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A Comparative Study of Adsorbents Prepared from Industrial Wastes for Removal of Dyes

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A Comparative Study of Adsorbents Prepared from Industrial Wastes for Removal of Dyes

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ABSTRACT

Waste materials such as blast furnace dust, sludge and slag from steel plants and carbon slurry from fertilizer plants were treated and activated to prepare low-cost adsorbents. The adsorbents were chemically characterized and the surface area determined. The carbonaceous adsorbent prepared from carbon slurry had appreciable surface area (380 m^2/g); whereas, the other three adsorbents had poor surface area (4–28 m^2/g). The adsorption of three basic dyes, that is, chrysoidine G, crystal violet, and meldola blue was studied on all the adsorbents and the results indicated that only carbonaceous adsorbent removed the dyes from solution to an appreciable extent compared to the others. The carbanaceous adsorbent can, therefore, be a useful material for dye removal. All further studies were, therefore, done on the carbonaceous adsorbent. The adsorption isotherms of the dyes were found to conform to the Langmuir equation. The thermodynamic parameters calculated

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indicated that the dye adsorption was exothermic and physical in nature. The kinetic studies of the adsorption process showed it to be first order and pore diffusion controlled. The adsorption with the carbonaceous adsorbent is about 70–80% of the amount taken up by standard activated charcoal. Thus, the prepared carbonaceous adsorbent is efficient and can be used for the removal of dyes from solution.

Key Words: Low cost adsorbents; Adsorption; Basic dyes; Carbonaceous adsorbent.

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INTRODUCTION

The treatment of wastewater for the removal of inorganic and organic contaminants is getting increased attention. Among the organic pollutants, the dyes find a prominent place as they impart color besides toxicity to fish and other aquatic organisms.[1] The removal of dyes, therefore, is of prime importance. Although, a number of methods, such as coagulation,[2] ozonation,[3] membrane process,[4] filtration with coagulation,[5] and ozonation with coagulation,[6] have been used for this purpose, the adsorption process[7] remains the best one as it is universally applicable. Activated carbon is normally used as an adsorbent for the removal of dyes from various effluents generated in the dyes, textile, and paper industry. However, the main problem with this procedure is the high cost of the adsorbent. Keeping this in view, a number of attempts have been made to develop alternative adsorbents from various natural and industrial waste products. Some of the important studies have made use of peat,[8] wood,[9] wool carbonizing waste,[10] eucalyptus bark,[11] bagasse pith,[12] and chitosan fibers[13] as adsorbent. However, they have not proved to be very promising and, as such, the search is still on for adsorbents that may be cheaper and also efficient for removing colored materials from various wastewaters.

Natural as well as industrial wastes that are available may be inorganic, organic, or of mixed nature. We have, therefore, thought it desirable to investigate several wastes, that is, blast furnace (BF) dust, sludge and slag (mainly inorganic in nature) from steel plants, and a carbonaceous slurry (organic waste) from a fertilizer plant as a possible adsorbents for the removal of dyes from solution. The results were compared with those of standard activated charcoal to determine the efficiency of the prepared adsorbent.

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EXPERIMENTAL

Reagents and Materials

The three basic dyes, chrysoidine G, crystal violet, and meldola blue, were purchased from Fluka (Switzerland), Spectrochem (India) and Sigma (USA), respectively and were used as such. The other reagents used were of analytical grade. Standard activated charcoal was procured from E. Merck. Double distilled water was used throughout.

Preparation of Adsorbents

The adsorbents were prepared from wastes obtained from steel and fertilizer plants.

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Carbonaceous Adsorbent

One of the wastes generated in national fertilizer plants in India using fuel oil and low sulphur heavy stock (LSHS) as a feed stock is carbon slurry, which is available at a very cheap rate (~US $7 per ton). This slurry is dumped in large tanks and allowed to dry. The dried cake material was procured from National Fertilizer Limited, Panipat (India) and powdered. It was found to consist of small, black and greasy granules and was treated[14] with hydrogen peroxide to oxidize the adhering organic material. It was then washed with distilled water and heated at 200°C until the evolution of black soot stopped. This material was then activated at different temperatures in a muffle furnace for 1 hour in air atmosphere. After the activation, the material was treated with 1 M HCl to remove the ash content and washed with distilled water and then dried (yield ~90%). The dried product is now called carbonaceous adsorbent. It was sieved to get different mesh sizes and kept in a desiccator. Preliminary adsorption studies revealed that the activation at 500°C imparts maximum adsorption characteristics and, therefore, all investigations were carried out on the samples activated at this temperature.

Blast Furnace Slag, Dust, and Sludge Adsorbent

Among the various wastes produced in steel plants, the BF slag is in the largest amount. Besides this, BF dust and sludge are also waste products of steel plants. Gases generated during the manufacture of pig iron carry a dust

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load that is removed before their release into atmosphere. In the beginning, the coarse particles in the exhaust gases are removed by passing the gases through a large brick-lined chamber where the velocity of gases is reduced to allow the settling of the dust load. The chamber where some dust settles down is called a dust catcher and the waste material collected is "BF dust." The finer particles, which still remain in the gas, are removed in wet scrubbers wherein the gas is subjected to water sprays. The waste material collected here is termed as "BF sludge." The BF dust and sludge procured from Malvika Steel Ltd., Jagdishpur, India, were subjected to treatment similar to the carbon slurry treatment and then activated. The 400°C temperature was found to be optimum for activation. After activation, the wastes were washed with water and dried. During manufacture of pig iron in a blast furnace, the impurities combine with quicklime from limestone to form a molten product "slag," which floats on the surface of molten iron and is taken out from time to time. Molten slag is cooled to yield different types of slag depending on the mode of cooling. The foamed slag is formed by rapid chilling of slag with a limited amount of water, applied in such a way as to trap steam in the mass, producing porous, honeycombed material. As the foamed slag has some porosity, it was studied as adsorbent. The foamed slag was treated with H_2O_2 to remove impurities, if any, and washed with water and dried. The product was sieved and stored in a desiccator.

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Instrumentation

A Shimadzu 160A UV–VIS spectrophotometer (Japan) was used for spectrophotometric determination of dyes. The pH of solutions was measured with a ELICO LI 127 pH meter and a LEO 435 VP was used for scanning electron microscopy.

Analysis

The BF slag, dust and sludge were analyzed[15] and the results obtained are compiled in Table 1. The carbonaceous slurry waste was ignited at 1000°C and produced ash content of 0.9%. The volatile matter is 3.2% and the rest being mainly carbon. The analysis of the ash showed iron to be 0.25%. The surface area of the adsorbents was determined by N_2 gas adsorption and their porosity was seen by scanning electron microscopy. To further determine adsorption properties, the iodine and methylene blue numbers were also determined by standard methods.[16]

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Table 1. Chemical analysis of blast furnace sludge, dust, and slag.

	Sludge (%)	Dust (%)	Slag (%)
Loss on ignition	40.5	24.6	0.6
Insoluble residue	3.2	4.3	4.1
SiO_2	12.7	15.8	32.7
R_2O_3	35.4	44.9	22.8
CaO	3.5	4.7	31.7
MgO	3.0	4.2	6.8

Adsorption Studies

Adsorption on all four adsorbents prepared was studied by batch method. For this, a fixed amount of the adsorbent (0.01 g) was added to 10 mL of dye solution of varying concentrations taken in stoppered glass tubes, which were placed in thermostat with a shaking assembly. The solutions were stirred continuously at constant temperature for 2 h to achieve equilibration. The concentration of the dye in the solution after complete equilibrium adsorption was determined spectrophotometrically at λ_{max} of 448, 588, and 570 nm for chrysoidine G, crystal violet, and meldola blue, respectively. Kinetic studies of adsorption were also carried at two concentrations of the adsorbates wherein the extent of adsorption was investigated as a function of time. The pH of all solutions in contact with the adsorbents was found to be in the range 6.5 to 7.5.

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RESULTS AND DISCUSSION

Characterization of the Prepared Adsorbents

It is seen from analytical results given in Table 1 that silica and calcium oxides are the main constituents of BF slag; whereas, coke (loss on ignition), silica, and R_2O_3 (mainly iron oxide, R = Fe, Al) are the prominent components of BF dust and sludge. Thus BF slag is inorganic in nature. BF dust and BF sludge are inorganic with partial organic character (carbon content). On the other hand, carbonaceous adsorbent consisting of mainly carbon is organic in nature. The organic content generally imparts porosity to

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Table 2. Characteristics of adsorbents used.

	Standard activated charcoal	Carbonaceous adsorbent	BF sludge	BF dust	BF slag
Surface area (m^2/g)	710	380	28	13	4
Methylene blue number	198	90	6	3	2
Iodine number	635	330	24	11	3

the adsorbent. This is reflected in surface area of the four adsorbents given in Table 2. As the carbon content decreases, the surface area correspondingly decreases. The higher surface area is due to the porous nature of the adsorbent and SEM results showed that the porosity order is: carbonaceous adsorbent > BF sludge > BF dust > BF slag. To further evaluate the adsorption characteristics, the methylene blue and iodine numbers were also determined and are given in Table 2. It is seen that these numbers decrease in the order: carbonaceous adsorbent > BF sludge > BF dust > BF slag. This order of adsorption is parallel to the surface area of the adsorbents, which reflects the fact that the adsorption of organic molecules is a surface phenomenon and the carbonaceous adsorbent, having the largest surface area, is the best one. The methylene blue number for carbonaceous adsorbent (surface area: $380\,m^2/g$) was also worked out theoretically by taking the dye molecule area as $197\,\text{Å}^2$ and found to be 114. This is slightly higher than the experimental value (90) determined. The low value of the experimental methylene blue number indicates that some pores of the carbonaceous adsorbent are not accessible to methylene blue. To compare the efficiency of adsorbents, the results were compared with a standard activated charcoal sample. Table 2 shows that the carbonaceous adsorbent has about 50% of surface area compared to activated charcoal. Thus, it is expected that it would be half as efficient as the activated charcoal in removing organics. This conclusion is supported by relative values of the methylene blue and iodine numbers. The other three adsorbents, BF sludge, BF dust, and BF slag, are poor materials for this purpose.

Effect of Contact Time and Concentration

The adsorption of all the dyes at a fixed concentration on carbonaceous adsorbent was studied as a function of contact time to find an equilibration

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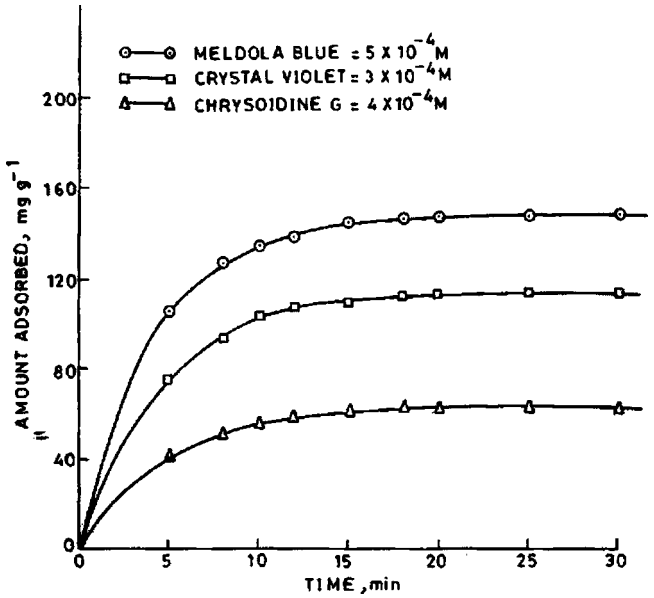

Figure 1. Effect of contact time on uptake of dyes on carbonaceous adsorbent (temperature: 25°C; particle size: 200–250 mesh).

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time for maximum adsorption. The results are shown in Fig. 1. It is seen that 25 minutes are required for the equilibrium adsorption to be attained. As such, for all adsorption studies, the equilibration time was kept 2 h. It is further seen from Fig. 1 that adsorption is very fast initially, showing that 50% adsorption in all the three dyes is completed in less than 3.5 min. After that, it slowly attains equilibrium adsorption. The effect of concentration on equilibration time was also investigated as a function of initial dye concentration and the results obtained in case of crystal violet adsorption are shown in Fig. 2. Similar plots were also obtained for the other two dyes. The plots in Fig. 2 show that time of equilibration, as well as time required to achieve a definite fraction of equilibrium adsorption, is independent of initial concentration. This type of response indicates that the adsorption process is first order, which is confirmed by Lagergren's plots discussed later under dynamic modelling. Similar observations were made by other workers.[17]

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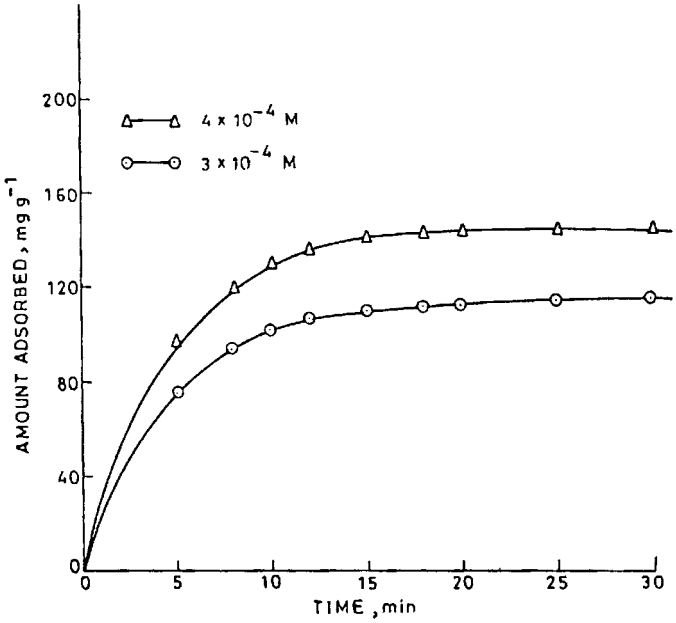

Figure 2. Effect of contact time on the uptake of crystal violet on carbonaceous adsorbent at different initial concentrations (⊙—3×10^{-4} M, Δ—4×10^{-4} M; particle size: 200–250 mesh; temperature: 25°C).

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Effect of Particle Size on Adsorption

The adsorption of dyes was investigated at three particle sizes 100–150, 150–200, and 200–250 BSS (British Standard Sieve) mesh, respectively. The results are shown for meldola blue adsorption on carbonaceous adsorbent in Fig. 3. The results indicate that adsorption capacity increases to some extent with the decrease in particle size of the adsorbent. This could not be due to substantial increase in surface area.[18] It is possible that large dye molecules are not able to penetrate to some of the interior pores of the particles, especially when their size is large. The access to all pores is facilitated, as particle size becomes smaller. Similar results were also obtained by Mckay et al.[19] As particles of size 200–250 mesh show maximum adsorption capacity, all further studies were carried out with this fraction only.

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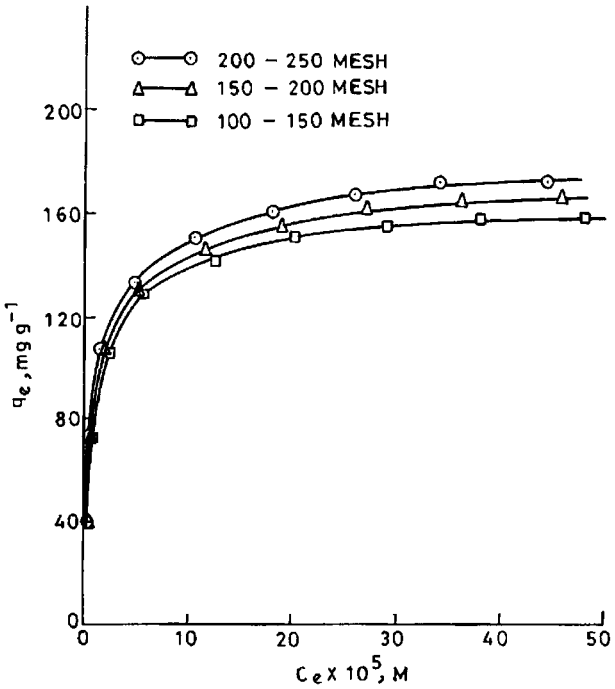

Figure 3. Effect of particle size on the adsorption of meldola blue on carbonaceous adsorbent (temperature: 25°C).

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Adsorption Isotherms

To know the adsorption capacity of the prepared adsorbents, the equilibrium adsorption of dyes was studied as a function of concentration. The amount of dye adsorbed (q_e) has been plotted against equilibrium concentration (C_e) for all the adsorbents in Figs. 4 through 6. It is seen that the extent of adsorption is in the order: carbonaceous adsorbent > blast furnace sludge > blast furnace dust > foamed slag for all the dyes, which is parallel to porosity and surface area of adsorbent. Further, the maximum adsorption on carbonaceous adsorbent, BF sludge, dust and slag is found to be 75, 10.1, 5.4, and 1.9 mg/g respectively for chrysoidine G; 161, 25, 11, and 3 mg/g for crystal violet, and 170, 67, 34, and 3.7 mg/g for meldola blue. It shows that the adsorption on BF sludge, dust and slag is much smaller than that on carbonaceous adsorbent. Thus, inorganic adsorbents having poor porosity and surface area are not suitable for the adsorption of dyes.

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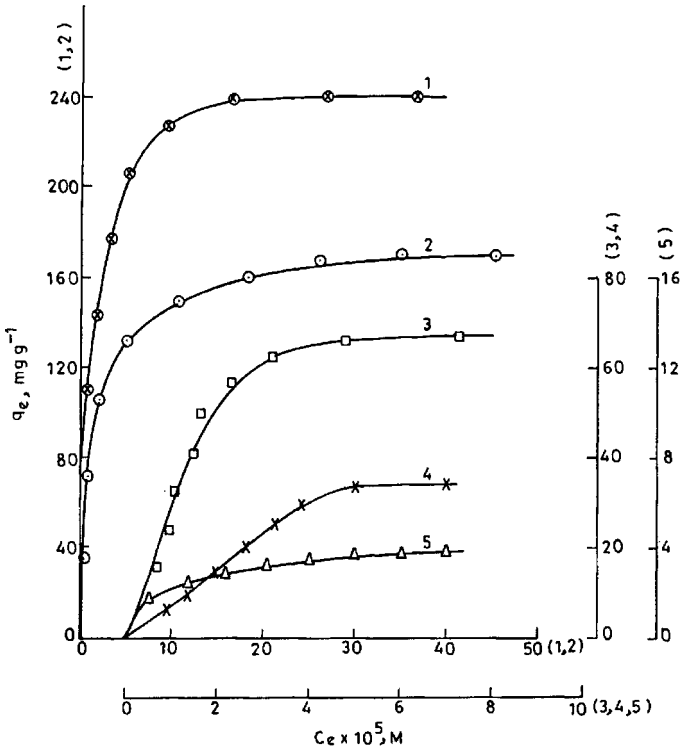

Figure 4. Adsorption isotherms of meldola blue on different adsorbents at 25°C (⊗1, Std. activated charcoal; ⊙2, carbonaceous adsorbent; □3, BF sludge; × 4, BF dust; Δ5 BF slag).

Only carbonaceous adsorbents are the materials that can be used for the removal of dyes. All further studies were carried out on this adsorbent only. In order to further assess the suitability of the carbonaceous adsorbent for dye removal, the adsorption was compared with that of standard activated charcoal. The results for adsorption of these dyes on standard activated charcoal are also incorporated in Figs. 4 through 6. The comparison shows that the maximum adsorption of dyes on carbonaceous adsorbent is about 70–80%, of the maximum on activated charcoal. This adsorption on carbonaceous adsorbent is much more than 50% of expectation on the basis of surface area alone. This appears due to large size of pores of carbonaceous adsorbent as compared to activated charcoal. Thus, the prepared adsorbent is appreciably efficient.

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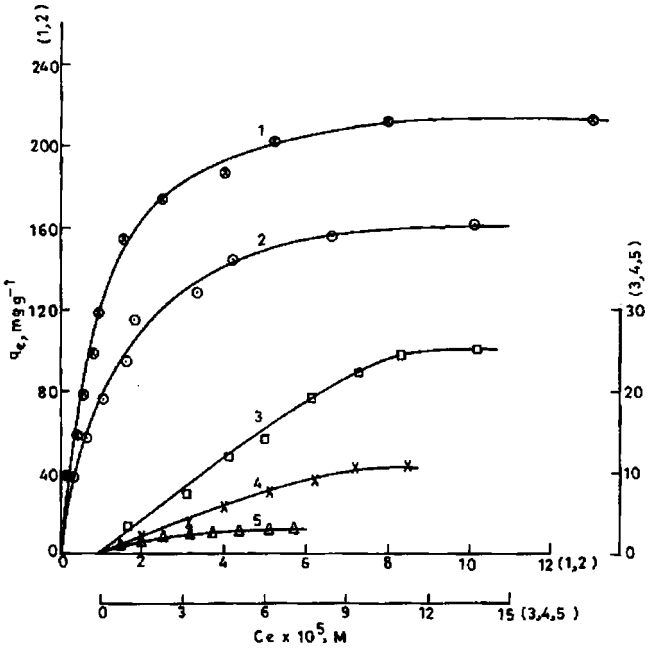

Figure 5. Adsorption isotherms of crystal violet on different adsorbents at 25°C (⊗1, Std. activated charcoal; ⊙2, carbonaceous adsorbent; □3, BF sludge; × 4, BF dust; Δ5 BF slag).

Effect of Temperature

The effect of temperature on the adsorption of dyes was also investigated. The results obtained at 45°C are shown in Fig. 7. The comparison of plots of the Fig.7 and Figs. 4 through 6 reveals that adsorption decreases with increase in temperature indicating that the process is exothermic.

The adsorption data was further analyzed and found to conform best to following Langmuir equation.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b C e}$$

where q_e is the amount adsorbed at equilibrium concentration, q_m the Langmuir constant related to maximum monolayer capacity, b the Langmuir constant related to energy of adsorption, and Ce the equilibrium concentration.

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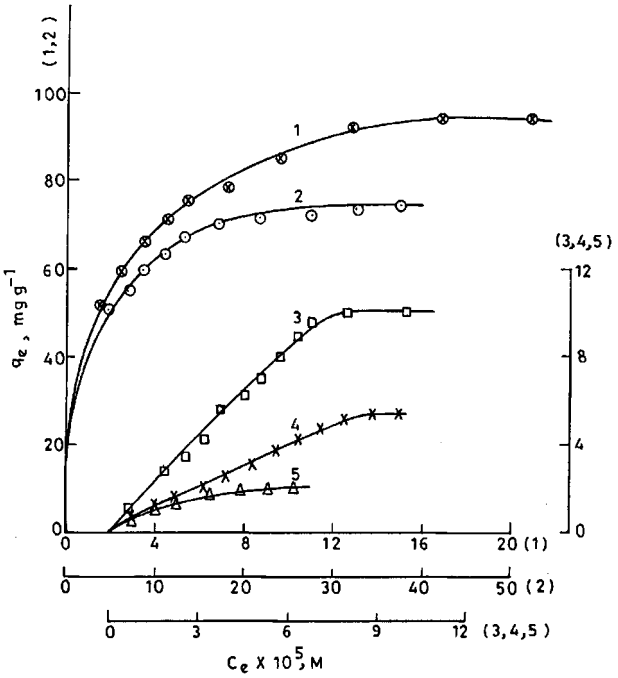

Figure 6. Adsorption isotherms of chrysoidine G on different adsorbents at 25°C (⊗1, Std. activated charcoal; ⊙2, carbonaceous adsorbent; □3, BF sludge; × 4, BF dust; Δ5 BF slag).

The plots between $1/q_e$ and $1/Ce$ for the adsorption of meldola blue dye were drawn and given in Fig. 8. Similar plots were also obtained for the other two dyes. The value of monolayer capacity (q_m) and equilibrium constant (b) have been evaluated from the intercept and slope of these plots and given in Table 3. It is seen from Table 3 that monolayer capacity (q_m) of the adsorbent for the dyes is comparable to the maximum adsorption as evaluated from adsorption isotherm of Figs. 4 through 7. Further, the q_m value decreases as expected with the rise in temperature as the adsorption process is exothermic. As b values reflect equilibrium constant for the adsorption process, it reflects the affinity of the adsorbent for dye. Thus, b values indicate that the adsorbent has maximum affinity for meldola blue and minimum for chrysoidine G. This is consistent with the results obtained where dye adsorption is in the order: meldola blue > crystal violet > chrysoidine G.

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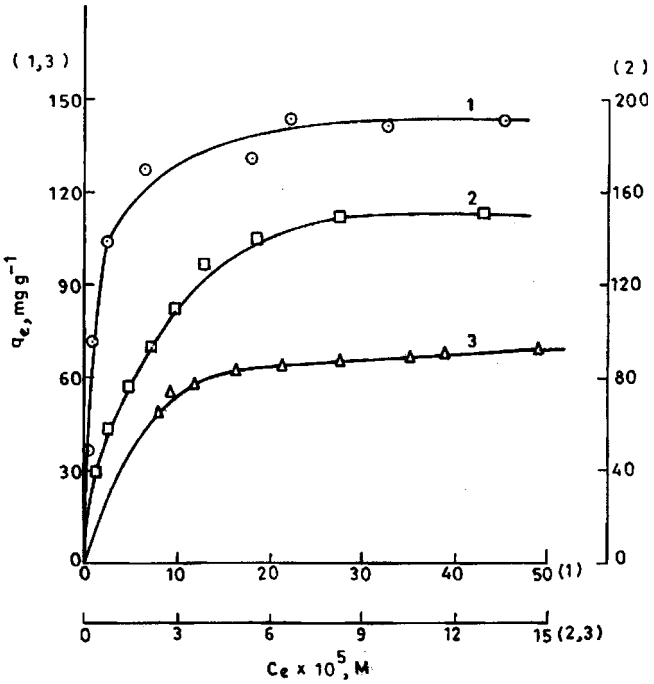

Figure 7. Adsorption isotherms of dyes on carbonaceous adsorbent at 45°C (⊙1, meldola blue; □2, crystal violet; Δ3, chrysoidine G).

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The influence of isotherm shape has been discussed[20] to know whether adsorption is favorable or not in terms of R_L, a dimensionless constant referred to as separation factor or equilibrium parameter. R_L is calculated[20] using the following equation.

$$R_L = \frac{1}{1 + bC_0}$$

where b is the Langmuir constant ($L\,mol^{-1}$) and C_0 the initial concentration ($mol\,L^{-1}$). The values of R_L calculated as per this equation are incorporated in Table 3. As the R_L values lie between 0 and 1, the adsorption isotherm is favorable.[20]

The free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were calculated using the following equations.

$$\Delta G^\circ = -RT \ln (b)$$

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Table 3. Langmuir constants and separation factor for adsorption of dyes on carbonaceous adsorbent at different temperatures.

Dye	Temperature (°C)	q_m (mgg^{-1})	b (L mol^{-1})	R_L
Chrysoidine G	25	80.6	8.55×10^4	3.5×10^{-2}
	45	76.3	8.40×10^4	3.6×10^{-2}
Crystal violet	25	163.0	9.75×10^4	4.2×10^{-2}
	45	148.4	9.26×10^4	4.4×10^{-2}
Meldola blue	25	171.2	9.91×10^4	3.1×10^{-2}
	45	150.4	9.35×10^4	3.7×10^{-2}

$$\ln(b_2/b_1) = -\frac{\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

for adsorption process to know the nature of adsorption, and are summarized in Table 4. The small negative value of ΔH° indicates that the adsorption is

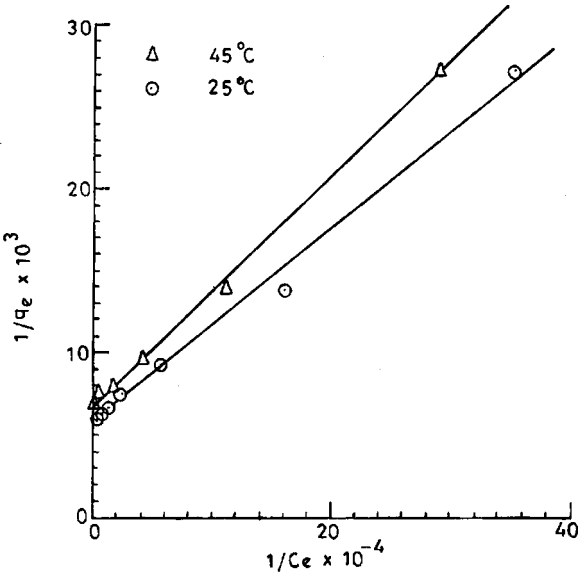

Figure 8. Langmuir adsorption isotherms of meldola blue on carbonaceous adsorbent at different temperatures.

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Table 4. Thermodynamic parameters for adsorption of dyes on carbonaceous adsorbent at different temperatures.

Dye	Temperature (°C)	$-\Delta G^0$ (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	$-\Delta H^0$ (kJ mol^{-1})
Chrysoidine G	25	28.1	91.9	0.7
	45	29.9	91.8	
Crystal violet	25	28.4	88.9	2.0
	45	30.2	88.7	
Meldola blue	25	28.5	87.9	2.3
	45	30.2	88.1	

physical in nature involving weak forces of attraction. The negative ΔH° values are in the order: meldola blue > crystal violet > chrysoidine G indicating that the adsorption forces decrease from meldola blue to chrysoidine G. This is consistent with experimental observations that dyes are adsorbed in the same order. The negative ΔG° value indicates the spontaneous nature of the adsorption process and the positive value of ΔS° indicates the affinity of adsorbent for dyes.

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Dynamic Modeling

The kinetics of adsorption is important from the point of view that it controls the process efficiency. Various kinetics models have been used by various workers, where the adsorption has been treated as a first order,[21,22] pseudo first order,[23,24] and pseudo second-order process.[25] Different systems conform to different models. The Lagergren's rate equation[26] is the one most widely used[21,22,27] for the sorption of a solute from a liquid solution. Thus, this first-order equation

$$\log (q_e - q) = \log q_e - \frac{k_{ads}}{2.303} t$$

where q_e and q are amounts of dye adsorbed at equilibrium and at time t, in mg/g respectively, and k_{ads} the first-order rate constant, was applied to the present studies of dye adsorption. As such, the values of $\log (q_e - q)$ were calculated from the kinetic data of Fig. 1 and plotted against time in Fig. 9. The plots are found to be linear with good correlation coefficients in the range of 0.995 to 0.999, indicating that Lagergren's equation is applicable to the dye adsorption on carbonaceous adsorbent and the adsorption process is

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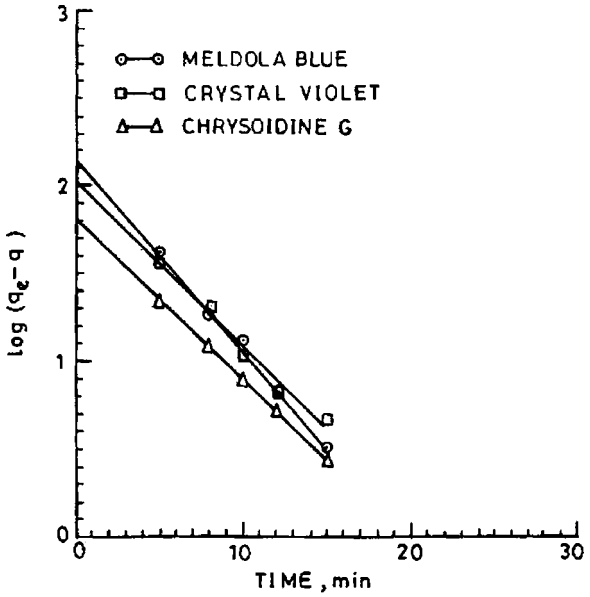

Figure 9. Lagergren's plot for dyes on carbonaceous adsorbent.

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a first-order process. The first-order rate constants calculated from the slope of the plots (see Fig. 9) are found to be 0.258, 0.227, and 0.209 min^{-1} for meldola blue, crystal violet, and chrysoidine G, respectively. A higher rate constant for meldola blue indicates that the adsorbent has higher affinity for this dye.

The kinetic data was further used to learn about the slow step occurring in the present adsorption system. The applicability of the following Bangham equation[28] to present dye adsorption studies was tested.

$$\log\log\left(\frac{C_0'}{C_0' - q'm'}\right) = \log\left(\frac{k_0 m'}{2.303V}\right) + \alpha \log t$$

where C_0' is initial concentration of adsorbate in solution (mmol/L), V the volume of solution (mL), m' the weight of adsorbent used per liter of solution (g/L), q' the amount of adsorbate retained at time t (mmol/g) and $\alpha(<1)$ and k_0 are constants. As such, $\log\log(C_0'/C_0' - q'm')$ was plotted against $\log t$ in Fig. 10. The linearity of these plots confirm the applicability of the Bangham equation and indicates that the diffusion of dye into pores of the adsorbent mainly controls the adsorption process.[23,29]

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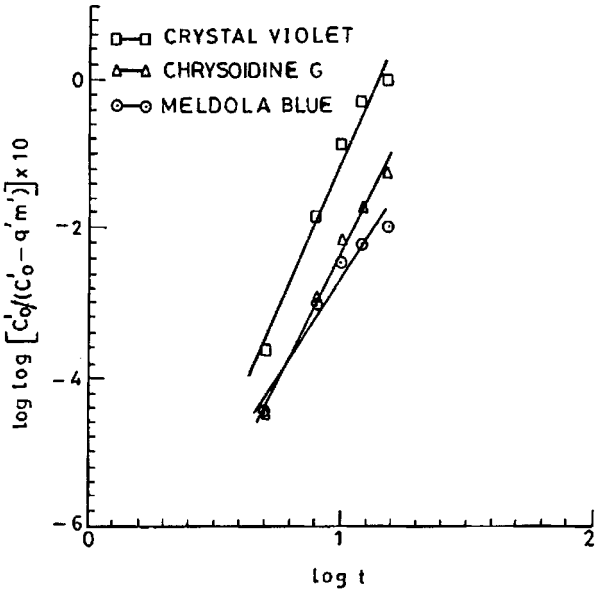

Figure 10. Bangham's plot for dyes on carbonaceous adsorbent.

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CONCLUSION

The present studies have led to the conclusions that carbonaceous adsorbent (organic nature), having a larger porosity and surface area, is more efficient compared to inorganic adsorbents, for adsorption of dyes. The adsorption of dyes on the carbonaceous adsorbent prepared is a first-order process, controlled by pore diffusion. The extent of adsorption of dyes is about 70–80% of that on standard activated charcoal, which is sufficient to use the adsorbent developed for the removal of dyes.

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