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Colour removal from a dyestuff industry effluent using activated carbon

K C Lakshmi Narayan Rao[a], K Krishnaiah & Ashutosh[b]

[a]Department of Chemical Engineering, Indian Institute of Technology, Madras 600 036, India

Research and Development Department, Chemiequip Ltd, Ambernath 421 501, India

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The objective of the present study is to identify the best commercially available activated carbon adsorbents to remove the colour of dye of the effluent (waste) water from dye using and dye manufacturing industry. The effect of different types of dyes, particle diameter of the adsorbent, intial dye concentration, carbon loading, *p*H of the effluent water and temperature on best available adsorbent is evaluated. Adsorption isotherms are developed for different dyes and represented by Freundlich isotherm which can be used for the design of waste water treatment plants.

The dyestuff manufacturing and consuming (mainly textile and paper) industries are some of the leading consumers of water. The effluents from these industries contain small proportions of dyes which impart colour to water and thus lower the aesthetic value of water. The removal of colour from waste water is often more important than the removal of soluble colourless organic contaminants which usually contribute to the major BOD load[1].

It is difficult to remove the dyes from the effluents since the dyes are stable to light and heat and are biologically non-degradable. Hence, the conventional methods of colour removal such as the primary and secondary treatment systems employed in the sewage plants are unsuitable[2]. So it is necessary to use tertiary treatment to remove colour before discharge the waste water into municipal sewer or directly into a natural stream. Adsorption processes have received considerable attention for colour removal from waste water and many adsorbents have been tried for the same. Parish[3] and Perrich[4] recommend the use of activated carbon since it is economically attractive as it can be regenerated for more than ten times.

This work deals with the performance evaluation of four types of commercial granular activated carbons available in India on different types of dyes, viz., basic, direct, hot and cold brand reactive dyes. Based on this, the best type is selected and its performance is further analyzed. The adsorption isotherms are also experimentally determined which will be of use in the design of adsorption equipment.

Experimental Procedure

Batch adsorption kinetics—Batch adsorption kinetic studies were carried out in a stainless steel cylindrical vessel of two litres capacity (height = diameter) fitted with a high speed impeller type stirrer. The vessel had four baffles to avoid vortex formation. In a typical experiment, 1.7 L of dye solution of known concentration was taken in the batch adsorber. A known amount of deaerated activated carbon was added to it. The speed of the stirrer was maintained at a value (1000 rpm) which ensures good mixing and also minimizes disintegration of particles. At different intervals of time, samples were drawn out of the adsorber using a syringe. Dye concentration was measured colorimetrically using a Spectrophotometer in the visible range. The effect of different parameters on adsorption of various dyes using different adsorbents was investigated. The range of variables investigated are summarised in Table 1 and the properties of the adsorbents and dyes are given in Tables 2 and 3, respectively. Even though surface area, pore size and pore volume are important, iodine number is frequently used to characterize the adsorbents for dye removal from waste water[4].

Adsorption isotherms—For batch adsorption studies, an isothermal (in water bath) flask shaker was used for agitation of the known volume of adsorbate solution with the known amount of activated carbon. At a time, four 250 mL conical flasks could be agitated for a specific interval of time of around four hours beyond which no significant amount of dye was adsorbed at a particular temperature. The solution was analysed for equilibrium concentration.

Results and Discussion

Batch adsorption kinetics—A large amount of experimental data on activated carbon are obtained[5] and a typical of results for each parameter are presented.

Comparison of different types of adsorbents—The performance of the commercial carbons with respect to basic and reactive dyes is compared with bentonite based activated clay in Figs 1a and 1b. It can be observed that in comparison with the reactive dye, the basic dye is easily removed by activated carbons studied (Figs 1a and b) and this may be due to the ionic attraction between the negatively charged active centres (associated with most carbons) and positively charged basic dye molecule. The comparison brings out the superiority of carbon D and hence this was used for further studies.

Table 1—Range of variables

Parameter	Range
Particle size, d_p	0.59-3.53 mm
Initial dye solution concentration, C_0	100-300 mg/L
Initial *p*H of the dye solution	2-10
Loading of carbon	2.6-10 g/L
Temperature, *T*	35-80°C

Table 2—Values of iodine number for different types of carbon

Carbon type	Iodine number
A	400-450
B	500-550
C	650-700
D	900-950

Table 3—Type of dyes and their molecular weights

Brand name	Dye type	Mol wt
Malachite Green	Basic	329.0
Direct Black 'E'	Direct	753.0
Chemictive Brill	Cold brand reactive	687.0
Chemictive Rose	Hot brand reactive	881.5

Table 4—Freundlich isotherm constants

	T, °C	*n*	*K*
Chemictive Brill	35	2.24	1.162
Chemictive Brill	45	2.40	2.675
Chemictive Brill	60	2.84	3.252
Chemictive Rose	35	2.15	1.058
Chemictive Rose	63	2.57	2.247

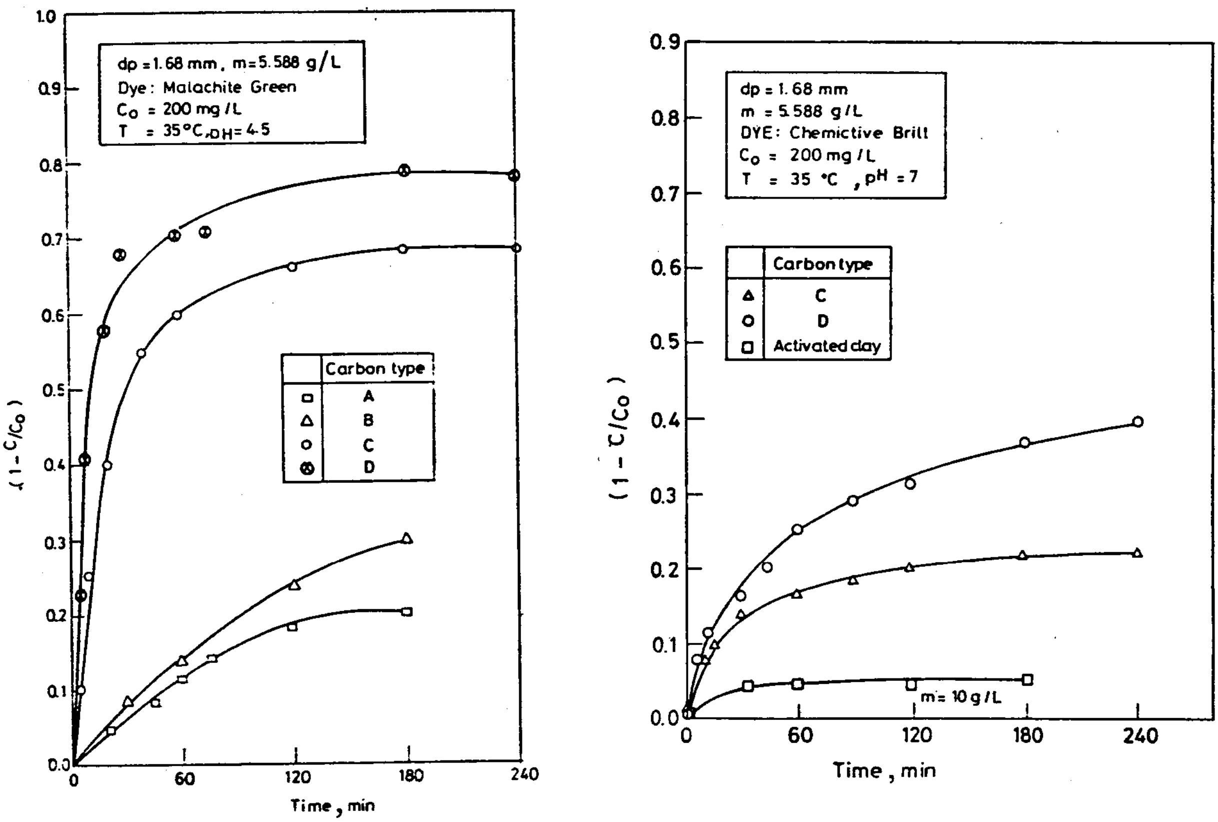

Fig. 1—Comparison of different types of adsorbents

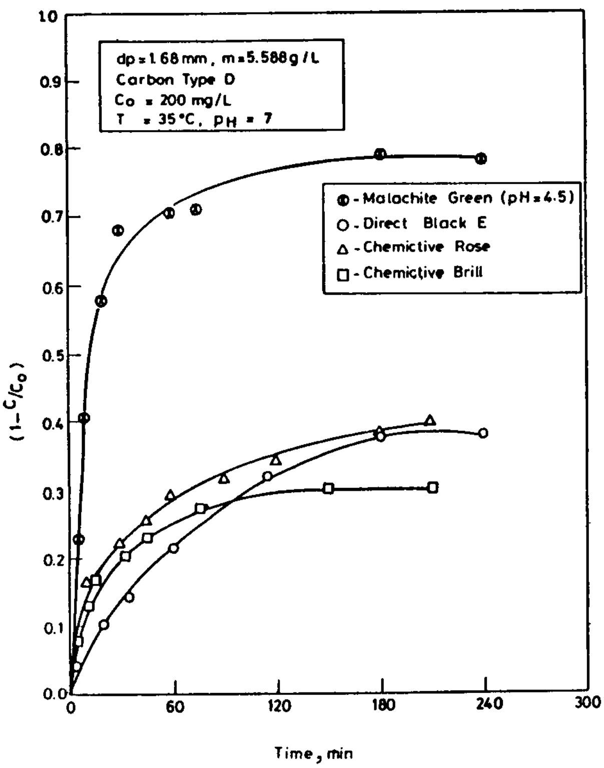

Fig. 2—Comparison of different types of dyes

Removal of different types of dyes—Fig. 2 shows the comparison of the fractional removal of various dyes. While the basic dyes can in general be easily removed from the effluents, the reactive dyes can not be so easily adsorbed. The hot brand reactive dye, Chemictive Rose is less adsorbed probably due to its larger molecular size which makes it difficult for the diffusion through the pores of activated carbon.

Effect of particle size—A typical result of the fractional removal of dye with time for different particle sizes and for two reactive dyes (Chemictive Brill and Chemictive Rose) is shown in Figs 3a and 3b. It can be observed as the particle diameter decreases, the removal of dye increases which is due to larger surface areas that are associated with small particles. For large particles the diffusional resistance to mass transport is higher and most of the internal surface of the particle may not be utilized for adsorption and consequently the amount of dye adsorbed is small. McKay[6] also observed that as the particle size decreases the dye uptake, i.e., the amount of dye adsorbed on the particles increases.

Even though small particles are better for colour removal from the effluents, one cannot use small particles in a continuous packed bed ad-

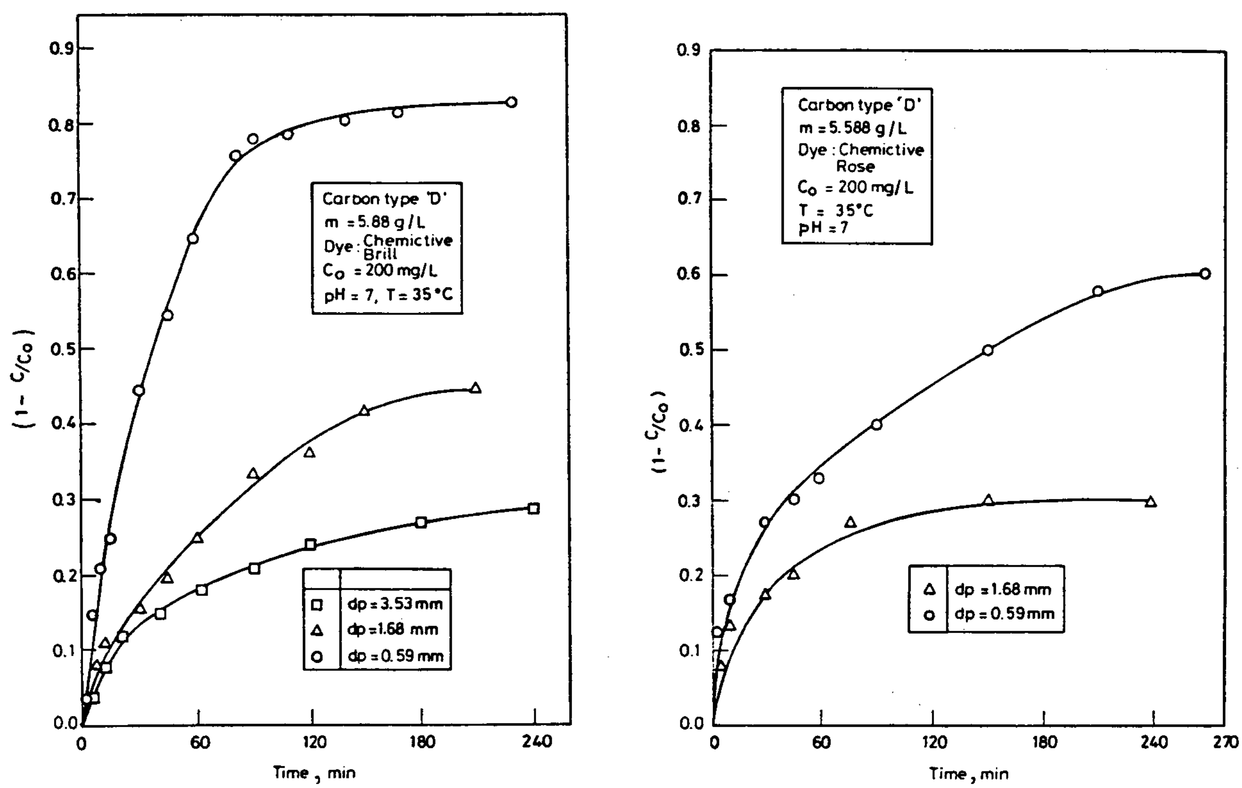

Fig. 3—Effect of particle size

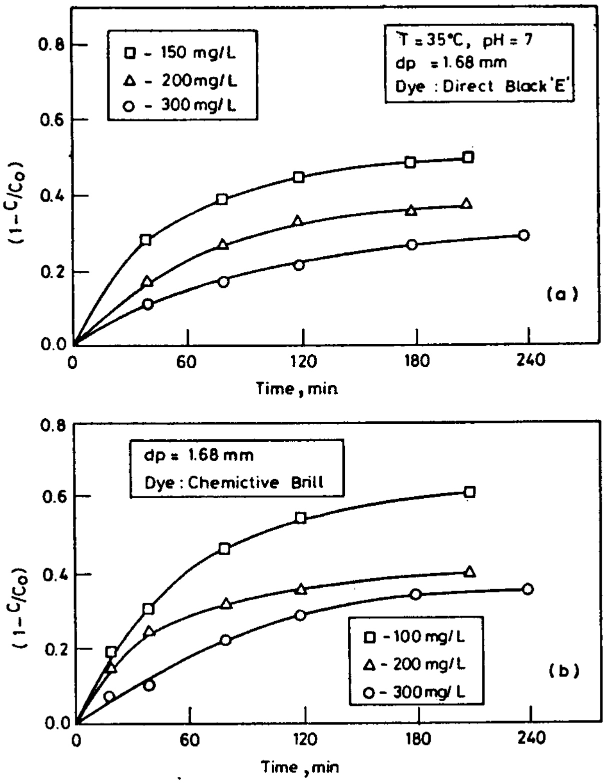

Fig. 4—Effect of initial dye concentration

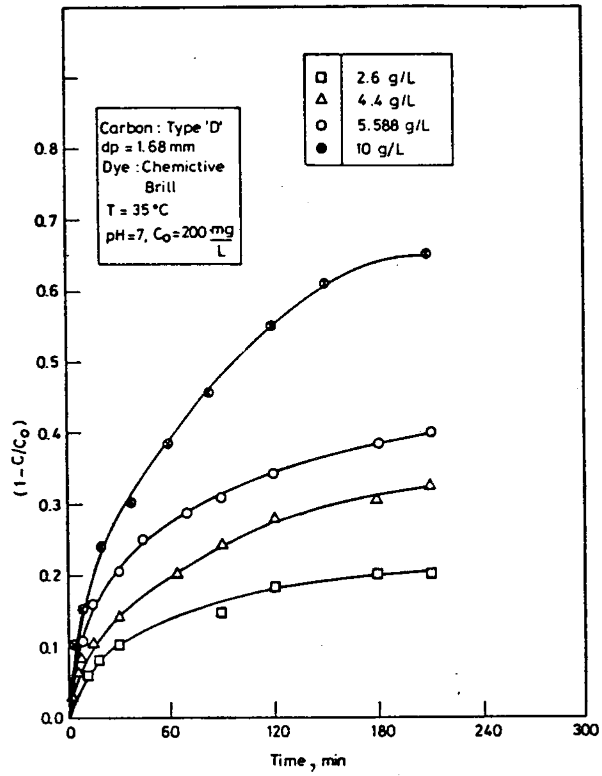

Fig. 6—Effect of carbon loading

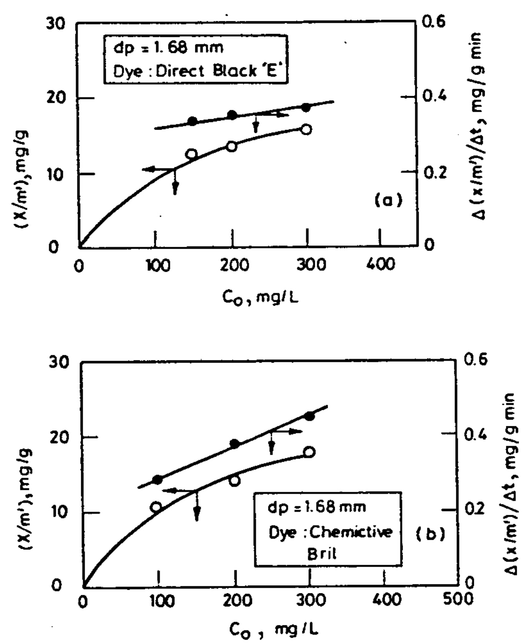

Fig. 5—Dye uptake and average rate of adsorption

sorber because of high pressure drops encountered.

Effect of initial dye concentration—Carbon has a fixed capacity for adsorption at a particular initial dye concentration. So the volume of the effluent that can be treated with a fixed amount of activated cabron depends upon the initial concentration of the dye. The effect of variation of initial dye concentration was studied for Direct Black 'E' and Chemictive Brill (Blue 'MR') with all other parameters being constant.

From Fig. 4, it is seen that for low initial concentrations the fractional uptake of the dye is more. Even though the fractional removal of dye is smaller at high initial concentration (Fig. 4), the actual amount of dye adsorbed increases with increase in initial dye concentration in the solution as shown in Fig. 5. In the same figure it is seen that overall rate of adsorption increases with the increase in initial dye concentration in the solution.

Effect of carbon loading—Carbon loading is an important parameter because this determines the capacity of an adsorber for a given initial concentration of the effluent. The effect of carbon loading (gram of carbon/litre of solution) was studied on Chemictive Brill keeping all other experimental conditions constant. As the carbon loading increases the fraction of dye removed increases as shown in Fig. 6. This is very obvious because a larger mass of carbon can adsorb larger amount of dye but in each case, at equilibrium, mass of

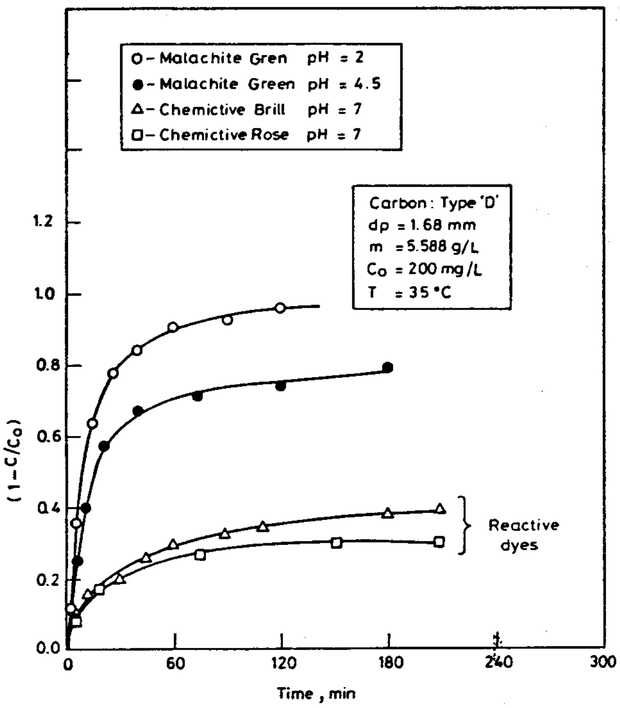

Fig. 7—Effect of initial pH of the solution

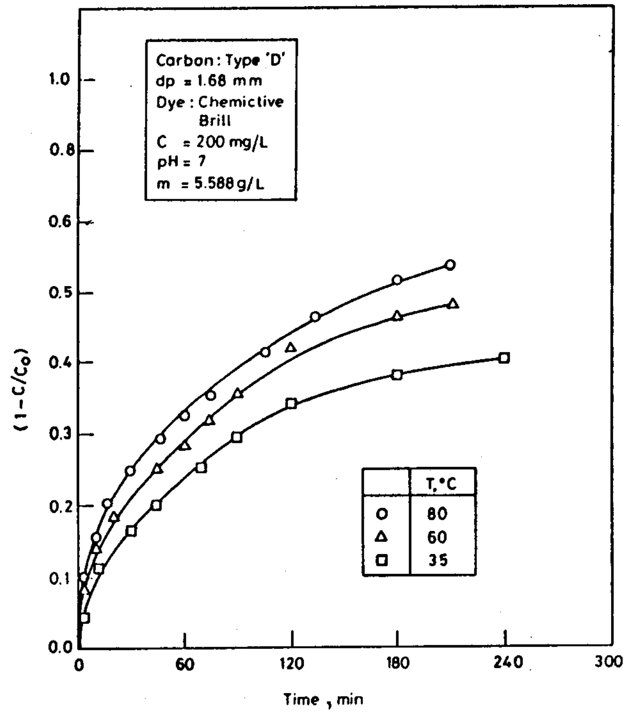

Fig. 8—Effect of temperature

dye adsorbed per unit mass of carbon is different. McKay[6] also reported similar observation that increasing carbon mass also increases the dye uptake.

Effect of initial pH of dye solution—The effect of initial pH of dye solution was studied on Malachite Green, Chemictive Brill and Chemictive Rose, with other parameters being kept constant. The adsorption of Malachite Green (basic dye) increased with a decrease in pH as shown in Fig. 7. It was found that change in pH does not significantly effect the adsorption characteristics of reactive dyes while a pronounced effect was observed for basic dyes for a pH of 4.5 indicating that basic dye removal is enhanced by acidic solutions[6].

Effect of temperature—The temperature of the dye containing effluent varies depending upon the process from which it originates. The effect of temperature on adsorption was investigated on Chemictive Brill in batch adsorber. Within the experimental range of temperatures studies, the fractional removal of dye increased with the increase in temperature as seen from Fig. 8. A similar observation was also made by McKay[6]. The capacity of the adsorbent to adsorb dye molecules increases with the increase in operating temperature which is due to increase in diffusion coefficient at higher temperatures[6]. However, the effect of temperature seems to be not very much pronounced.

Adsorption equilibrium isotherm—The equilibrium isotherms give the information on the maximum amount of dye that can be adsorbed at specific conditions. These adsorption isotherms are useful in the design and/or in developing a mathematical model that describes the dynamics of adsorption.

Adsorption isotherms were developed for two dyes, Chemictive Brill and Chemictive Rose at different temperatures. The experimentally obtained equilibrium data are shown in Figs 9a and 9b. The shape of the isotherms gives an indication whether the adsorption is favourable or unfavourable as indicated by Weber and Smith[7]. The shape of curves obtained in the present investigations is favourable for adsorption (Figs 9a and 9b).

More practicle and easy to handle semi-empirical adsorption model, such as Fruendlich isotherm generally fits experimental data of dilute solutions which is the case in most of the effluents. The experimental adsorption data is found to be satisfactorily modelled by Fruendlich isotherm

$$\left(\frac{X}{m'}\right) = K\,(C_e)^{1/n} \qquad \ldots (1)$$

as can be seen from Figs 10a and 10b. The values of constants are given in Table 4.

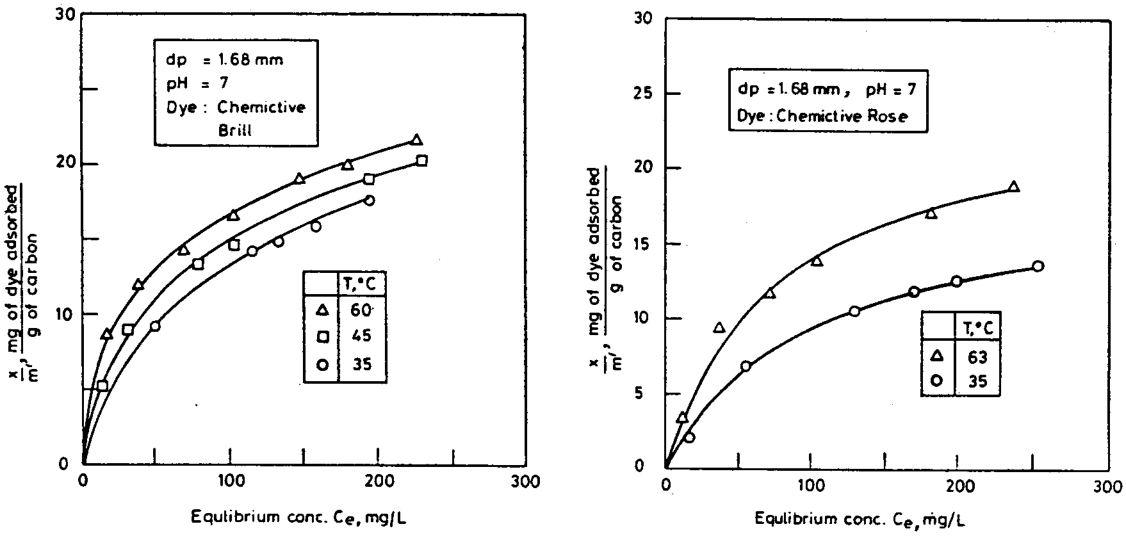

Fig. 9—Equilibrium isotherm

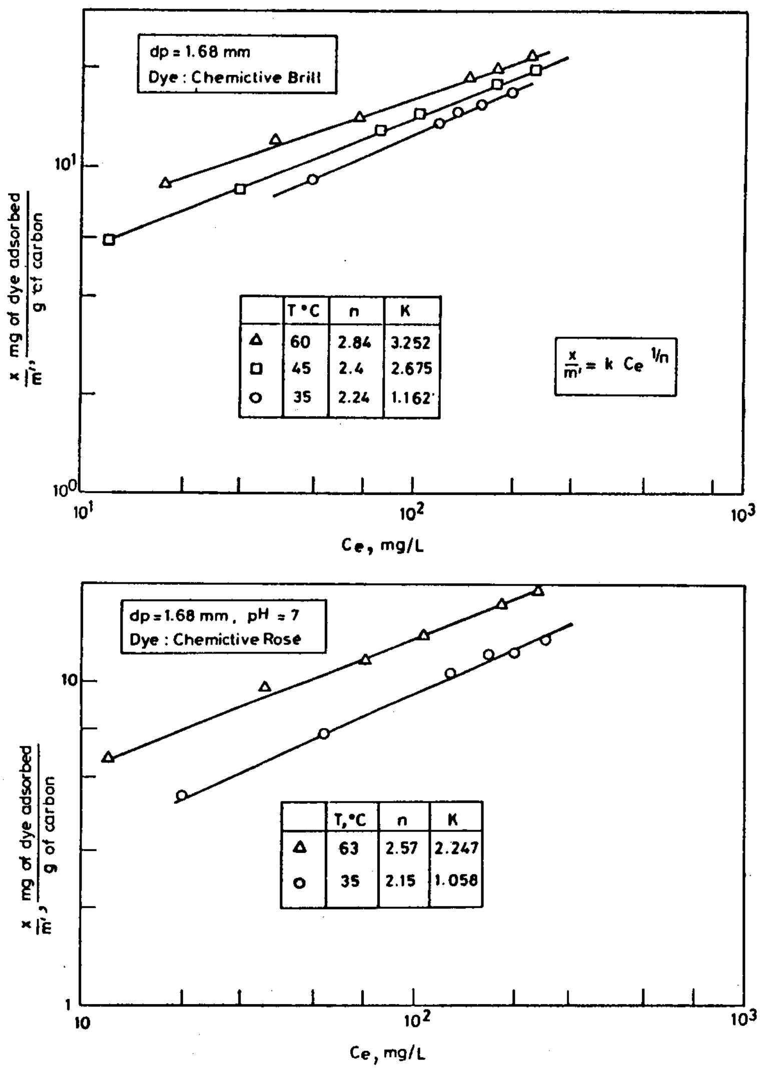

Fig. 10—Freundlich isotherm

Higher values of n and K for basic dyes (when compared with values obtained for reactive dyes, Table 4) are reported by McKay[6], which indicates that basic dyes are easily adsorbable than the reactive dyes. When dyes are adsorbed on activated carbon it is very difficult to differentiate between physical adsorption and chemisorption[8]. In this work, in all experiments, it was found that higher temperature aids the adsorption process. This may be due to increase in diffusivity with temperature which can eventually transport more dye molecules to the carbon surface or may be due to the increased surface activity which increases adsorption or may be due to both the effects.

Conclusions

The adsorption characteristics of basic, direct and reactive dyes on granular activated carbons from four different indigenous manufacturers were studied. The best of these carbons was selected and the factors like type of dye, particle size, initial dye concentration, carbon loading, *p*H and temperature affecting the adsorption of dyes from aqueous solutions were investigated. Activated carbon was found to be a very good adsorbent for basic dyes and good for reactive dyes.

The simple and semi-empirical Freundlich adsorption isotherm constants were evaluated experimentally for reactive dyes at different temperatures.

In all the experiments, granular carbon was used because granular carbons can be easily regenerated and reused. The cyclic usage of regenerated carbon holds the key to the economic viability of activated carbon adsorption for waste water treatment.

Acknowledgement

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Nomenclature

C = dye concentration in water at any time, mg/L
C_o = initial dye concentration in water, mg/L
C_e = equilibrium dye concentration in water, mg/L
d_p = average particle diameter, mm
K = constant in Freundlich isotherm
m = mass loading of carbon, g/L
m' = mass of carbon, g
n = constant in Freundlich isotherm
t = time, min
T = temperature, °C
X = mass of dye adsorbed, mg

References

1 Vaidya A A & Datye K V, *Colourage*, 29 (1982) 3.
2 McKay G, Allen S J, Mcconney I F & Otterburn M S, *J Colloid Interface Sci*, 80 (1981) 323.
3 Parish G J, *Rev Prog Color*, 7 (1976) 55.
4 Perrich J R, *Activated carbon adsorption for waste water treatment* (CRC Press, London), 1981.
5 Rao K C L N, *Some Studies on Color Removal from a Dyestuff Industry Effluent using Activated Carbon*, M. Tech Thesis, Indian Institute of Technology, Madras, 1987.
6 McKay G, *J Chem Technol Biotechnol*, 32 (1982) 759.
7 Weber W J & Smith E H, *Environ Sci Technol*, 21 (1987) 1040.
8 McKay G, *J Chem Technol Biotechnol*, 33 (1983) 196.