

Utilisation of a solid waste generated in leather industry for removal of dye in aqueous solution

G Sekaran*, K A Shanmugasundaram, M Mariappan & K V Raghavan

Department of Environmental Technology, Central Leather Research Institute, Adyar, Madras 600 020, India

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Buffing dust generated from leather industry can be considered as a source for obtaining activated carbon for the removal of dyes from wastewater. The adsorption capacity of buffing dust based activated carbon was 6.24 mg/g at a pH 3.5, temperature 30°C for dye concentration of 125 mg/L and carbonisation temperature 900°C. Effect of initial dye concentration, pH, temperature and particle size on dye adsorption and pore diffusion were also determined. The enthalpy of adsorption was determined to be - 15.69 kJ/mol.

Synthetic dye stuffs (acid and azo dyes), sulphated, sulphited, phosphorylated fatliquors and other tanning materials having aromatic characteristics are generously added during the manufacture of leather. Under normal circumstances biological treatment units are seldom effective for removal of dyes. It has been reported that dye stuffs were passed through activated sludge wastewater treatment system without getting removed¹. The discharge of highly coloured wastewater is not acceptable to statutory bodies. Also, the penetration of light and photosynthetic activity in the aquatic medium are impaired².

The techniques like dissolved air floatation, coagulation, ion-exchange, adsorption and oxidation with H_2O_2 were employed³ for the removal of dyes from wastewater. Coagulants⁴⁻⁷ used for the removal of dyes from wastewater were $FeSO_4$, lime, $MgCO_3$, $Fe_2(SO_4)_3$ and $FeCl_3$. Percentage removal of dyes by coagulation method is only partial (in the range of 60-80%) while adsorption technique is an ultimatum for the removal of dyes from wastewater⁸.

Activated carbon has been obtained from various sources like sawdust, poly furfuryl alcohol, phenolic resins, bark and wood chips, waste saran, PVC resin, shells of gokru fruit, asphalt, rice bran and paper mill solid waste. In this present study, activated carbon obtained from buffing dust, a solid waste generated in leather industry, has been used.

High degree of leather finish is achieved while carrying out buffing operation at room tempera-

ture in a separate chamber provided with a facility to collect the buffing dust produced in the process. In leather industry 2 kg of buffing dust is generated for every 1000 kg of skins/hides processed or 200 kg of leather produced. Buffing dust is a finely divided leather substrate which contributes towards dust pollution within tannery premises and also in the surrounding environment. Hence, leather industries are advised by pollution control authorities to dispose off this solid waste in an environmentally sound manner. One of the possible approaches for the disposal of buffing dust is to convert it into activated carbon.

Wastewater discharged from leather industry after extensive biological (anaerobic and aerobic) treatment possess straw yellow to orange colour, contributed by residual organics like dye stuffs and tannins. This necessitates the inclusion of polishing treatment unit for safe disposal of tannery effluent. Segregation of spent dye wastewater from composite effluent and its separate treatment might ease the biological treatment of tannery effluent to meet the discharging standard. The objective of this study was to optimise the conditions for the removal of dye from water by activated carbon obtained from buffing dust, one of the solid wastes generated in leather industry to be disposed off.

Experimental Procedure

The temperature required for carbonization of buffing dust was selected from thermogravimetric analysis. Thermogram of buffing dust shows (Fig. 1) that moisture movement takes place in the

*Author to whom correspondence should be addressed.

temperature range 95-210°C. The impregnated volatile organics are removed in the temperature range from 210 to 445°C. Carbonisation of buffing dust occurred at a temperature range between 500 to 900°C. The buffing dust collected from the tannery was dried at 210°C. The temperature of furnace was increased to 450°C to remove volatile organics. The contents were cooled and impregnated with activant MgO in the ratio 1:1. The mixture was homogenised and carbonised at elevated temperature for two hours in muffle furnace. The contents were cooled and soaked in 2N H₂SO₄ for removing ash and the activant used during carbonisation. The experiment was repeated at other carbonisation temperatures 600, 700, 800 and 900°C.

The IR spectrum (Fig. 2) of activated carbon obtained from buffing dust has no characteristic stretching band indicating the absence of any functional group in it.

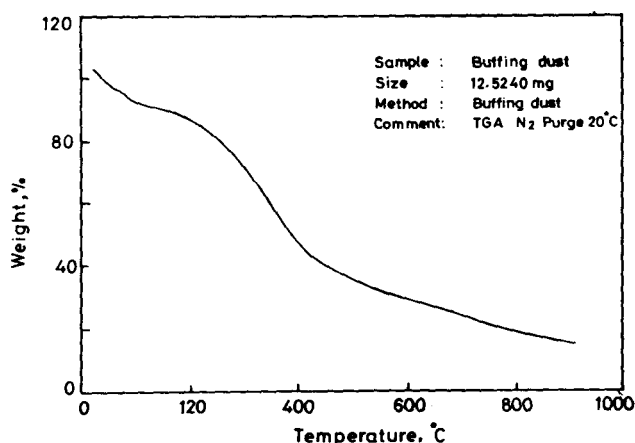


Fig. 1—TGA

Acid brown dye, widely used in leather industry, was selected as a reference dye compound for adsorption studies. Adsorption of acid brown dye by buffing dust based activated carbon was studied analytically in the range of dye concentrations 50, 75, 100 and 125 mg/L. In each of the dry well stoppered bottles 100 mL of dye solution was taken. 1g of accurately weighed activated carbon, dried over H₂SO₄, was added in one bottle while the other bottle without activated carbon was taken as reference. The contents were agitated at constant temperature in a shaking water bath. At the end of the predetermined time intervals the adsorbent was centrifuged and the supernatant was analysed for acid brown dye spectrophotometrically (Bausch & Lomb, Spectronic 21) at maximum absorbance wavelength, 464.4 nm. From the known concentration of dye before and after adsorption milligram of acid brown dye adsorbed per gram of activated carbon (X/m , q_e) was calculated. Sodium formate, 0.05 M was used to provide ionic strength during adsorption of dye on activated carbon. The solution was adjusted to the required pH by using 0.05 M HCl/0.1 M NaOH.

Results and Discussion

Effect of contact time—Fig. 3 shows that dye remaining in the aqueous solution decreased with time and achieved equilibrium in 60 min, and is different for each concentration indicating independent nature of equilibrium period. Initial portion of the curve is linear and after a certain time the linear portion of the curve is changed into a smooth curve and there after plateau region is reached. Geundi⁹ found that the mechanism of

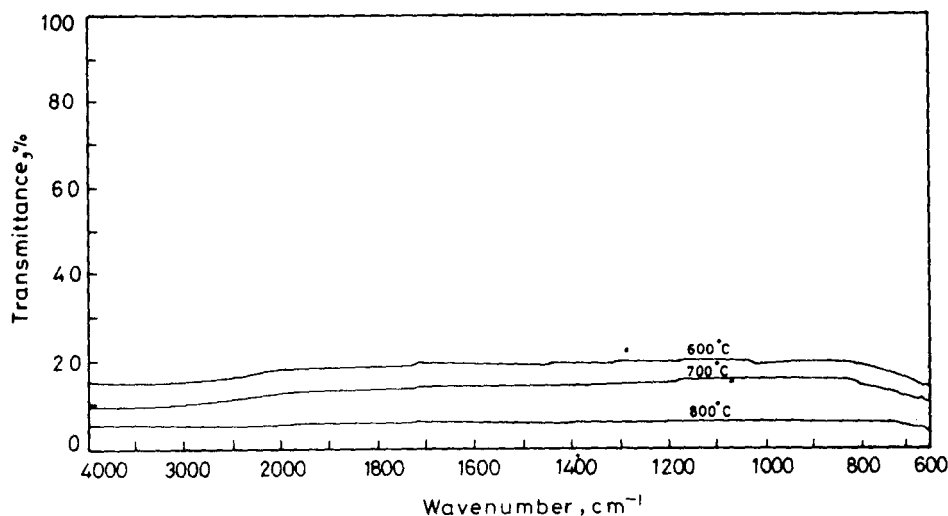


Fig. 2—IR spectra of activated carbons obtained at different heat treatment temperatures

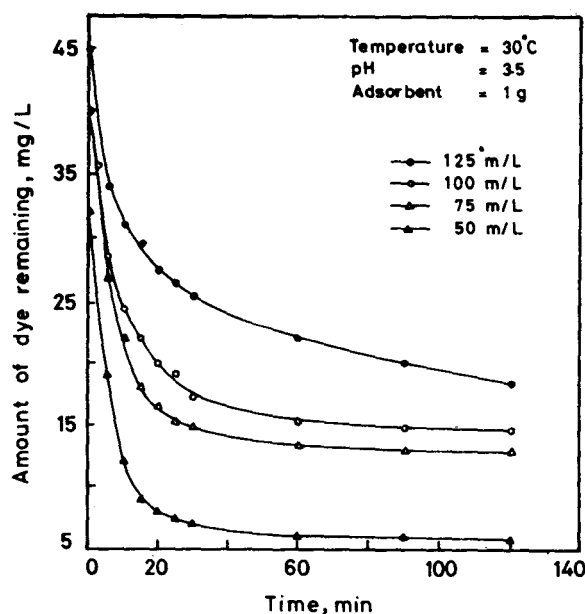


Fig. 3—Effect of contact time and dye solution concentration on the removal of dye by activated carbon

colour removal from the bulk solution involves migration of dye molecules from the bulk solution to outer surface of activated carbon and diffusion of dye molecules into pores of it. The transport of adsorbate from solution into the pores of the adsorbent is the rate controlling step^{10,11}. This the saturation of dye molecules on activated carbon surface takes place after a contact time of 60 min. The amount of dye removal increased from 2.84 to 6.13 mg/g of adsorbent respectively for the initial dye concentrations from 50 to 125 mg/L at pH 3.5 and at temperature 30°C. The removal curves are smooth and continuous indicating the formation of monolayer coverage of the adsorbate on the outer surface of the adsorbent¹².

The rate constant for the adsorption of acid brown dye on activated carbon was calculated by using Lagergren's equation¹³

$$\log(q_e - q) = \log q_e - (k_{ad}/2.303 t)$$

where q_e is dye removed at equilibrium, q is dye removed at any time t , and k_{ad} is rate constant for dye adsorption. The plot of $\log(q_e - q)$ versus t gives a straight line. This confirms the validity of the equation to our experimental observation. The slope of this line gives k_{ad} . The values of k_{ad} at different temperatures are given in Table 1. Table 1 shows that the values of rate constant k_{ad} are in the same order of magnitude indicating that the removal of dye follows first order kinetics.

Adsorption capacity of activated carbon increased with increase in carbonisation temperature. Fig. 4 shows that the amount of dye removal

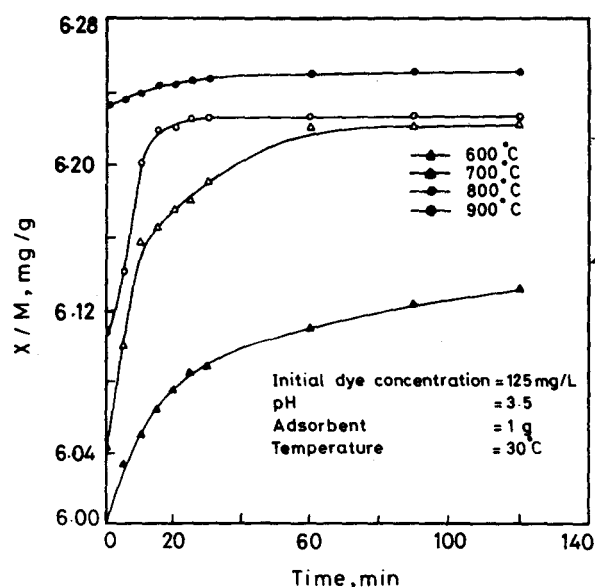


Fig. 4—Effect of contact time and heat treatment temperature on adsorption of acid brown dye on activated carbon

versus time at different carbonisation temperatures. Adsorption capacity of activated carbon increased from 6.13 to 6.24 mg/g for the carbonisation temperatures from 600 to 900°C.

Rehman *et al.*¹⁴ showed that the adsorbate diffuses through the film layer and adsorb on the external surface of the carbon particle with simultaneous filling of the micropore volume. When the adsorption capacity of the external carbon surface is exhausted the transport to the transitional pores and subsequent filling of it occurs and followed with filling of the macropore and final adsorption results. The intra-particle diffusion in a rapidly stirred batch reactor is the rate limiting step in many adsorption processes¹⁵. The rate constant for intra-particle diffusion at different temperatures are determined by plotting the amount of dye adsorbed on activated carbon versus squareroot of time (Fig. 5). The double nature of these plots was explained as the initial curved portions are attributed to boundary layer diffusion of adsorbate and final linear portion was due to its intra-particle diffusion. Rate constant k_p at various temperatures were obtained from the slope of linear portions of the respective plots and are presented in Table 1. Extrapolation of the initial curved portions of the curve to $t_{0.5}$ gives intercepts which is directly proportional to boundary layer thickness¹². The larger the intercept the greater is the boundary layer effect.

Adsorption isotherms—The study of adsorption isotherms is helpful in determining the adsorption capacities of various adsorbents for the removal of dyes at certain temperature. Adsorption iso-

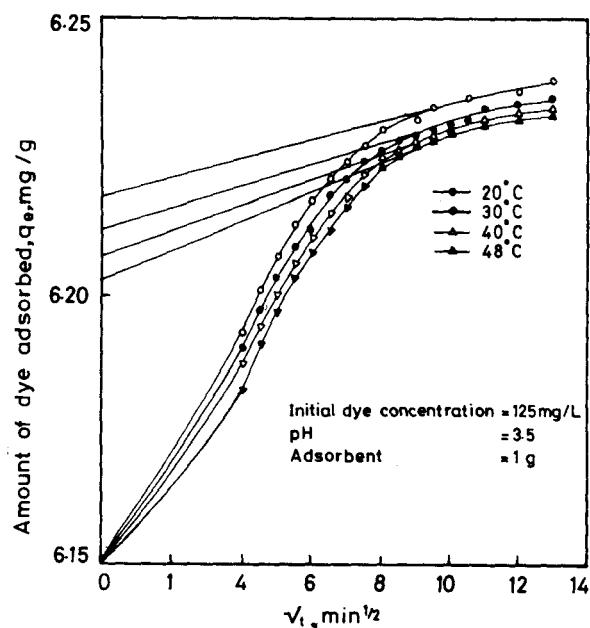


Fig. 5—Intra-particle diffusion plot for the adsorption of the dye on activated carbon

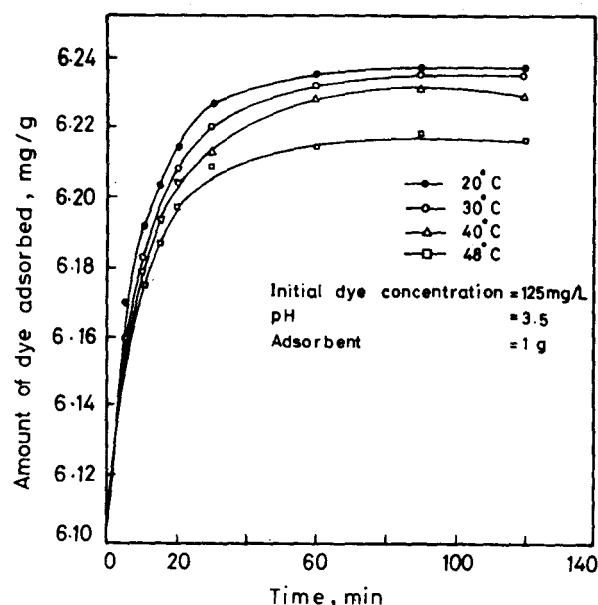


Fig. 6—Effect of temperature on adsorption of acid brown dye on activated carbon

Table 1—Adsorption kinetic parameters at different temperatures for adsorption of acid brown dye on buffing dust based activated carbon

Temperature °C	k_{ad}, min^{-1}	$k_p, \text{min}^{-1/2}$	Thickness, $\text{min}^{0.5}$
20	0.067	0.002060	2.00
30	0.050	0.002058	1.16
40	0.040	0.002000	0.84
48	0.016	0.002000	0.74

therms were developed at different temperatures 20, 30, 40 and 48°C (Fig. 6). Fig. 7 shows the saturation curve for the acid brown dye adsorbed on the activated carbon. The isotherm rises sharply in the initial step for low C_e and q_e values and eventually a plateau portion is reached. The dye molecules adsorb on the surface due to the secondary force of attraction between adsorbent and adsorbate (corresponds to linear portion of the isotherm). When all of the available monolayer sites are taken up^{16,17} some fresh internal surface like macropore and micropore are created. This process will tend to further increase the adsorption capacity of the adsorbent (corresponds to plateau portion of isotherm). The curvature of the isotherm decreased as the C_e value increased considerably for a small increase in q_e . This is possibly due to less number of active sites available at the end of the adsorption process and/or penetration of the edge molecules into the adsorbent and into the layer of dye molecules partially covered the

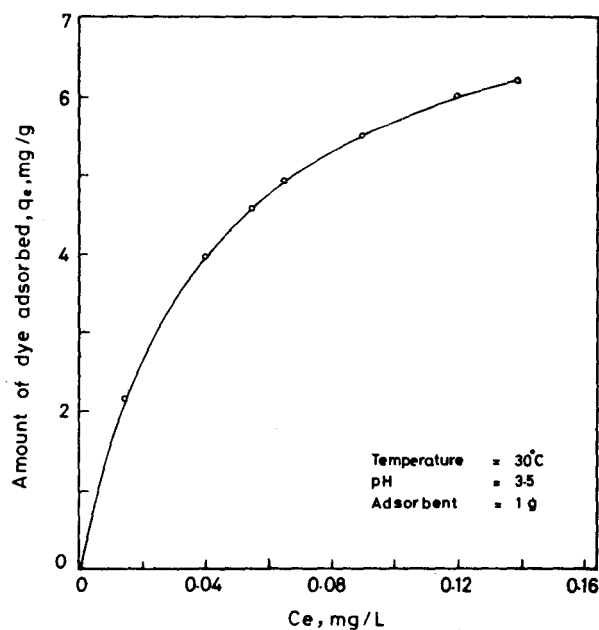


Fig. 7—Adsorption isotherm of acid brown dye on activated carbon

surface sites¹⁸ becomes difficult. The equilibrium data for the removal of acid brown dye by activated carbon at 30°C and at pH 3.5 have been found to follow the rearranged Langmuir isotherm model.

$$C_e/q_e = 1/Q_0 b + C_e/Q_0$$

The linear plot of C_e/q_e versus C_e suggest the applicability of Langmuir isotherm. The constant Q_0 and b were obtained from slope and intercepts of

Table 2—Langmuir constants at different temperatures for adsorption of acid brown dye on buffing dust based activated carbon

Temperature °C	Langmuir Constants				Equilibrium parameter, R
	Graphical values		Regression values		
	Q_0 , mg/g	b , L/g	Q_0 , mg/g	b , L/g	
20	7.69	1.64	7.86	1.54	5.6×10^{-3}
30	9.47	1.70	8.62	1.79	4.2×10^{-3}
40	8.66	2.58	8.78	2.25	2.9×10^{-3}
48	8.71	11.15	8.40	5.30	6.2×10^{-3}

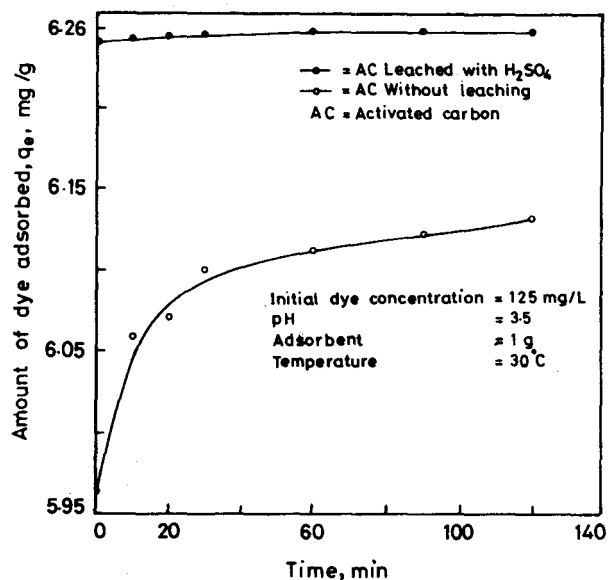


Fig. 8—Effect of leaching with acid on adsorption of dye on activated carbon

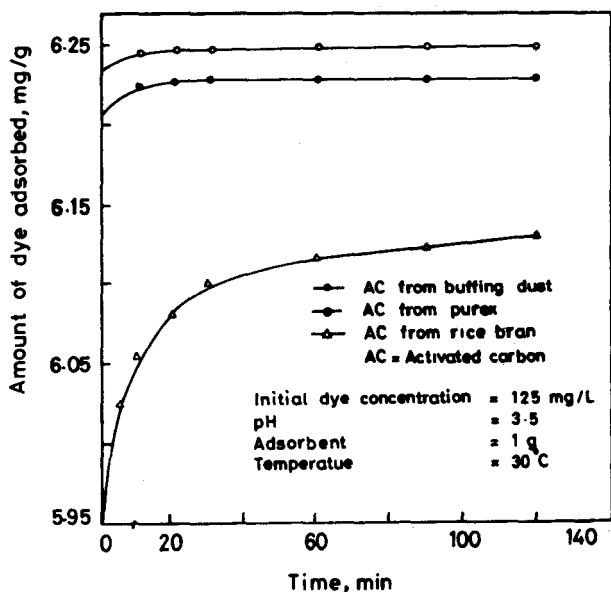


Fig. 9—Comparison of adsorption capacities of different activated carbons

the linearised plots of Langmuir isotherm developed at various temperatures. The value Q_0 is a measure of maximum adsorption capacity $q_{\max}$ in such system. The maximum adsorption capacity is a useful criterion in assessing the greatest uptake of a selected adsorbent. The maximum adsorption capacity values are used to calculate the quantity of adsorbent required to remove 1 kg of dye. These quantities are used for working out cost of the adsorption process. Table 2 contains the values of constants Q_0 and b obtained by graphical methods and regression analysis.

Ash content of activated carbon determines its adsorption capacity. Adsorption capacity of buffing dust based activated carbon was improved after washing with $2\text{NH}_2\text{SO}_4$ (Fig. 8).

Adsorption isotherms for commercial activated carbon supplied by Purex Company and activated carbon obtained from rice bran¹⁹ were compared with activated carbon obtained from buffing dust as shown in Fig. 9. The results obtained in the experiment on dye removal from wastewater by activated carbons suggested that the adsorption capacity of activated carbon derived from the buffing dust was found to be greater than others.

The equilibrium parameter R has been calculated from the relationship

$$R = \frac{1}{1 + aC_0}$$

The values of R shown in Table 2 indicate that adsorption of acid brown dye on activated carbon

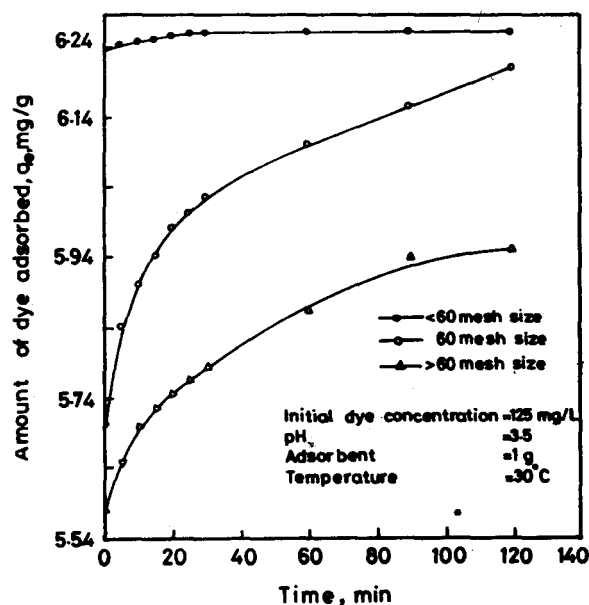


Fig. 10—Effect of adsorbent particle size on the removal of acid brown dye by carbon obtained from buffing dust

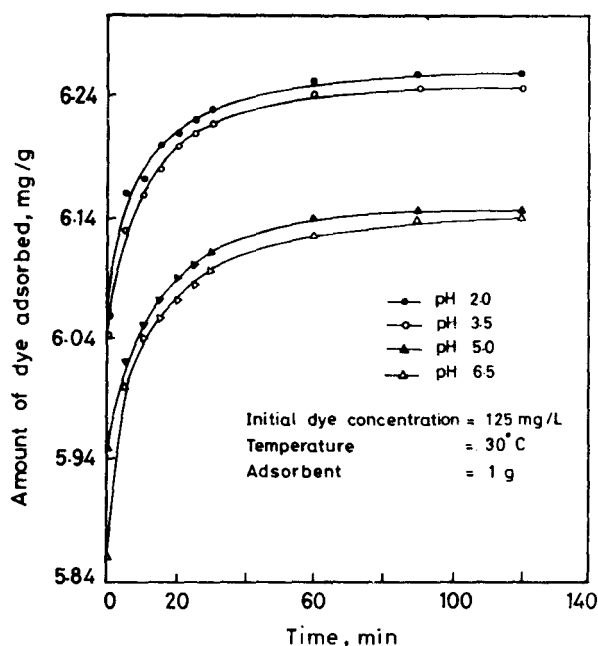


Fig. 11—Effect of pH on adsorption of acid brown dye on activated carbon

from buffing dust is a favourable process because R values lies between 0 and 1.

Effect of particle size on adsorption—Fig. 10 shows the effect of contact time on adsorption of acid brown dye on activated carbon for different particle sizes. The initial rate of adsorption is controlled by film diffusion from the bulk solution to the particle surface. The adsorption rate is influenced with the variation in particle size while mass of carbon is kept constant. Since the amount of external surface area for adsorption is varied, the smaller the particle diameter greater is the external surface area. The amount of dye adsorbed on the carbon surface was increased for decrease in particle size.

Activation energy of adsorption—The k_p values determined from the results of adsorption of acid brown dye on activated carbon at several temperatures are shown in Table 1. The activation energy of adsorption was calculated from the slope of linear curve obtained in the plot of $\log k_p$ versus $1/T$ and it was found to be -15.69 kJ for 1 mol of dye. The value suggested the exothermic nature of the process and the possibility of weak bonding between the adsorbate and adsorbent species.

Effect of pH—Fig. 11 shows the effect of pH on the removal of acid brown dye from aqueous solution. It was observed that the concentration of dye left in solution increased with increase in pH. This study was carried out in the pH range of 2–6.5. It showed that at pH 2 percentage removal

of dye was 99.8 and at pH 6.5 it was about 98.2% at 125 mg/L dye concentration, 30°C and 60 mesh carbon particle size.

Conclusion

Activated carbon obtained from buffing dust generated in leather industry as solid waste (2 kg for every 200 kg leather produced) was able to remove 6.24 mg of dye per gram at a concentration of 125 mg/L. Maximum removal of dye from the wastewater occurred at pH 3.5 and temperature 30°C. The adsorption capacity of the activated carbon was found to be increased with carbonisation temperature. The adsorption of dye from aqueous solution on surface of buffing dust based activated carbon was physical in nature involving very little heat of adsorption (-15.69 kJ/mol). The adsorption capacity of buffing dust based activated carbon was found to be greater than with commercially available activated carbons.

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