Interaction of Acid Yellow 29 with Activated Carbon Prepared from Cellulosic Precursor: 1. Kinetics

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Summary: Carbon prepared from the wood of *Paulownia tomentosa* (PT) was treated with mixture of acids (HCl and HNO_3), KOH and *n*-hexane and activated at 400 and 800 °C. Activation removed the surface oxygen functional groups (carboxyl's, lactones or phenols and ethers) and exposed the pores. Increase in the amount of carbon with respect to oxygen resulted which enhanced the dye adsorption. First order and Bangham kinetic equations were found to apply to the data, indicating the adsorption to be diffusion controlled. Rate constant increased with the increase in both the adsorption temperature and the activation temperature of carbon. Thermodynamic parameters of adsorption (Ea, $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$) were calculated. The endothermic nature adsorption was indicated by the positive values of $\Delta H^{\neq}$. Negative values of $\Delta S^{\neq}$ found for adsorption, reflect decrease in the disorder of the system at the solid-solution interface during adsorption. Gibbs free energy ($\Delta G^{\neq}$), that represent the driving force for the affinity of dye for the carbon, increased with the decrease in adsorption temperature but increased with activation temperature of the carbon.

Introduction

There are more than 100,000 commercially available dyes with over 7×10^5 tonnes produced annually [1]. It is estimated that 2 % of dyes produced annually are discharged in to effluents from the manufacturing operations, while 10 % are discharge from textile and associated industries [2]. Besides the aesthetic problem, the greatest environmental concern with dyes is their absorption and reflection of sunlight entering the water, which interferes with the growth of bacteria, limiting it to levels insufficient to biologically degrade impurities in the water. Color in effluents can cause problems in several ways: dyes can have acute and /or chronic effects on exposed organisms depending on the exposure time and dye concentration; dyes are inherently highly visible, meaning that concentrations as low as 0.005 ppm capture the attention of both the public and the authorities [3,4]. It is therefore evident that the removal of such colored agents from aqueous effluents is environmentally significant. Adsorption techniques employing solid sorbents are widely used to remove certain classes of chemical pollutants from water [5-10]. However, amongst all the sorbent materials proposed, activated carbon is the most popular one for the removal of a wide variety of dyes [11]. This study deals with the characterization of activated carbon prepared from the wood of *Paulownia tomentosa* and its interaction kinetics with acid yellow 29 dye in aqueous solution.

Results and Discussion

Characterization

The surface area ($m^2 . g^{-1}$) of Raw carbon, 400 and 800°C activated carbons have values of 184 , 234 and 278 respectively. The increase in the surface area with rise in temperature is due to the escape of the surface organic compounds that were trapped in the porous structure [12]. The porous structure and the openings are evident in the SEM of the samples (Fig. 1-4). The EDS which gives semi quantitative analysis, showed the carbon contents of the samples as; 78.84 % (Raw carbon), 83.78 % (400 °C activated) and 92.59 % (800 °C activated). The oxygen content was 21.01 % (Raw carbon), 15.93 % (400 °C activated) and 6.870 % (800 °C activated). Other elements like sodium, chlorine, sulfur, potassium, calcium, magnesium and zinc were found in trace quantities.

Adsorption Kinetics

The rate of adsorption of the dye molecules, measured up to 15 seconds, was high at both 10 and 45°C and then it declined due to the possible diffusion in to the micropores. The increase in temperature has increased adsorption (Fig. 5), indicating the endothermic nature of the process. Acid yellow 29 is an anionic azo dye that have sulphonic acid group which ionizes to SO^-_3 group, in the aqueous solution. This anionic group has affinity to attract to

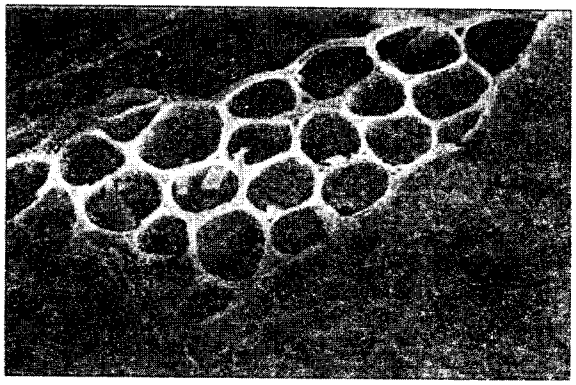


Fig.1. Scanning electron micrograph of Raw carbon. (Mag=1000x, AccV =20kV, Signal = SEI, WD = 16mm, Spot Size = 25, —20 μm)

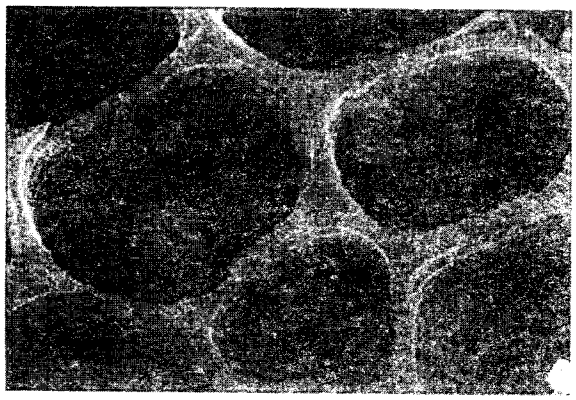


Fig. 2. Scanning electron micrograph of Raw carbon. (Mag = 3500x, AccV =20kV, Signal = SEI, WD = 16mm, Spot Size = 25, —5.71 μm)

the positively charged carbon surface during adsorption [13]. In the cases of Raw carbon and 400 °C degassed carbon samples, the dye on approaching to the surfaces also experience the Columbic repulsion due to the oxygen containing functional groups present on the samples. As a consequence of the decomposition of some of the acidic oxygen surface functionalities at high temperature, that decrease polarity of the carbon surface, the adsorption of dye on the sample activated at 800 °C is greater than that activated at 400 °C. Activation opens the blind pores, and thus increase in the surface area and pore volume resulting in the increase in adsorption on samples activated at high temperatures A non-polar surface of the 800 °C activated carbon is

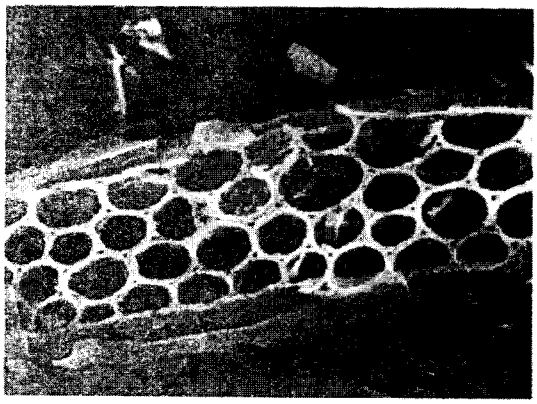


Fig. 3. Scanning electron micrograph of 400 °C activated carbon. (Mag =1100x, AccV =20kV, Signal = SEI, WD = 16mm, Spot Size = 18.18 μm)

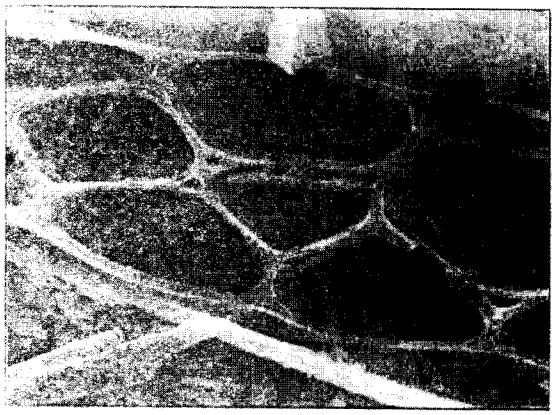
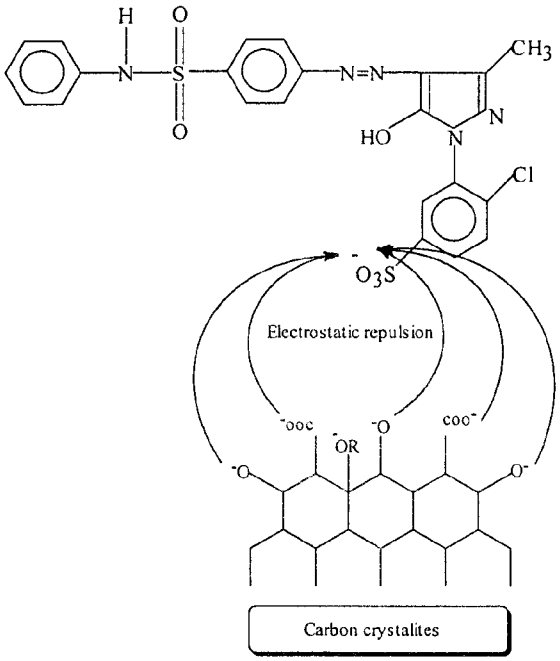


Fig. 4. Scanning electron micrograph of 800 °C activated carbon. (Mag = 3500x, AccV =20kV, Signal = SEI, WD = 16mm, Spot Size = 25, —5.71 μm)

another reason for the high adsorption of the dye. Lower adsorption of dye on the Raw carbon and 400 °C activated carbon samples was due also to the fact that polar functional groups situated at the pore opening adsorb water strongly through hydrogen bonds that in turn result in pore constriction or pore blockage [13]. A schematic representation of the electrostatic repulsion between the acid yellow 29 ions and the negatively charged carbon surface is depicted in scheme 1.

Kinetic Models

The rate constant for adsorption of acid yellow 29 on carbon surface was determined by the first



Scheme 1. Electrostatic repulsion between acid yellow 29 ion and negatively charged carbon surface

order kinetic equation. Such an equation in the linear form can be expressed as [14]:

$$\ln D_\sigma = \ln D_o - K_{ad} t \qquad (1)$$

Here D_o and D_σ are the solution concentration (mol dm^{-3}) at t = 0 and t = t respectively and k_{ad} is the 1st order rate constant. Linear plots of ln D_σ vs. t for adsorption of the dye on carbon surface at 10 and 45 °C are shown in Fig. 6. Values of k_{ad} at different temperatures are shown in Table 2. It was noted that the rate constant increased with the increase in the temperature of adsorption and also for the sample activated at high temperature. The r^2 values (around 0.800-0.960) for the first order model indicate the better fit of the model. The energy of activation for the adsorption was calculated using the Arhenius equation [14] in the form:

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{T_2 - T_1}{T_1\ T_2}\right) \qquad (2)$$

Table-1: Some characteristics of carbon samples

Sample	Physical parameters			
	pH	Ash content (%)	Bulk density (kg/m^3)	Moisture content (%)
Raw carbon	9.30	9.89	260	1.20
400 °C	9.53	5.32	245	0.90
800 °C	9.90	5.00	220	0.30

Where E_a is the activation energy, k_1 and k_2 are rate constants at T_1 and T_2, R is the gas constant (8.314 J K^{-1} mol^{-1}). The energies of activation for acid yellow 29 in case of carbon activated at different temperatures are given in Table-2. The data showed that for the samples activated at high temperature the activation energy of adsorption was low. The high activation energy of dye adsorption on the less activated sample might be due to the presence of polar functional groups at the pore opening that block the entrance of dye molecules resulting in the energy barrier for adsorption to occur. From the values of activation energies, other thermodynamic parameters such as Gibbs free energy of activation $(\Delta G)^{\neq}$, enthalpy of activation $(\Delta H)^{\neq}$ and entropy of activation $(\Delta S)^{\neq}$ were calculated (Table-3) by using the following equations [14].

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \qquad (3)$$

$$\Delta H^{\#} = Ea - RT \qquad (4)$$

$$\Delta S^{=} = R\left[\ln\frac{kh}{k_B T} + \frac{\Delta H^{=}}{RT}\right] \qquad (5)$$

Where k = Rate constant

k_B = Boltzmann constant (1.3806×10^{-23} J K^{-1})

$\Delta H^{\neq}$ = Enthalpy change of activation.

h = Planck constant (6.626×10^{-34} J s)

Table-2: Thermodynamic parameters for the adsorption of acid yellow 29 on carbon samples.

Sample	k_{ad} (s^{-1})		E_a (kJ.mol^{-1})	$\Delta H^{\neq}$ (kJ.mol^{-1})		$\Delta S^{\neq}$ (J.mol^{-1}. K^{-1})		$\Delta G^{\neq}$ (kJ.mol^{-1})	
	10 °C	45 °C		10 °C	45 °C	10 °C	45 °C	10 °C	45 °C
Raw carbon	0.01190	0.01240	21.3774200	19.024561	18.733569	-214.0929	-223.9988	-79.612851	-89.965187
400 °C	0.03540	0.08230	18.0352600	15.682400	15.391408	-216.8390	-218.7729	-77.047837	-84.961190
800 °C	0.06350	0.12220	13.9940000	11.641210	11.350218	-226.2600	-228.1947	-75.67279	-83.916132

Table-3:Bangham equation constants for the adsorption of acid yellow 29 on carbon samples

Sample	α		k_o	
	10 °C	45 °C	10 °C	45°C
Raw carbon	0.28010	0.13910	0.36760	0.68690
400 °C	0.30160	0.47550	0.42360	0.40190
800 °C	0.20050	0.29660	0.76320	0.75590

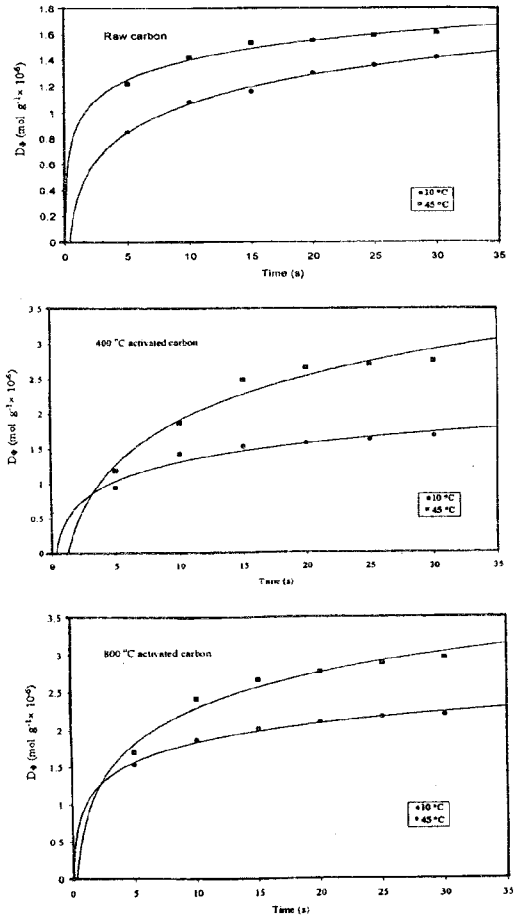


Fig. 5. Adsorption kinetics of acid yellow 29 on carbon samples.

The tendency of the dye to pass from aqueous phase onto the adsorbent surface is determined by the Gibbs free energy ($\Delta G^{\neq}$) that represents the driving force for the affinity of dye for the carbon [15]. Negative values of free energy ($\Delta G^{\neq}$) indicate the spontaneity of the adsorption process. It was also noted that $\Delta G^{\neq}$ values decrease with increase in temperature. The enthalpy of activation, $\Delta H^{\neq}$, calculated from energy of activation, was found to

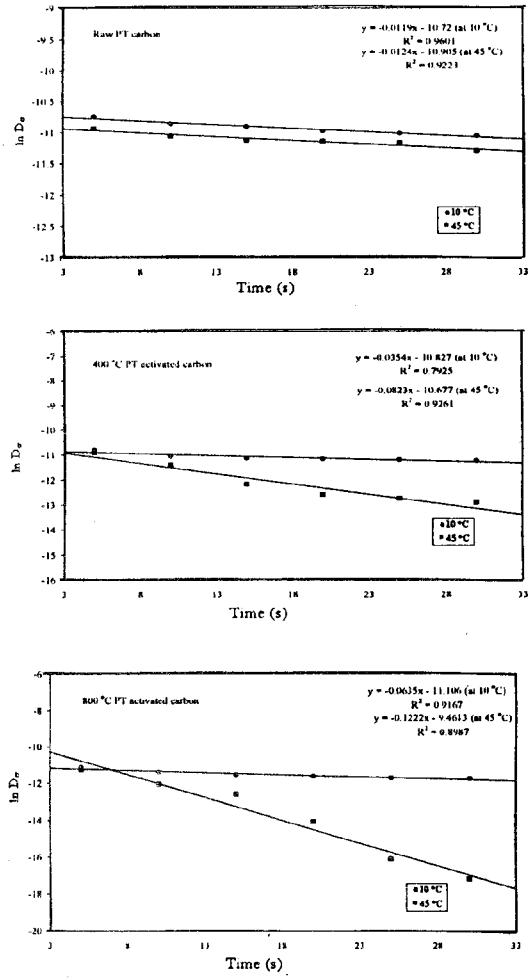


Fig. 6: First order kinetics plots for the acid yellow 29 adsorption on carbon samples.

decrease with the increase in the adsorption temperature indicating the process to be endothermic in nature. Negative values of the entropy of activation, $\Delta S^{\neq}$, reflects the affinity of the dye toward the carbon which decreased with the increase in adsorption temperature (Table-2) meaning that the dye molecules have more stable oriented position on the carbon surface.

The Bangham equation in the linear form as given below, was used to check the pore diffusion during the adsorption process .

$$\log \log \frac{D_o}{D_o - D_e} W = \log \frac{k_o W}{2.303 V} + \alpha \log t \qquad (6)$$

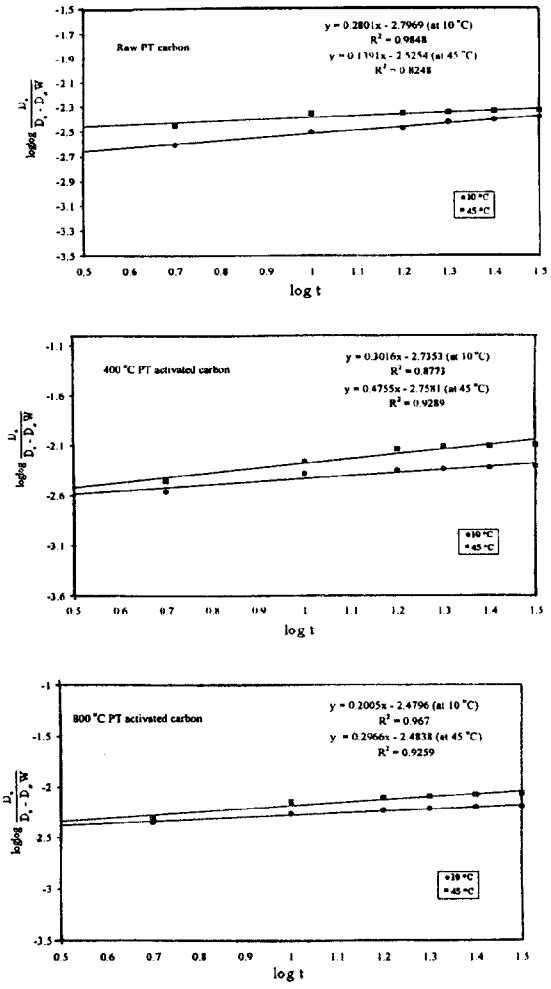


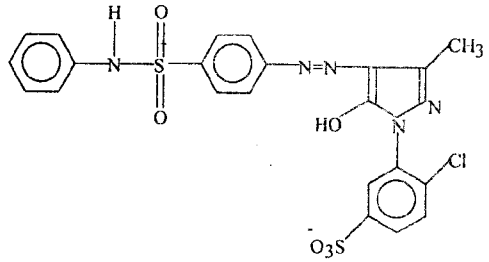
Fig. 7. Bangham plots for the acid yellow 29 adsorption on carbon samples.

Where D_o is the initial concentration (mol dm^{-3}) of the dye in solution, V is the volume (dm^3) of solution, W is the weight (g) of carbon, D_σ is the amount of dye adsorbed at time t, while $\propto$ and k_o are constants. Plots of log log (D_o / D_o- D_σ W) against log t are linear (Fig. 7). The values of $\propto$ and k_o calculated from the slopes and intercepts are given in Table-3. The decrease in α and increase in k_o values with temperatures of adsorption and also in the samples activated at high temperatures indicate that the diffusion of dye into pores of the carbon is important and that adsorption in to the pores is a diffusion controlled process [16].

Experimental

Acid yellow 29

The dye used was supplied by Sigma-Aldrich (Catalogue No. =21,036-6, dye contents = 60 %, formula weight =569.98, $\lambda_{max.}$ 409 nm),



Molecular structure of acid yellow 29

Preparation and characterization of carbon

The wood of *Paulownia tomentosa* collected from Pakistan forest institute Peshawar, was air dried and then heated continuously for 8 hours on a flame burner in a specially designed iron container with an outlet for the emission of volatile matter. Carbon obtained (about half of the mass of wood used) was cooled in the container and ground with the help of pestle and mortar and screened with US standards mesh 150-180 μ m. It was then treated with 0.5 M aqueous solution of KOH for 24 hours with occasional stirring. The mixture was then filtered and washed with double distilled water for the complete removal of basicity. The carbon was then leached with 0.2N solution of HNO_3 : HCl (1: 1) and allowed to stand for 24 hours at room temperature with regular mixing. It was then filtered and washed with double distilled water until free from Cl^- and NO_3^- ions. The carbon thus obtained was then air-dried in an oven at 105 ± 2 °C. This treated carbon was then extracted with n-hexane for two hours in a soxhlet extractor and allowed to dry for 8 hours in a vacuum oven. The sample was then degassed by placing in silica (SiO_2) tubes and heated at 400 and 800 °C in a tube furnace (FS. 215 Gallenkamp England) with a vacuum facility. The samples were allowed to cool and then stored under nitrogen atmosphere. pH of the prepared sample suspension in CO_2 free water (1: 50) was determined by pH meter. The moisture content was found by measuring the weight loss of the sample, by heating for about two hours at 105 ± 1 °C

in an air dried oven. Ash content was obtained by weighing ignited sample at 600 °C in a Muffle furnace, with door partially open to provide stream of air until the sample has been totally burned [17]. The surface area of the samples was determined as described elsewhere [18]. Surface morphology of the samples was studied by SEM (Model-JSM-5910, Japan JEOL) with EDS (INCA 200 Oxford Instruments) for the elemental analysis.

Adsorption studies

0.2 g of activated carbon and 20cm^3 of acid yellow 29 (3.0×10^{-5} mol.dm^{-3}) was shaken in a laboratory syringe (Hamilton CO.) for 5 - 30 seconds at 10 °C and 45 °C and filtered through 0.2 μ filter paper already fitted in the syringe adopter. The residual concentration of the dye in the filtrate was determined by UV visible spectrometer.

Acknowledgement

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