Utilization of industrial waste products as adsorbents for the removal of dyes

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Abstract

A number of low cost adsorbents from steel and fertilizer industries wastes have been prepared and investigated for the removal of anionic dyes such as ethyl orange, metanil yellow and acid blue 113 from aqueous solutions. The results indicate that inorganic wastes, i.e. blast furnace dust, sludge and slag from steel plants are not suitable for the removal of organic materials, whereas a carbonaceous adsorbent prepared from carbon slurry of fertilizer industry was found to adsorb 198, 211 and 219 mg/g of ethyl orange, metanil yellow and acid blue 113, respectively. The adsorption of dyes on this adsorbent was studied as a function of contact time, concentration, particle size and temperature by batch method. The adsorption isotherm conformed to Langmuir model and the adsorption was found to be exothermic and physical in nature. Kinetic data conforms to Lagergren's equation with good correlation coefficients varying from 0.9998 to 0.9999 indicating that the adsorption is a first-order process. The adsorption data on carbonaceous adsorbent was compared to a standard activated charcoal sample and it was found that the prepared adsorbent is about 80% as efficient as standard activated charcoal and therefore, can be used as low cost alternative (∼US$ 100 per ton) for colour removal from effluents.
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1. Introduction

Wastewater generated as a result of domestic, industrial and agricultural activities often contains various regulated compounds [1], both organic and inorganic in nature. Effluents from industries such as dyeing, paper and pulp, textile, etc. contain many dyes which are toxic [2,3] and need to be removed. Removal techniques for dyes include coagulation

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[4], ozonation [5], membrane process [6], filtration with coagulation [7], ozonation with coagulation [8] and adsorption [9,10]. Among these, the adsorption process gives the best results as it can be used to remove different types of colouring materials. Although activated carbon is a preferred adsorbent for colour removal, its widespread use is restricted due to high cost. As such, alternative adsorbents, including peat [11], plum kernels [12], wood [13], coal [14], resin [15], coir pith [16], chitosan fibres [17], etc. and various industrial wastes [18,19], have been investigated. However, the results have not been promising and often not compared with activated charcoal which shows high removal efficiencies. Thus, efforts are still going on to develop alternative low cost materials. In the present study, industrial wastes of both inorganic and organic nature have been tried as adsorbents for the removal of ethyl orange, metanil yellow and acid blue 113 which are toxic and are used in many industries such as textile, soap, leather and shoe polish [20–22]. The results are compared with those obtained on standard activated charcoal.

2. Experimental

2.1. Reagents and materials

Ethyl orange was procured from Riedel–deHaën and metanil yellow and acid blue 113 from Aldrich. All other reagents used were of AR grade. Double distilled water was used throughout.

2.2. Adsorbents

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

(i) *Carbonaceous adsorbent*: Fertilizer plants in India generate large amounts of carbon slurry waste as a result of partial oxidation of fuel oil/ low sulphur heavy stock (LSHS) as feed stock. This slurry is stored in large tanks and allowed to dry. The dried cake material, which is available at very cheap rates (∼US$ 7 per ton), was procured from National Fertilizer Limited, Panipat (India) and powdered. It was found to consist of small, black and greasy granules, and was treated [23] 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 ceased. This material was then activated at different temperatures in muffle furnace for 1 h 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. The dried product is referred to as carbonaceous adsorbent and was sieved to obtain particles sizes corresponding to 100–150, 150–200 and 200–250 British Standard Sieve (BSS) mesh, and the sieved material was kept in a desiccator. The cost of the processed products is ∼US$ 100 per ton. 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.

(ii) *Blast furnace (BF) slag, dust and sludge adsorbent*: The waste products include BF slags, dust and sludge and were procured from Malvika Steel Ltd., Jagdishpur, India.

Of these wastes produced in steel plants, the BF slag is in largest amount while dust and sludge occurs in lesser amounts. The gases generated during the manufacture of pig iron carry a dust load, which is removed before their release in 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 dust load and the waste material collected is called 'BF dust'. The finer particles, which still remain in the gas, are removed in wet scrubbers. The waste material collected here is referred to as 'BF sludge'. The BF dust and sludge were subjected to treatment similar to the carbon slurry treatment and then activated. The temperature of $400\,^{\circ}C$ was found to be optimum for activation. After activation, the wastes were washed with water and dried. Of the BF slags, only foamed slag having some porosity was used as an 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.

2.3. Instrumentation

The determination of dyes was done spectrophotometrically on a Shimadzu 160A UV-Vis spectrophotometer. The pH of solutions was measured with a ELICO LI 127 pH meter and a LEO 435 VP was used for scanning electron microscopy.

2.4. Analysis

The dried carbon slurry waste was ignited at $1000\,^{\circ}C$ and found to produce ash content of 0.9%. The analysis of ash showed iron to be 0.25%. The carbon content of slurry was found to be 89.8%. The BF slag, dust and sludge were also analyzed [24] and the results obtained are compiled in Table 1. The surface area of the adsorbents was determined by N_2 gas adsorption and their porosity was estimated using a scanning electron microscope (SEM).

2.5. Adsorption studies

Adsorption on all the four adsorbents prepared was determined using the batch method. 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 agitated and stirred continuously

Table 1
Chemical analysis of blast furnace (BF) sludge, dust and slag

	BF sludge (%)	BF dust (%)	BF 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 (R: Fe, Al)	35.4	44.9	22.8
CaO	3.5	4.7	31.7
MgO	3.0	4.2	6.8

under constant temperature for 3 h to achieve equilibration. The concentration of the dye in the solution after equilibrium adsorption was determined spectrophotometrically by measuring absorbance at λ_{max} of 475, 432 and 532 nm for ethyl orange, metanil yellow and acid blue 113, respectively. Kinetic studies of adsorption were also performed 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 adsorbents was found to be in the range 7 ± 0.5.

3. Results and discussion

3.1. Characterization of the prepared adsorbents

The chemical analysis results of BF sludge, dust and slag given in Table 1 show that silica and calcium oxides are the main constituents of BF slag, whereas coke (loss on ignition), silica and R_2O_3 (R: Fe, Al) are the prominent components of BF dust and sludge. Thus, BF slag is inorganic in nature whereas BF dust and sludge are inorganic but with partial organic character (carbon content). The carbonaceous adsorbent is mainly organic in nature. The organic content generally imparts porosity to the adsorbent. This is reflected in the surface areas of the adsorbents which were found to be 380, 28, 13 and 4 m^2/g for carbonaceous adsorbent, BF sludge, dust and slag, respectively. 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 show that the porosity order is, carbonaceous adsorbent > BF sludge > BF dust > BF slag. On the basis of surface area, the carbonaceous adsorbent is expected to be a useful material for the removal of organic molecules. A comparison of surface area of these adsorbents with a standard activated charcoal sample having surface area of 710 m^2/g, indicates that carbonaceous adsorbent is expected to be about half as efficient as the activated charcoal in removing organics. The other three adsorbents, BF sludge, BF dust and BF slag, with small surface area are poor materials for this purpose.

3.2. 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 in order to determine the equilibration time for maximum adsorption (Fig. 1). Nearly 45 min are required for the equilibrium adsorption for all three dyes. Therefore, the equilibration time was set conservatively at 3 h for further experiments. Fig. 1 suggests that adsorption is very fast initially, showing 50% adsorption for all three dyes in less than 5.5 min, and gradually tails off thereafter.

The effect of concentration on equilibration time was also investigated as a function of initial dye concentration. The results for ethyl orange are shown in Fig. 2. Similar plots were also obtained for the other two dyes. The independence of time required to achieve definite fraction (Fig. 2) of equilibrium adsorption on initial concentration indicates that the adsorption process is first-order, which is confirmed by Lagergren's plots [25] discussed later under dynamic modelling. Similar observations were made by other workers [26].
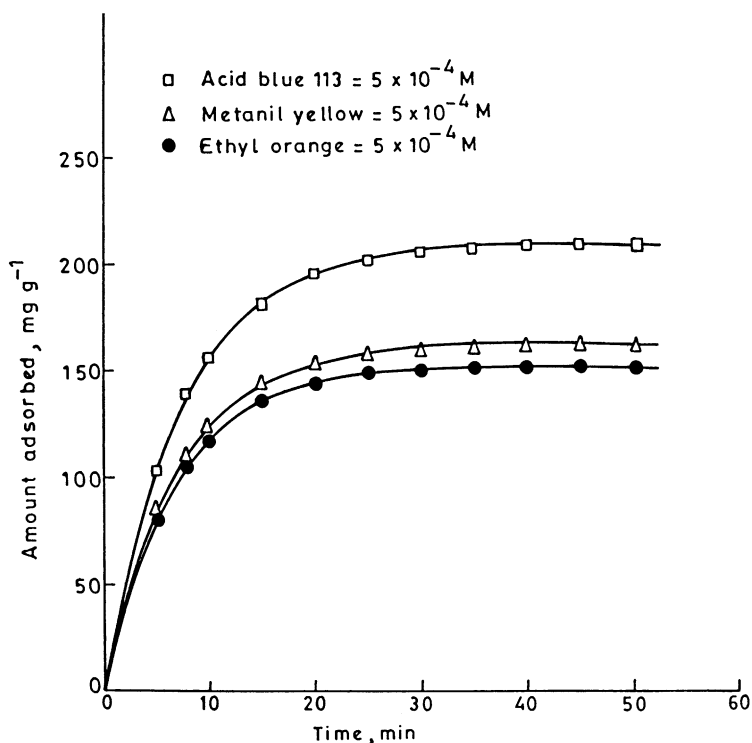
Fig. 1. Effect of contact time on the uptake of dyes on carbonaceous adsorbent (25 °C; particle size: 200–250 mesh).

3.3. Effect of particle size on adsorption

The adsorption of acid blue 113 at three particle sizes given in Fig. 3 shows that adsorption capacity increases to some extent with decreasing particle size. Similar results were also obtained with the other two dyes. Since this could not be due to substantial increase in surface area [27], it is possible that large dye molecules were not able to penetrate the interior pores of the particles. Similar results were also obtained by McKay et al. [28]. As the 200–250 mesh size particles show maximum adsorption capacity, all studies were carried out using only this fraction.

3.4. Adsorption isotherms

The equilibrium adsorption of dyes was studied as a function of concentration. The amount of dye adsorbed (q_e) has been plotted against the equilibrium concentration (C_e) for all the adsorbents and shown in Fig. 4 for ethyl orange. Similar plots were also obtained for metanil yellow and acid blue 113. The adsorption is in the order carbonaceous adsorbent > BF sludge > BF dust > foamed slag, which is well correlated to the porosity and surface area of the adsorbent. The maximum adsorption of ethyl orange, metanil yellow and acid
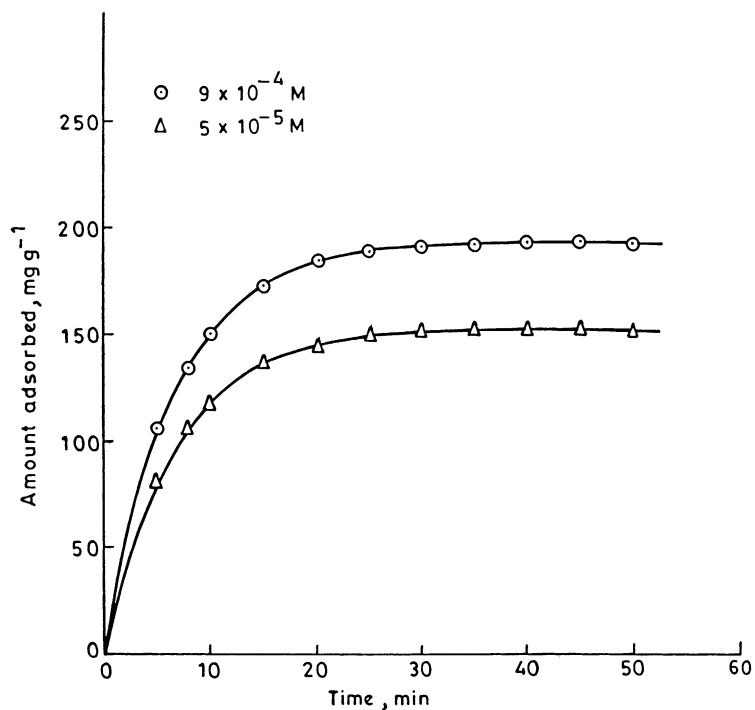
Fig. 2. Effect of contact time on the uptake of ethyl orange on carbonaceous adsorbent at different initial concentrations (25 °C; particle size: 200–250 mesh).

blue 113 on the carbonaceous adsorbent and BF sludge were found to be 198, 211 and 219 mg/g and 1.3, 1.4 and 2.1 mg/g, respectively. The adsorption was negligible on BF dust and foamed slag, suggesting that inorganic adsorbents characterized by poor porosity and surface area are not suitable for the adsorption of organics. Carbonaceous adsorbents possessing high surface area and porosity are the preferred materials for the removal of organics. Therefore, further studies were carried out on the carbonaceous adsorbent. A comparison (Fig. 4) of adsorption data to that with standard activated charcoal shows that the maximum adsorption of dyes on the carbonaceous adsorbent is about 77–86% of the activated charcoal.

3.5. Effect of temperature

The adsorption of dyes at higher temperatures (Fig. 5) decreases with increase in temperature indicating that the process is exothermic. The adsorption data were fitted and found to conform best to the Langmuir equation as follows:

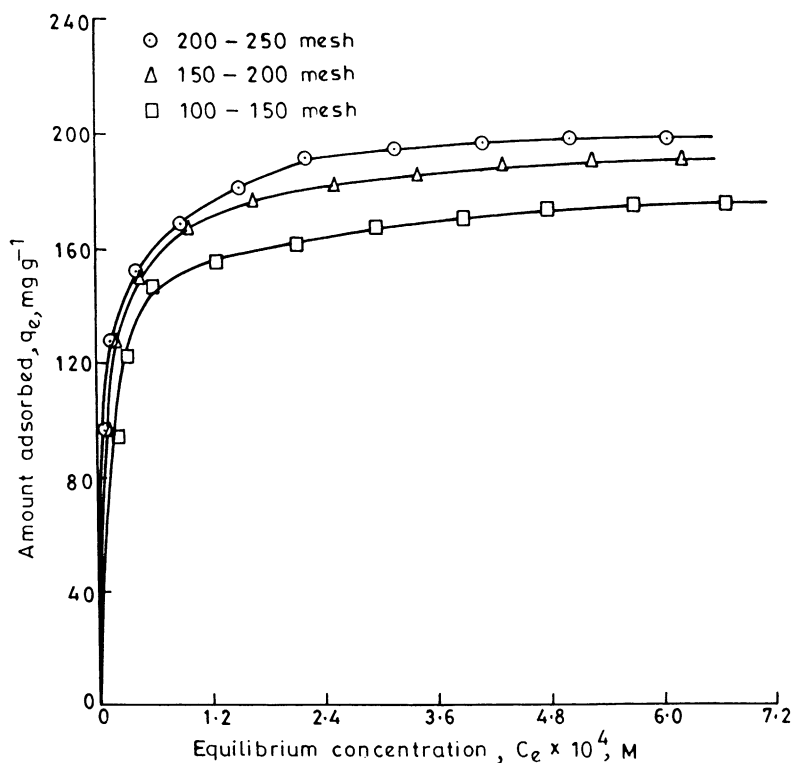$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b C_e} \tag{1}$$

Fig. 3. Effect of particle size on the adsorption of ethyl orange on carbonaceous adsorbent at 25 °C.

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

Plots of $1/q_e$ versus $1/C_e$ were prepared for each dye (ethyl orange shown in Fig. 6). The values of monolayer capacity (q_m) and equilibrium constant (b) are reported in Table 2. The monolayer capacity (q_m) of each adsorbent is comparable to the maximum adsorption observed. As expected, the q_m values decrease with increasing temperature. The 'b' values indicate that the adsorbent has maximum affinity for ethyl orange and minimum for acid blue 113.

The influence of adsorption isotherm shape to know whether the adsorption is favourable or not, has been discussed in terms of a dimensionless constant R_L, referred to as separation factor [29], defined as follows:

$$R_L = \frac{1}{1 + bC_0} \tag{2}$$

where b is Langmuir constant ($1\,\text{mol}^{-1}$) and C_0 the initial concentration ($\text{mol}\,1^{-1}$). The values of R_L for this study are reported in Table 2, and their magnitude between 0 and 1 suggest that the adsorption was favourable [29–31].
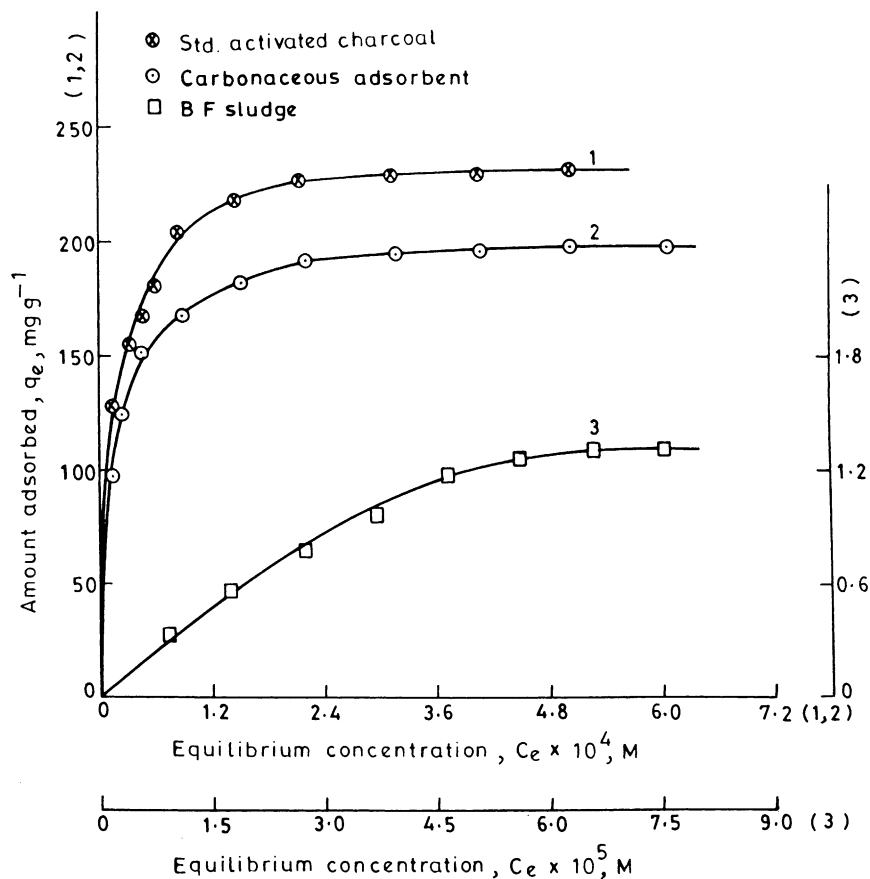
Fig. 4. Adsorption isotherms of ethyl orange on different adsorbents at 25 °C.

Table 2
Langmuir constants and separation factor for adsorption of dyes on carbonaceous adsorbent at different temperatures

Dye	Temperature (°C)	q_m		b ($1\,mol^{-1}$)	R_L
		(mg g^{-1})	(mmol g^{-1})		
Ethyl orange	25	198.4	59.5×10^{-2}	91.6×10^{3}	1.7×10^{-2}
	45	162.6	48.8×10^{-2}	78.3×10^{3}	2.1×10^{-2}
Metanil yellow	25	211.9	56.5×10^{-2}	64.5×10^{3}	4.2×10^{-2}
	45	182.8	48.7×10^{-2}	55.3×10^{3}	3.1×10^{-2}
Acid blue 113	25	221.2	32.5×10^{-2}	44.3×10^{3}	6.4×10^{-2}
	45	193.8	28.4×10^{-2}	38.2×10^{3}	7.3×10^{-2}

q_m: monolayer capacity in the Langmuir equation (see Eq. (1)); b: Langmuir constant related to energy of adsorption (see Eq. (1)); R_L: dimensionless separation constant (see Eq. (2)).
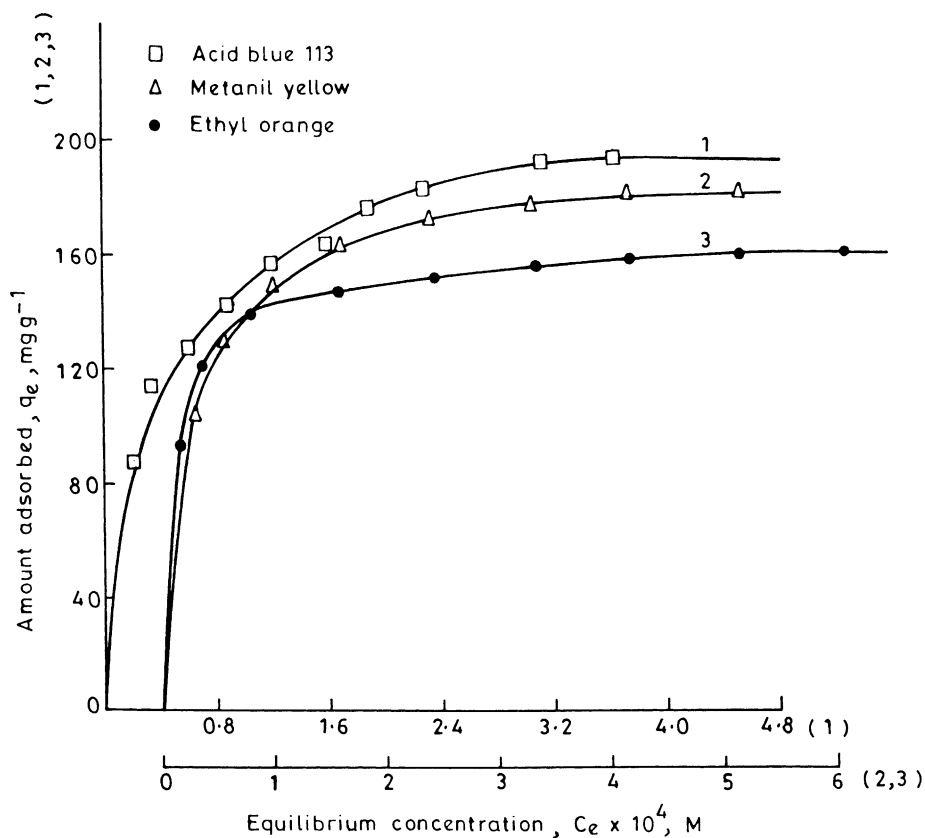
Fig. 5. Adsorption isotherms of dyes on carbonaceous adsorbent at 45 °C.

The free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were also evaluated using following equations [32]:

$$\Delta G^\circ = -RT \ln(b) \tag{3}$$

$$\ln \left(\frac{b_2}{b_1} \right) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \tag{4}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{5}$$

The results are reported in Table 3. The small negative value of ΔH° suggests the adsorption to be physical, and indicate that the adsorption forces decrease from ethyl orange to acid blue 113 which is consistent with experimental observations. The negative ΔG° values show spontaneous nature of adsorption process and the positive values of ΔS° indicate the affinity of the adsorbent for dyes.
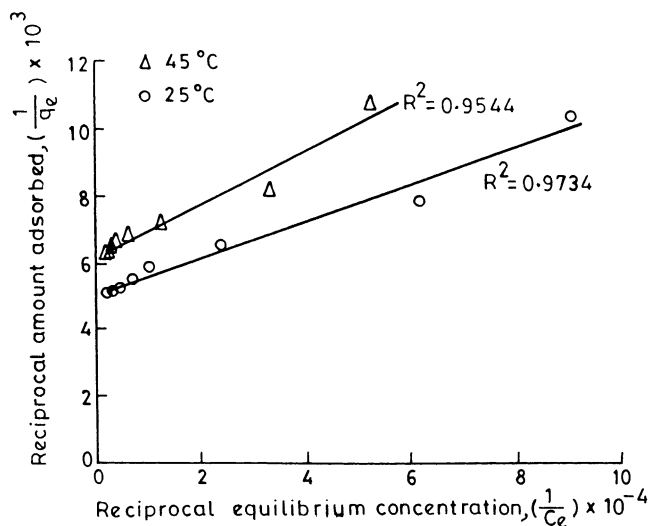
Fig. 6. Langmuir adsorption isotherms of ethyl orange on carbonaceous adsorbent for two temperatures.

3.6. Dynamic modelling

A study of kinetics of adsorption is desirable as it provides information about the mechanism of adsorption, which is important for efficiency of the process. Adsorption has been treated as a first-order [33,34], a pseudo first-order [35,36] and a pseudo-second-order [37] process. The Lagergren's rate equation [25], which is the one most widely used [31,33,34] for the sorption of a solute from a liquid solution, may be written as follows:

$$\log(q_e - q) = \log q_e - \frac{k_{ads}}{2.303}t \tag{6}$$

where "q_e" and "q" are amount of the dye adsorbed at equilibrium and at time t, in mg/g, respectively, and k_{ads} the first-order rate constant. The values of $\log(q_e - q)$ were calculated from the kinetic data (Fig. 1) and plotted against time as Fig. 7. Good correlation coefficients (0.9998–0.9999) indicate that Lagergren's equation is applicable and the adsorption process

Table 3
Thermodynamic parameters for adsorption of dyes on carbonaceous adsorbent at different temperatures

Dye	Temperature (°C)	$-\Delta G^\circ$ (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	$-\Delta H^\circ$ (kJ mol^{-1})
Ethyl orange	25	28.3	74.2	6.2
	45	29.8	74.2	
Metanil yellow	25	27.4	71.5	6.1
	45	28.9	71.7	
Acid blue 113	25	26.5	69.5	5.8
	45	27.9	69.5	

$-\Delta G^\circ$: change in standard free energy; ΔS°: change in standard entropy; $-\Delta H^\circ$: change in standard enthalpy.
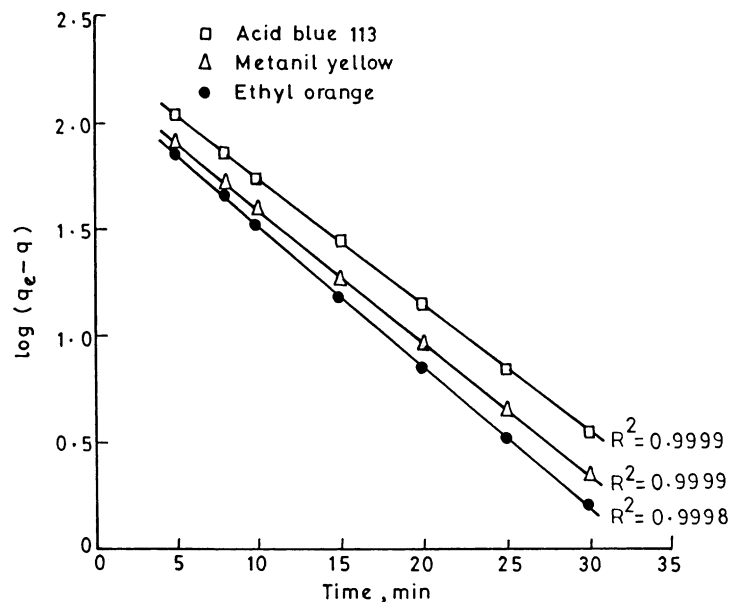
Fig. 7. Lagergren's plot for dyes on carbonaceous adsorbent at 5×10^{-4} M.

is first-order. The first-order rate constants calculated from Fig. 7 are 0.153, 0.143 and 0.136 min^{-1} for ethyl orange, metanil yellow and acid blue 113, respectively. A higher rate constant for ethyl orange indicates that the adsorbent has higher affinity for this dye, consistent with its higher adsorption (q_m).

4. Conclusions

Sorption studies using ethyl orange, metanil yellow and acid blue 113 have shown that: (i) inorganic adsorbents are not suitable for the sorption of organics, whereas carbonaceous adsorbent (organic nature) are appropriate; (ii) dye adsorption on a carbonaceous adsorbent is both exothermic and physical in nature; (iii) the adsorption process is first-order; and, (iv) the carbonaceous adsorbent prepared is about 80% as efficient as standard activated charcoal and thus can be suitable for the removal of toxic substances from effluents. Carbonaceous adsorbent being a low cost material need not be regenerated after being loaded with pollutants and can be disposed of by burning.

Acknowledgements

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