

A comparative assessment of adsorbents prepared from industrial wastes for the removal of cationic dye[†]

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Carbon slurry waste from fertilizer plant and blast furnace slag, dust and sludge from steel plant have been investigated after some processing as adsorbents for the removal of methylene blue dye. The results have indicated that the carbonaceous adsorbent prepared from carbon slurry waste of fertilizer industry has high porosity and much larger surface area (380 m²/g) as compared to other three adsorbents (4–28 m²/g). This has resulted in large adsorption of the dye (92 mg/g) on this adsorbent whereas the adsorption on the other three adsorbents is poor (2.1–6.4 mg/g). The adsorption of methylene blue on carbonaceous adsorbent conforms to Langmuir model, and is a first order process and pore diffusion controlled. A comparison of its performance with standard activated charcoal sample shows that its efficiency is 45% as compared to standard sample and thus can be used as alternative in view of its low cost.

The present day industrial, agricultural and domestic activities have adversely affected water with both inorganic and organic pollutants. These contaminants are often toxic and cause harmful effects to human and animal life. It has, therefore, become important to treat wastewater for the removal of toxic substances before they are discharged into natural waterbodies having good quality water. Although a number of methods^{1–6} are used for the removal of pollutants, the adsorption process has been found to be versatile as it can remove both inorganics and organics. The most common adsorbent in practice for pollution control is activated carbon. The high cost of activated carbon has, however, sometimes restricted its use in pollution control simply on economical considerations. In view of the importance of adsorption process in effluent treatment, attempts have been made to develop low cost adsorbents which may be good alternative to activated carbon. Towards this end, various solid materials of different industries like fly ash⁷, slag⁸, bottom ash⁹, red mud¹⁰, blast furnace sludge¹¹ have been investigated as adsorbents. These materials have not proved to be very promising in view of low adsorption efficiency and tendency to adsorb inorganic contaminants more than the organics. Further, their adsorptive properties in general have not been compared with standard activated carbon to assess their potentiality. In the present communication, we have evaluated adsorbents prepared from carbon slurry waste of fertilizer industry and blast furnace slag, dust and sludge from steel industry. Methylene blue, a cationic dye, has been taken to investigate adsorptive power of these adsorbents, keeping in view that dyes are important pollutants. The results obtained are compared with those on standard

activated charcoal in order to assess the efficiency of prepared adsorbents.

Results and discussion

Effect of contact time, concentration and particle size :

The effect of contact time on uptake of the dye is shown in Fig. 1. It is seen that it takes about 25, 40, 55 and 75 min for equilibrium adsorption to reach on carbonaceous adsorbent, BF sludge, dust and slag, respectively. In case of carbonaceous adsorbent, 50% adsorption is reached in less than 4 min. Further, time required to achieve a definite fraction of equilibrium adsorption was found to be

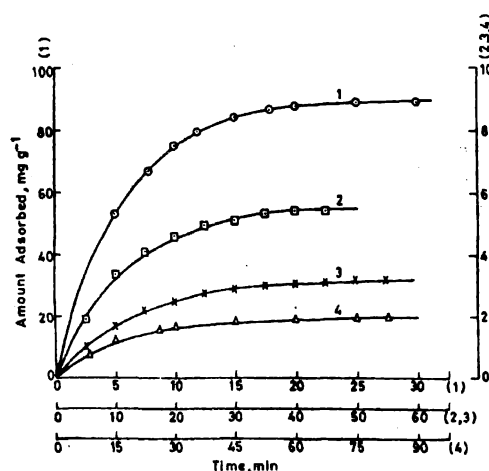


Fig. 1. Effect of contact time on uptake of methylene blue on different adsorbents : (○) carbonaceous adsorbent, (□) BF sludge, (X) BF dust, (Δ) BF slag; initial dye concentration : (○) 4×10^{-4} M, (□) 6×10^{-5} M, (X) 6×10^{-5} M, (Δ) 3×10^{-5} M.

[†]Dedicated to Professor R. P. Rastogi.

independent of initial concentration. Similar observations were also made by other workers¹² and indicate a first order process¹³. The effect of particle sizes, viz. 100–150, 150–200 and 200–250 BSS mesh, was also studied and the results show that adsorption capacity increases to some extent with decrease in particle size of the adsorbent. This could not be due to substantial increase in surface area¹⁴. It is possible that large dye molecules are not able to penetrate to some of the interior pores of the particles, specially when their size is large. The reach to all pores is facilitated, as particle size becomes smaller. Similar results were also obtained by McKay *et al.*¹⁵. As particles of size 200–250 mesh show maximum adsorption capacity, all detailed studies were carried out with this fraction only.

Adsorption isotherms :

In order to assess the adsorptive power of the adsorbents, the equilibrium adsorption studies after an equilibration time of 2 h were carried out and the adsorption isotherms are shown in Fig. 2. It is seen that the extent of adsorption is in the order : carbonaceous adsorbent > blast furnace sludge > blast furnace dust > foamed slag, which may be explained on the basis of surface area and porosity of the carbonaceous

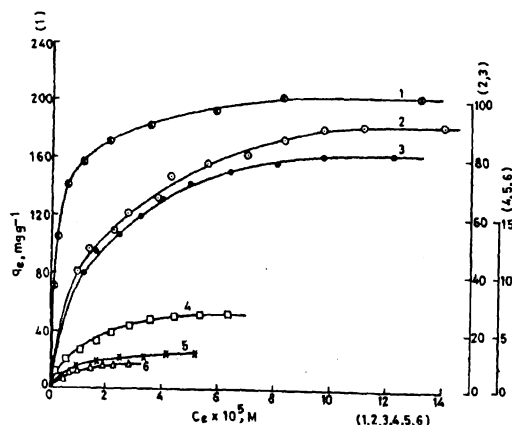


Fig. 2. Adsorption isotherms of methylene blue at 25° on (●) std. activated charcoal, (○) carbonaceous adsorbent, (□) BF sludge, (X) BF dust, (Δ) BF slag; (●) isotherm on carbonaceous adsorbent at 45°.

adsorbent possessing large surface area (380 m²/g) as compared to other adsorbents. It has a larger area due to highly porous structure as indicated by SEM studies. The high porous structure is on account of high carbon content (~90%) whereas the other three adsorbents are basically materials having inorganic constituents¹⁶ resulting in poor porosity and low surface area (4–28 m²/g). Thus results show that adsorption of dye (organic molecule) is a surface phenomenon and it is therefore expected that this adsorbent

will adsorb organics in appreciable quantity. In order to assess the efficacy of adsorbents, the results of methylene blue adsorption are compared with a standard activated charcoal (E. Merck) having surface area of 710 m²/g (Fig. 2). It was found that carbonaceous adsorbent with removal capacity of 92 mg/g is nearly 45% as efficient as standard activated charcoal, while the other adsorbents : BF sludge, dust and slag with removal capacity of 6.4, 3.3 and 2.1 mg/g, respectively, are poor materials for this purpose. Thus only carbonaceous adsorbent possessing high surface area and porosity is the material that can be used for the removal of the organics. Therefore, further studies were carried out on this adsorbent only.

Effect of temperature :

Equilibrium adsorption experiments were also carried out at higher temperature for methylene blue - carbonaceous adsorbent system to understand the nature of process. The results are presented in Fig. 2. It is seen that with increase in temperature adsorption decreases, reflecting the process to be exothermic in nature. Further, the adsorption data fitted the following Langmuir equation best

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

where q_e is 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 C_e the equilibrium concentration.

The plots between $1/q_e$ and $1/C_e$ for adsorption of the dye are shown in Fig. 3. The values of q_m and b have been evaluated from the intercept and slope of these plots (Table 1). It is seen that monolayer capacity (q_m) of the adsorbent for the dyes is comparable to the maximum adsorption as evaluated from adsorption isotherm of Fig. 2. Further, the q_m value decreases expectedly with rise in temperature as the adsorption process is exothermic.

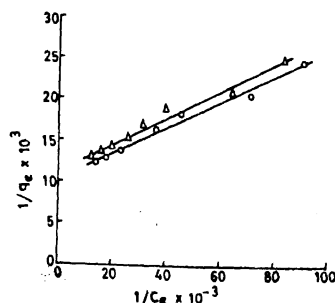


Fig. 3. Langmuir adsorption isotherms of methylene blue on carbonaceous adsorbent at different temperatures : (○) 25°, (Δ) 45°.

Table 1. Langmuir constants and separation factor for the adsorption of methylene blue on carbonaceous adsorbent at different temperatures

Temp. °C	q_{\max} mg/g	b dm ³ /mol	R_L
25	96.2	6.67×10^4	0.06
45	90.9	6.59×10^4	0.07

The influence of isotherm shape has been discussed¹⁷ 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 calculated¹⁷ using the equation,

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

where C_0 is the initial concentration (mol dm⁻³). The values of R_L calculated as above are incorporated in Table 1. As the R_L values lie between 0 and 1, the adsorption isotherm is favourable¹⁷.

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

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

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

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

for adsorption process and are summarized in Table 2. The small negative value of ΔH° indicates that the adsorption is physical in nature involving weak forces of attraction. The negative ΔG° value indicates spontaneous nature of adsorption process and the positive value of ΔS° indicates the affinity of the adsorbent for the dye.

Table 2. Thermodynamic parameters for adsorption of methylene blue on carbonaceous adsorbent

Temp. °C	$-\Delta G^\circ$ kJ mol ⁻¹	ΔS° J mol ⁻¹ K ⁻¹	$-\Delta H^\circ$ kJ mol ⁻¹
25	27.5	90.6	0.5
45	29.3	90.6	

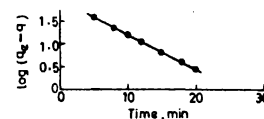
Dynamic modelling :

In order to understand the adsorption process and for optimum and efficient utilization of the adsorbent, the adsorption data was kinetically analyzed. Various kinetics models have been used by various workers, where the adsorption has been treated as first order^{18,19}, pseudo-first order^{20,21} and pseudo-second order²² process. Different systems conform to different models. The Lagergren's rate equation²³ is the most widely used^{18,19,24} for the sorption

of a solute from a liquid solution. Thus, this first order equation,

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

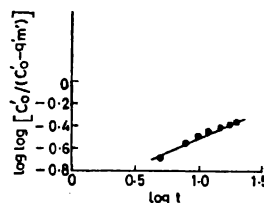
where, q_e and q are the amounts (mg/g) of dye adsorbed at equilibrium and at time t , respectively, and k_{ads} the first order rate constant, was applied to the present studies of dye adsorption. As such, the values of $\log(q_e - q)$ were calculated from the kinetic data of Fig. 1 and plotted against time. The plots (Fig. 4) were found to be linear with good correlation coefficients in the range 0.996–0.999, indicating that Lagergren's equation is applicable to the dye adsorption on carbonaceous adsorbent and the adsorption process is a first order process with rate constant 0.177 min⁻¹.

**Fig. 4.** Lagergren's plot for methylene blue on carbonaceous adsorbent.

In order to know rate-controlling step in adsorption process, the applicability of the Bangham's equation²⁵ to present dye adsorption studies was tested,

$$\log \log \left(\frac{C'_0}{C'_0 - q'm'} \right) = \log \left(\frac{k_0 m'}{2.303 V} \right) + \alpha \log t$$

where C'_0 is the initial concentration of adsorbate in solution (mmol dm⁻³), V the volume of solution (ml), m' the weight of adsorbent used per liter of solution (g dm⁻³), q' the amount of adsorbate (mmol g⁻¹) retained at time t and α (<1) and k_0 are constants. As such $\log \log [C'_0/(C'_0 - q'm')]$ was plotted against $\log t$. The plots (Fig. 5) obtained were linear with good correlation coefficients. The results thus conform to Bangham's equation and indicate that the adsorption of the dye is pore diffusion controlled process^{20,26}.

**Fig. 5.** Bangham's plot for methylene blue on carbonaceous adsorbent.

Conclusions : The present investigation on the adsorption of dye on a number of adsorbents indicates that (i) the carbonaceous adsorbent having high carbon content, porous structure and large surface area is a much better adsorbent than BF slag, dust and sludge which contain mainly inorganic constituents resulting in poor porosity and

surface area, (ii) the adsorption of the dye on carbonaceous adsorbent is a first order process and pore diffusion controlled and (iii) the prepared carbonaceous adsorbent is about 45% as efficient as a sample of standard activated charcoal. In view of good efficiency of carbonaceous adsorbent and its cheaper cost, it can be used as an alternative to activated carbon for the removal of dyes in particular and organics in general.

Experimental

Methylene blue (Loba) was purified. Other reagents used were of A.R. grade. Double-distilled water was used throughout.

Preparation of adsorbents :

Carbonaceous adsorbent : Carbon slurry waste was procured from NFL Plant, Panipat (India) which operated on fuel oil/LSHS as feed stock. It was treated with hydrogen peroxide^{16,27} to oxidize the adhering organic material and then washed with water and dried. The dried material was then activated at different temperatures in muffle furnace for 1h in air. The activated product (now called carbonaceous adsorbent) was sieved to get different mesh sizes and stored in desiccator. The optimum temperature of activation was found to be 500°.

Blast furnace slag, dust and sludge adsorbent : Blast furnace (BF) slag, dust and sludge were procured from Malvika Steel Ltd., Jagdishpur (India) and treated¹⁶ to impart adsorption characteristics. The products were then sieved and stored in desiccator.

A Shimadzu 160A UV-VIS spectrophotometer was used. pH was measured with an a Elico LI 127 pH meter. A Leo 435 VP was used for scanning electron microscopy.

Adsorption studies : Batch method was used to study the adsorption on the prepared adsorbents. A fixed amount of the adsorbent (0.01 g) was added to the dye solution (10 ml) of varying concentrations in stoppered glass tubes, which were placed in thermostat-cum-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} 664 nm. Kinetic studies of adsorption were also carried at two concentrations of the adsorbate 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 ± 0.5 .

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