fact that polar functional groups situated at the pore opening have adsorbed water strongly through hydrogen bonds that in turn has resulted in the pores constriction or blockage. Freundlich, Langmuir, DR isotherm, and distribution coefficient models were used to compare the efficiency of the carbon activated at different temperature (400, 800 °C). The data generated from all isotherms, show that 800 °C activated sample has greater dye adsorption capacity.

Introduction

Activated carbon is one of the most useful porous adsorbents from an environmental concern. It has a very porous structure, with pore sizes ranging from micropores (<20 Å slit width) to macropores (>500 Å slit width), and has a variety of surface groups, impurities, and irregularities. Activated carbon can be produced from a number of precursor materials such as coal, peat, coconut shell, and any other inexpensive materials with high carbon content. The adsorption capacity of a certain material is generally related to the nature of the adsorbents surface functional groups. The surface area is also known to play an important role in the adsorption process. Generally, carbon surface characteristics can be related to adsorption capacity from solutions. These characteristics include both chemical and physical properties. Chemically, carbon can be imagined as plates of carbon atoms arranged hexagonally in basal planes [3]. Many chemical groups are assumed to be attached to that complicated geometry. Reactivity of carbon in solution can be attributed to strength and concentration of these chemical groups. Physically, on the other hand, carbon performance can be attributed to the presence of high surface area, channels, and porosity system. Such a structure can

accommodate, or attract, adsorbate species onto the surface by different forces [3]. Since the surface characteristic and internal pore structure of the activated carbon play an important role in adsorption processes and depend both on the precursor used and the method of preparation, therefore, characterization of these are crucial to the adsorption and separation processes [1-3].

In spite of extensive research into color removal from textile wastewater, problems of costly plant requirements or operating expenses; lack of effective color reduction, particularly for sulphonated azo dyes, and sensitivity to variable wastewater inputs are experienced in the application of the chemical and physical treatment methods in reactive dye wastewater treatment. Two properties of reactive dyes limit the rate of color removal: the highly soluble hydrolyzed azo structure and low biodegradability. Due to the chemical nature, molecular size, and structure, activated carbon appears to offer some prospects for effluent treatment. A number of investigations were conducted to evaluate adsorption of reactive dyes onto a range of natural and synthetic, organic and inorganic sorbents [4-9]. This paper presents

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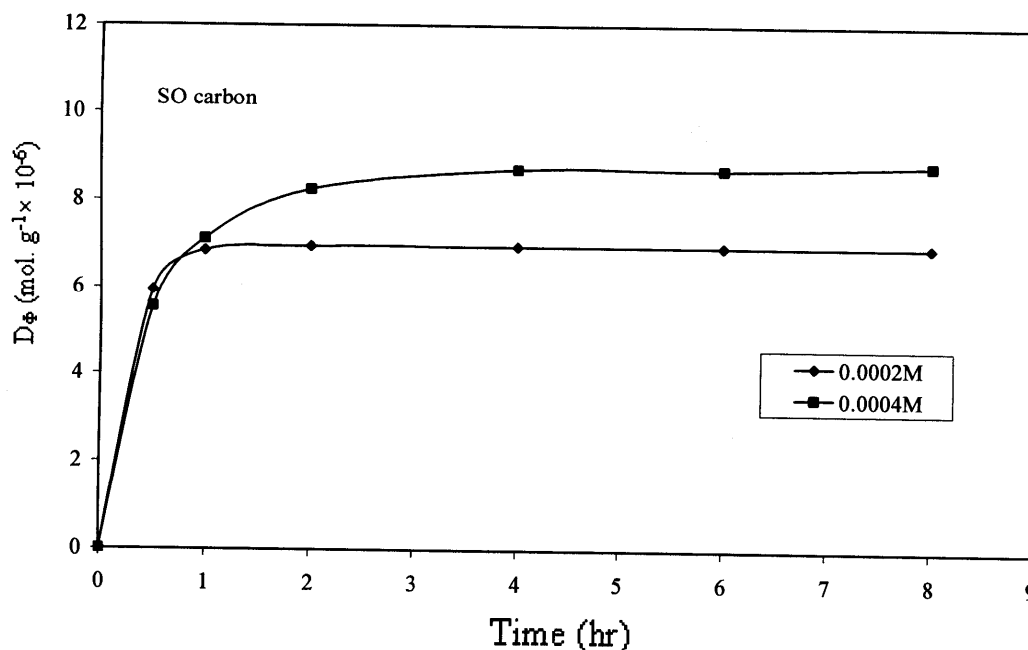


Fig. 1: Equilibration time for the adsorption of acid yellow 29 on SO carbon sample.

adsorption of acid yellow 29 on activated charcoal prepared from fast growing tree and to compare the efficiency of the carbon activated at different temperatures, using the adsorption models of Freundlich, Langmuir, and DR.

Results and Discussion

Equilibrium Studies

Adsorption of acid yellow 29 on activated carbon was high in the initial thirty minutes and then it became slow due to the diffusion in to the micropores. The slow process continued and reached to equilibrium in two hour time giving a plateau in the adsorption curves (Fig. 1).

The equilibrium uptake for two hours, of the acid yellow 29 with the initial dye concentration of $8.0 - 26 \times 10^{-5} \text{ mol dm}^{-3}$ are shown in Fig. 2. The adsorption increased with the dye concentration reaching a plateau that indicates the monolayer surface coverage, with slow adsorption still continued. The study at 10 and 45 °C show that the dye adsorption increased with increase in temperature indicating endothermic nature of the process. The effect of temperature of activation of the sample is also important as high temperatures have the effect of

removing surface acidic oxygen functionalities, leaving the surface pores open for the dye entrance [10]. It is thus shown that carbon samples activated at 800 °C adsorbed more dye than 400 °C carbon samples.

Freundlich equation in the following straight line form [11] was also found to apply to the dye adsorption data,

$$\ln D_{\phi} = \ln K + \frac{1}{n} \ln D_0 \quad (1)$$

The values of parameters n and K (adsorption capacity) calculated from the plots are given in Table-1. The empirical constant n gives information about the surface heterogeneity and affinity for the solute. A larger value of $1/n$ indicates effectiveness of adsorbent. When $1/n > 1.0$, the adsorbed concentration of the solute is greater than that of the solution concentration. The values of constant, K (mol/g) are higher for samples activated at high temperatures.

Langmuir isotherm in the straight line form [12] was applied to the data,

$$\frac{D_{\phi}}{D_0} = \frac{1}{K_1 d} + \frac{D_{\phi}}{d} \quad (2)$$

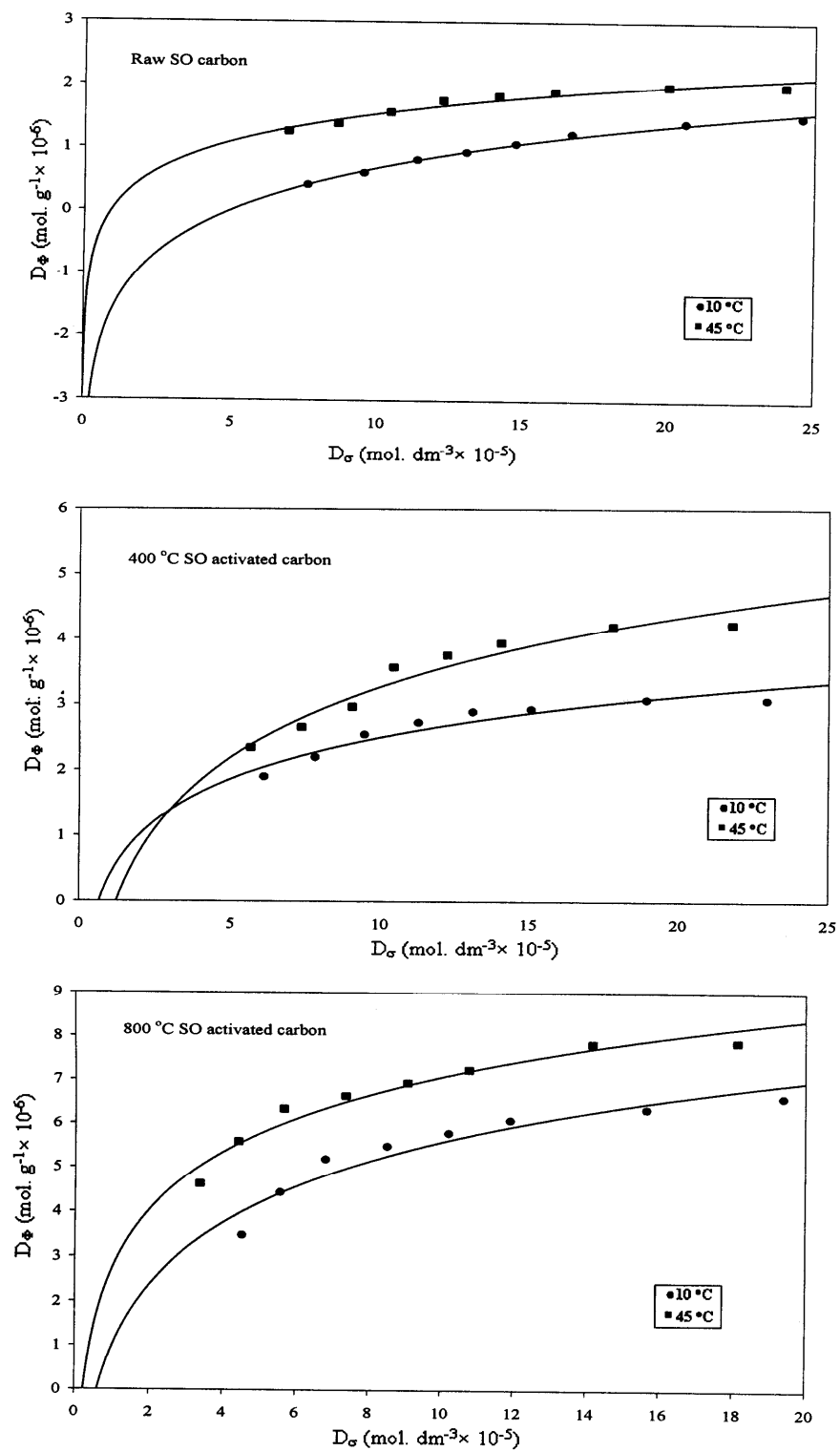


Fig. 2: Adsorption isotherms of acid yellow 29 on the SO carbon samples.

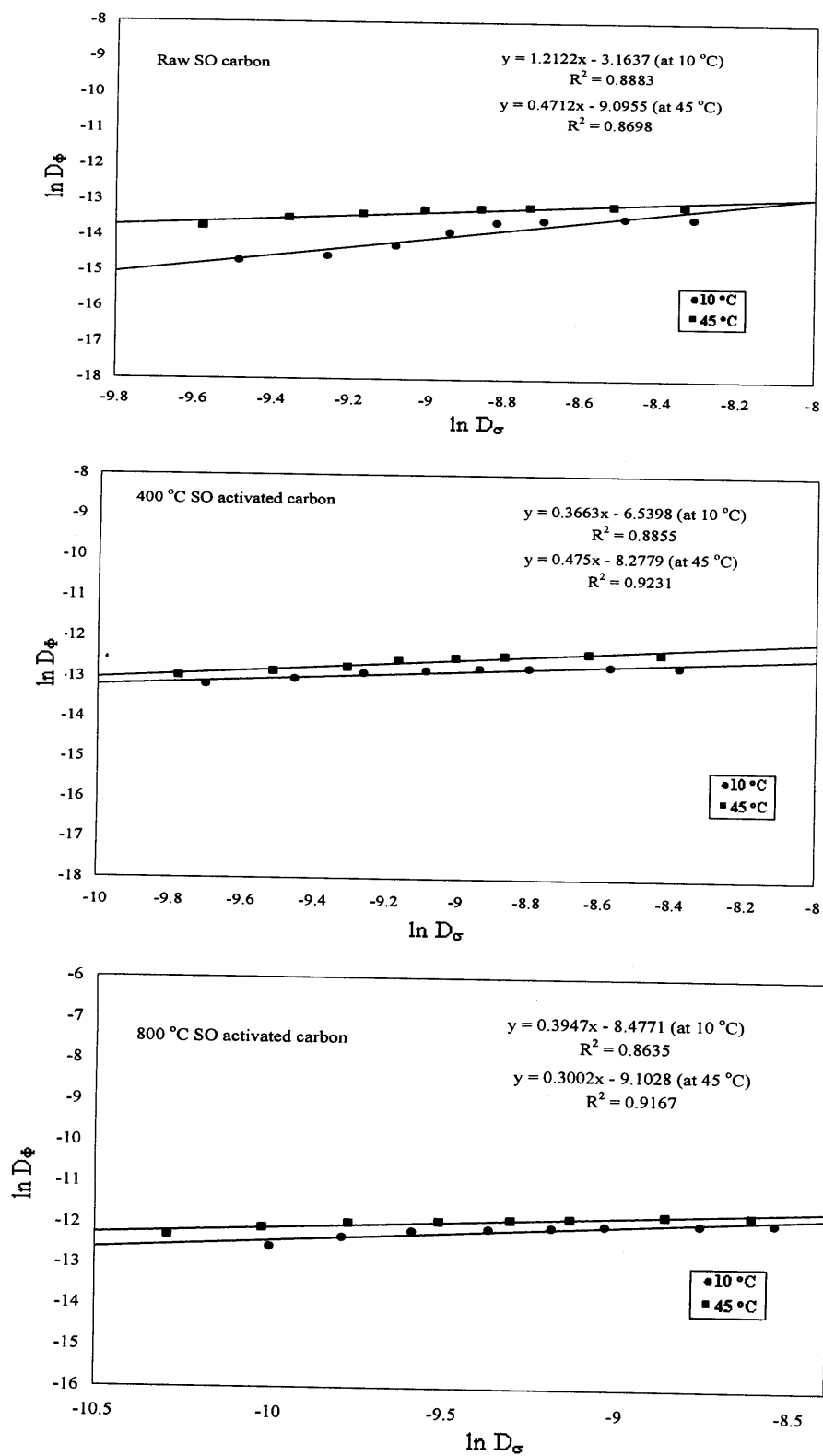


Fig. 3: Freundlich plots for the adsorption of acid yellow 29 on the SO carbon samples.

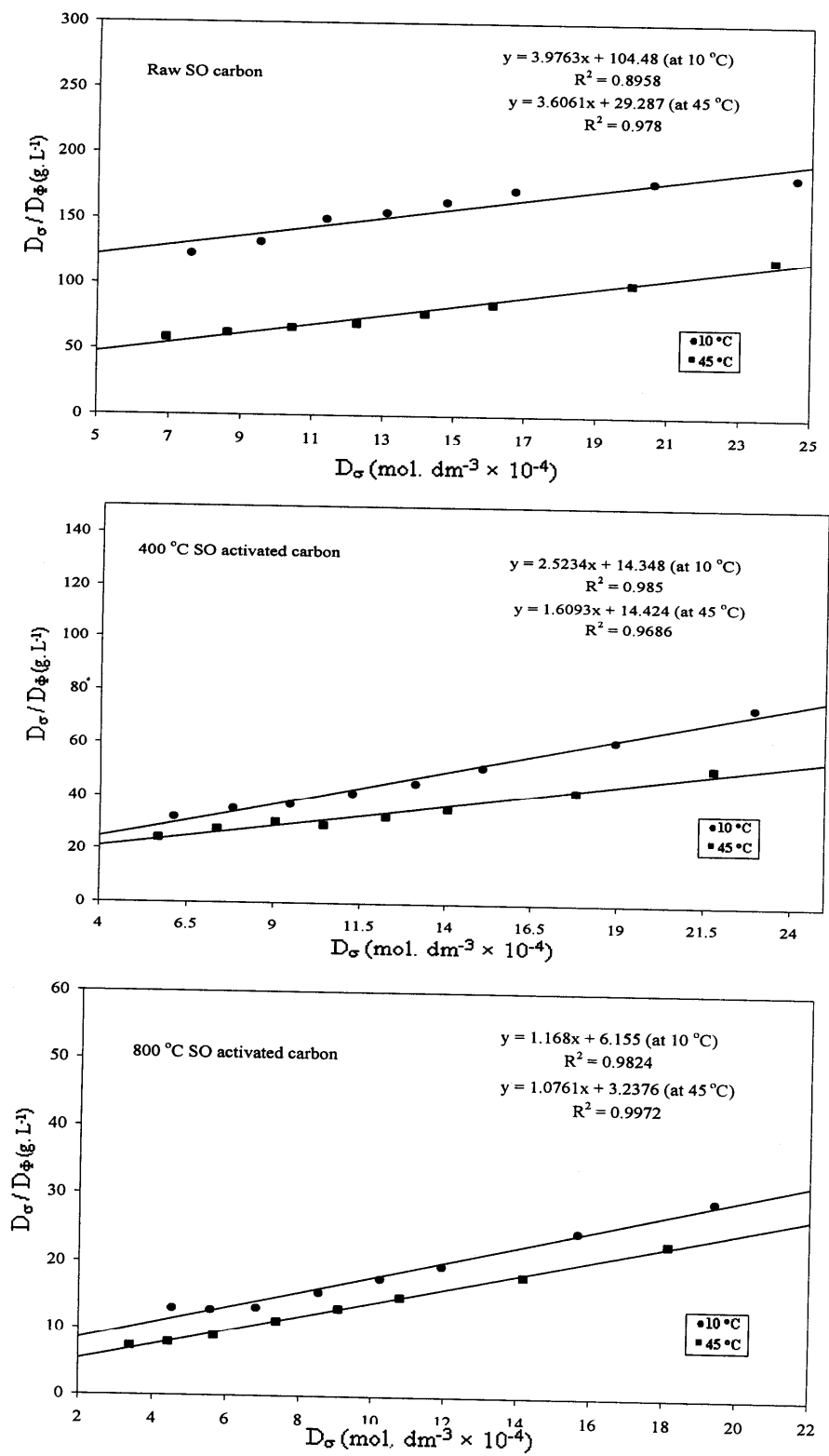


Fig. 4 Langmuir plots for the adsorption of acid yellow 29 on the SO carbon samples.

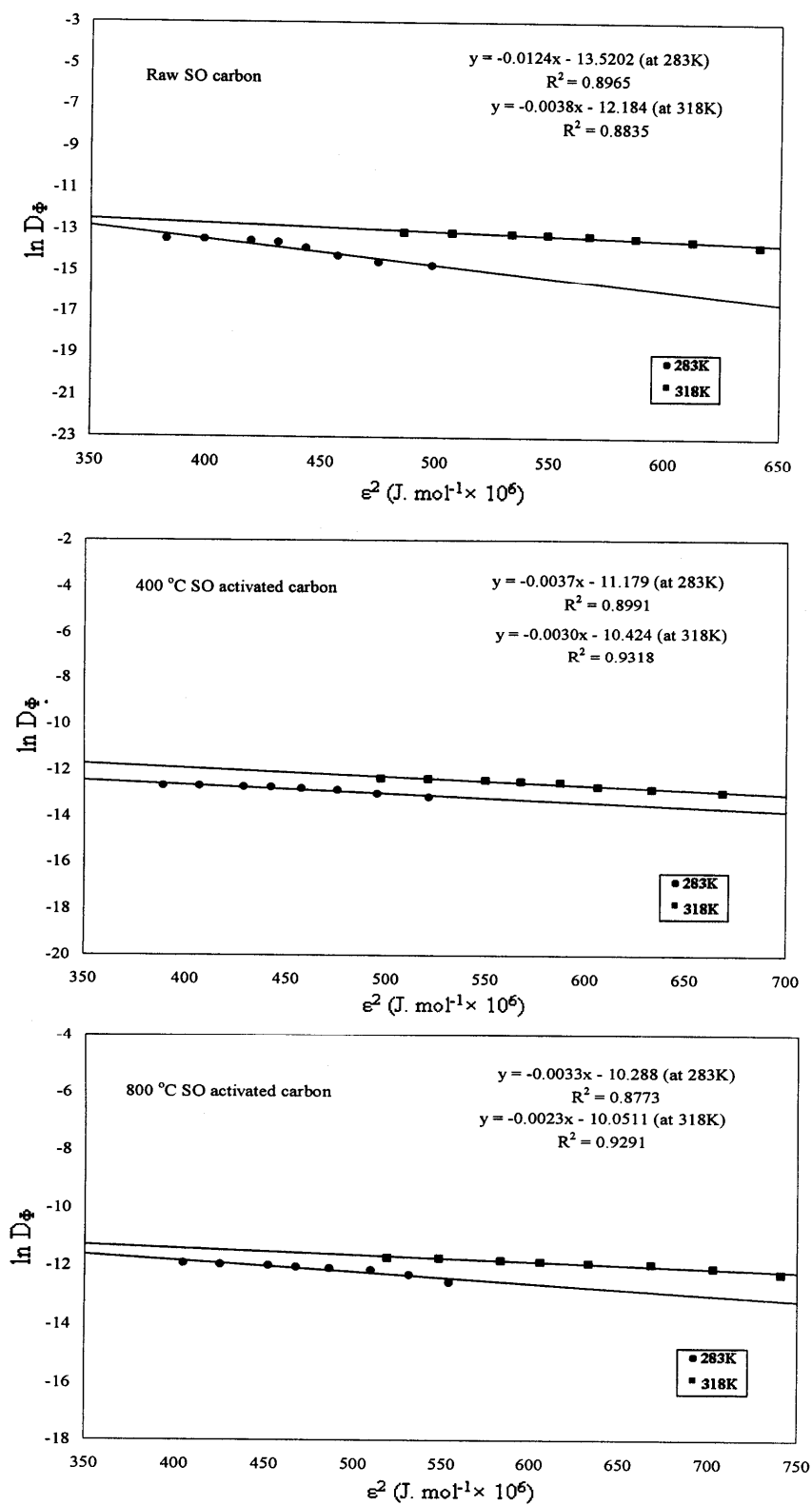


Fig.5: Dubinin-Radushkevich (DR) plots for the adsorption of acid yellow 29 on the SO carbon samples.

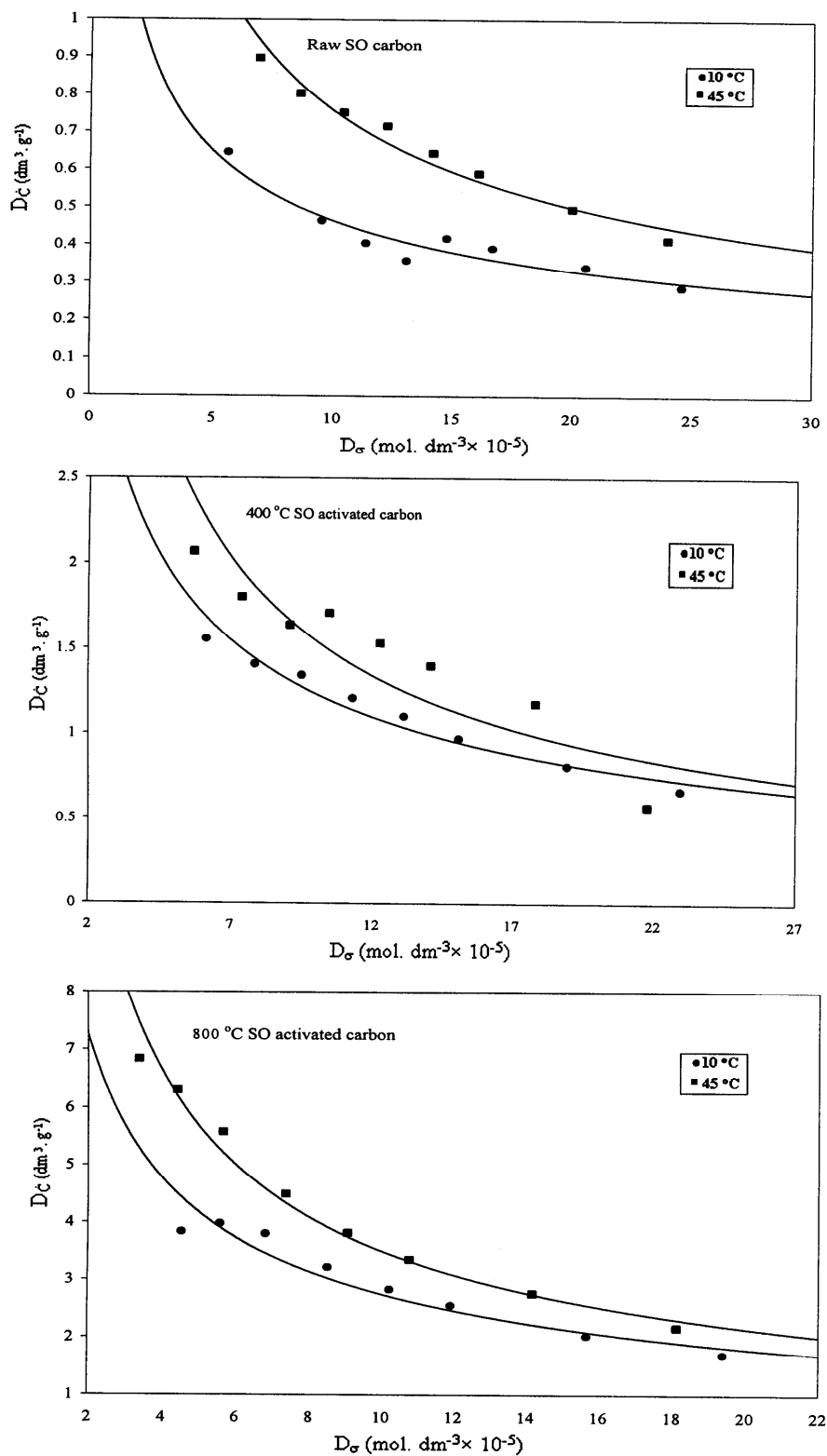


Fig. 6: Distribution coefficient plots for the adsorption of acid yellow 29 on the SO carbon samples.

where d is the amount of adsorption (mol g^{-1}) corresponding to complete monolayer coverage and K_l ($\text{dm}^3 \text{g}^{-1}$) is the binding energy constant. Linear plots of D_σ/D_ϕ (g dm^{-3}) against D_σ (mol dm^{-3}) gave K and d values (Fig. 4). The isotherm was best fit to the data with correlation coefficient, $r^2 > 0.984$. The adsorption capacity (d) for dye adsorption were more at high temperature and also for the samples that are activated at high temperatures (Table-1).

Table-1: Constants for the adsorption of acid yellow 29 on the SO carbon samples.

Sample	Langmuir constants				Freundlich constants			
	b ($\mu\text{mol g}^{-1}$)		K_l ($\text{dm}^3 \text{g}^{-1}$)		n		K (mol g^{-1})	
	10 °C	45 °C	10 °C	45 °C	10 °C	45 °C	10 °C	45 °C
Raw	0.2515	0.277	0.038	0.123	0.825	2.123	23.6	8915.1
400 °C	0.3963	0.621	0.176	0.043	2.730	2.105	692.1	3935.9
800 °C	0.8562	0.929	0.189	0.332	2.534	3.331	4803.5	8980.4

Plots of the data according to the Dubinin-Radushkevich straight line equation [13] are given in Fig. 5.

$$\ln D_f = \ln D_{f_m} - B\varepsilon^2 \quad (3)$$

where ε is the Polanyi potential, D_ϕ is the amount of dye adsorbed in mol g^{-1} , D_σ is the equilibrium concentration (mol dm^{-3}), R is a gas constant and T is the absolute temperature. Linear plots of $\ln D_\phi$ vs. ε^2 were obtained. D_{ϕ_m} gives values of adsorption maximum, as given in Table-2, which increase with the increase in adsorption temperature.

Table-2: DR Adsorption maximum (D_{ϕ_m}) of acid yellow 29 on the SO carbon samples.

Sample	10 °C	45 °C
Raw	0.134	0.511
400 °C	1.396	2.971
800 °C	3.403	4.313

Affinity of the dye for the carbon matrices was determined by calculating the distribution coefficient, using the following equation [14]:

$$D_c = \frac{D_o - D_\sigma}{WD_\sigma} \quad (4)$$

The plots of D_c vs. D_σ are given in Fig. 6. These plots show that, for a fixed amount of adsorbent, the extent of adsorption and the

distribution coefficient, D_c , decreased as the dyes concentration was increased over the concentration ranges of $8.0 - 26 \times 10^{-5} \text{ mol dm}^{-3}$. Distribution coefficients can be predicted from Fig. 6 which show that the samples activated at high temperatures have high values. Their values for the same initial dye concentration are in the sequence: $D_{c, 800^\circ\text{C}} > D_{c, 400^\circ\text{C}} > D_{c, \text{Raw}^\circ\text{C}}$, indicating that carbon activated at 800 °C had higher affinity as compared to 400 °C and Raw samples. The temperature of activation is thus important factor in considering the efficiency of the carbon produced from corncobs for the removal of dyes from aqueous solutions. High temperatures opens the pores, increases the surface area, and eliminates the oxygen containing surface functional groups, leaving the surface exposed for the adsorption.

Experimental

The surface area was determined in a study submitted to this journal earlier [10]. Determination of pH, moisture contents, ash contents, bulk density, FTIR, XRD, SEM and EDS of the prepared activated carbon have also been reported in part-I (Kinetics).

Equilibration Time

0.2 g of activated carbon and 20 cm^3 of acid yellow 29 (20×10^{-5} and $40 \times 10^{-5} \text{ mol dm}^{-3}$) were shaken by a water bath shaker for different intervals of time (0.5 - 8 hours) at 25 °C. The mixture was then filtered. The residual concentration of the dye in the filtrate was determined by Uv-Visible spectrophotometer. Equilibrium time was established from the plots of amount adsorbed vs. time.

Equilibrium Adsorption

Experiments were carried out at 10 and 45 °C by shaking 0.2 g of the sample with 20 cm^3 of the dye solutions of various concentrations ($8.0 - 26 \times 10^{-5} \text{ mol dm}^{-3}$) for two hours equilibrium time. The slurry was filtered and the concentration of dye in the filtrate was determined by Uv-Visible spectrophotometer. Amount adsorbed was found as the difference of the initial dye concentration and that at equilibrium time.

Conclusion

The carbon samples (Raw, 300 and 400 °C), prepared from *Salvadora oleoides* have oxygen

containing surface functional groups which disappear by activation at 500 - 1000 °C. High activation temperatures favor in the removal of dye from aqueous solution. Straight line equations of Freundlich, Langmuir and DR were found to apply to the adsorption isotherm data and found fit to the adsorption data.

References

1. S. Ismadji, Y. Sudaryanto, S. B. Hartono, L. E. K. Setiawan, and A. Ayucitra. *Bioresource Technology*, **96**, 1364 (2005).
2. J. Laine, A. Calafat, and M. Labady, *Carbon*, **27**, 191 (1989).
3. A. Ahmadpour, D. D. Do. *Carbon*, **34**, 471 (1996).
4. Y. S. Al-Degs, M. I. El-Barghouthi, M. A. Khraisheh, M. N. Ahmad, and S. J. Allen, *Separation Science and Technology*, **39**, 97 (2004).
5. F. K. Bangash, and A. Manaf, *Journal of the Chemical Society of Pakistan*, **28**, 20 (2006).
6. F. K. Bangash and A. Manaf, *Journal of the Chemical Society of Pakistan*, **26**, 111(2004).
7. F. K. Bangash, S. Alam, and M. Iqbal, *Journal of the Chemical Society of Pakistan*, **23**, 215 (2001).
8. F. K. Bangash, and A. Manaf, *Journal of the Chinese Chemical Society*, **52**, 489 (2005).
9. H. Freundlich, *Colloid and Capillary Chemistry*, E. P. Dutton, and Co., New York (1928).
10. Y. Iqbal, M. A. Khan, and N. A. Ihsanullah, *International Journal of Environmental Studies*, **62**, 47 (2005).
11. G. Chen, B. Dussert, and I. Suffet, *Water Research*, **31**, 1155 (1997).
12. C. Ng, J. N Losso, W. E. Marshall, and R. M. Rao, *Bioresource Technology* **85**, 131 (2005).
13. M. M. Dubinin, and L. V. Radushkevich, *Proceeding Academy of Science USSR*, **55**, 331 (1947).
14. L. B Khalil, A. A. Amina, and El-Nabarawy, *Adsorption Science and, Technology*, **19**, 511 (2001).