Mixed Adsorbent for Colour Removal from Aqueous Solution

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ABSTRACT

A homogenous mixture of fly ash and wollastonite (1:1) has been used as mixed adsorbent to study the removal of victoria blue (CI Basic blue — 26, 44045) from its aqueous solution. The parameters studied were initial dye concentration, temperature and pH of the solution. The kinetics of adsorption indicate the process to be diffusion controlled. The equilibrium data at different temperatures fit well into the Langmuir isotherm. Maximum adsorption and desorption of victoria blue from the interface of fly ash-wollastonite was noted at pH 8.5 and pH 3.0 respectively.

INTRODUCTION

The colour of the effluents from the textile and carpet industry causes widespread industrial waste disposal problems. Dyes used in such industries are particularly difficult to remove by conventional waste treatment methods because of their stability towards light and oxidizing agents and resistance towards aerobic digestion (Weber and Morris, 1962; Poots et al., 1976). The adsorption technique using activated carbon (ICI, 1971; McKay, 1984) as adsorbent is generally employed for colour removal from water and wastewaters. However, high costs and difficult procurement of activated carbon restrict its use in developing countries like India. Recently a number of unconventional adsorbents have been used for colour removal from wastewater by several investigators (Alexander and McKay, 1977; Poots et al., 1976, 1978; Singh et al., 1984; Khare et al., 1987). There appears to be limited information on the use of mixed adsorbents for wastewater treatment. In some cases, the adsorption capacity of mixed adsorbents for the removal of undesirable substances from water was found to be more than its constituents (Panday et al., 1986). This paper describes the results of a feasibility study using a homogenous mixture (1:1) of fly ash and wolla-
stonite as an adsorbent for the removal of victoria blue from its aqueous solutions at different concentrations, temperatures and pH.

MATERIALS AND METHOD

The Adsorbent
Fly ash was obtained from Obera Thermal Power Plant, Mirzapur (U.P.) and wollastonite was supplied by M/s Wolkem Pvt. Ltd., Udaipur (Rajasthan), India. These materials were sieved to 59μ size and used as such without any treatment. An equal amount of sieved fly ash and wollastonite was mixed to obtain a homogenous mixture (1:1) and employed as mixed adsorbent in the present investigations. The surface area of the mixed adsorbent was determined using a "Three Point" N₂ gas adsorption method, model Q5-7 Quantasorb Surface Area Analyser (Quanta Chrome Corp., USA) and the average particle size was measured by HIAC-320, Model 8002917 (Royco Inst. Div., USA). The porosity and density of the adsorbent were determined using mercury porosimeter and specific gravity bottle respectively. The different constituents of the adsorbent were analysed by Indian Standard Methods of Chemical Analysis (1960) and the results are presented in Table 1 along with other characteristics.

The Adsorbate and its Solution
Victoria blue (Basic blue — 26) was supplied by BDH and used without further purification. All solutions of dye were prepared with deionised-distilled water and the desirable pH of the solution was maintained using 0.5 M HCl or NaOH solution.

Batch Experiments
Batch adsorption experiments were carried out by shaking different glass bottles containing 1.0g mixed adsorbent (fly ash-wollastonite) and 50ml aqueous solution of victoria blue of desired concentration at various temperatures and pH. The speed of shaking was maintained at 125 r.p.m. for each run. After predetermined time intervals, the suspensions were centrifuged and the residual dye concentrations were determined using a spectronic — 20, Spectrophotometer at 575nm. The desorption experiments were performed by shaking 1.0g used fly ash — wollastonite containing fixed amount of victoria blue with 50ml deionised — distilled water at different pH at 30°C.

RESULTS AND DISCUSSION

The chemical analysis of fly ash — wollastonite mixture (Table 1) shows that the oxides of silicon, calcium and aluminium are the main constituents while other oxides are present in trace amounts. It is thus expected that the dye will be mostly adsorbed either by any one or by a combined influence of the major oxides present.

| TABLE 1 |
| Chemical analysis of adsorbent and other characteristics |
| Constituents | % by weight |
| SiO₂ | 52.28 |
| CaO | 25.35 |
| Al₂O₃ | 13.07 |
| Fe₂O₃ | 0.76 |
| MgO | 0.47 |
| Ignition loss | 8.07 |
| Specific surface area (m² g⁻¹) | 3.05 |
| Mean particle diameter (μm) | 0.50 |
| Porosity | 0.18 |
| Density (g cm⁻³) | 3.055 |

Effect of Concentration
With an increase in victoria blue concentration from 1.0×10⁻⁶ to 1.0×10⁻⁵ M, the amount of dye adsorbed was noted to increase from 0.0246 to 0.1938mg g⁻¹ (Figure 1) while percentage removal decreased from 98.50 to 77.59%, indicating that dye removal using the adsorption technique is highly concentration dependent. The equilibrium time was noted to be 60 min. in all cases and is found to be independent of concentration of the solution. The plots in Figure 1 are single smooth and continuous leading to saturation, suggesting the possibility of the formation of monolayer coverage of victoria blue on the fly-ash wollastonite surface (Panday, et al., 1986).
MIXED ADSORBENT FOR COLOUR REMOVAL FROM AQUEOUS SOLUTION

To 30 20 80 120 160

Fig. 1: Time variation of removal of victoria blue by fly ash-wollastonite at different concentrations: (0) $1.0 \times 10^{-6}$ M, $5.0 \times 10^{-6}$ M and $1.0 \times 10^{-5}$ M.
Conditions: Temperature $30 \pm 0.1^\circ$C; pH: 8.5

Adsorption Dynamics

The rate constant of adsorption, $K$ (min$^{-1}$) of victoria blue on fly ash-wollastonite was determined using the following rate expression (Lagergren, 1898):

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

where, $q_e$ and $q$ are the amount of dye adsorbed (mg g$^{-1}$) at equilibrium and at time, $t$ respectively. A straight line plot of $\log (q_e - q)$ Vs $t$ (Figure 2) suggests the applicability of the above equation. The value of rate constant was calculated from the slope and found to be $6.60 \times 10^{-2}$ min$^{-1}$ at $30^\circ$C.

In a rapidly stirred batch reactor, the adsorbate molecules generally diffuse into the interior of the porous adsorbents. During such processes it is probably reasonable to assume that the rate of uptake of adsorbate is not limited by mass-transfer from the bulk liquid to the external surface of the particle. If this is the case, one might postulate that the rate limiting step is intraparticle diffusion and the amount adsorbed should vary almost proportionally with square-root of time rather than time itself (Weber and Morris, 1963). The plots of amount of victoria blue adsorbed $V_s$ $t^{0.5}$ (Figure 3a) are linear for a wide range of contact period. The slight deviations from linearity at the initial stages suggest that the pore diffusion is not predominant at the initial stages of the contact. The plots also do not pass through the origin suggesting that the mechanism of victoria blue adsorption proceeds from boundary layer mass-transfer across the interface to the intraparticle diffusion within the pores of adsorbent (Poots et al., 1978).

Adsorption Dynamics

The rate constants of intraparticle transport, $k$ (i.d.) (Table 2) were calculated from the linear portion of the plots of $q$ Vs $t^{0.5}$ (Poots et al., 1976) for different particle size range at $30^\circ$C and solution concentration of $1.0 \times 10^{-5}$ M. A self consistancy check is then possible, in which a plot of rate constant of intraparticle diffusion $V_s$ square of the inverse of particle
TABLE 2

<table>
<thead>
<tr>
<th>Particle size (um)</th>
<th>Rate constant $k_{id}$ (mg g$^{-1}$ min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>53</td>
<td>0.021</td>
</tr>
<tr>
<td>63-53</td>
<td>0.023</td>
</tr>
<tr>
<td>75-63</td>
<td>0.025</td>
</tr>
</tbody>
</table>

diameter (Figure 3b) yielded straight line. The value of pore diffusion coefficient, D was calculated using the relationship given below (Helfferich, 1962).

$$D = 0.030$$

where, $D$ is the pore diffusion coefficient (cm$^2$ sec$^{-1}$), $r$ the radius of adsorbent particle (cm and $t_{1/2}$ is the time for half adsorption (min)). The value of $D$ was found to be $2.50 \times 10^{-10}$ cm$^2$ sec$^{-1}$ suggesting that the rate of reaction is mainly governed by intraparticle diffusion during the latter stages of contact (Michelsen et al., 1975) although at the initial stages, a rapid surface adsorption takes place because at this stage the dye molecules have only to overcome the potential barrier across the boundary of the solid-solution interface (Poole et al., 1978).

The value of surface mass-transfer coefficient for the transport of victoria blue from bulk to the solid phase at 30°C was calculated using the following diffusion model (McKay et al., 1981):

$$\ln \frac{C - 1}{C_e} = \ln \left( \frac{mk}{1 + mk} \right) - \frac{1 + mk}{mk} \beta_S t$$

where, $C_e$ is the initial dye concentration (mg l$^{-1}$); $C$ (mg l$^{-1}$), the dye concentration in solution after time $t$; $k$ (1 g$^{-1}$) is the Langmuir constant obtained by multiplying $Q^o$ and $b$; $\beta_S$ (cm sec$^{-1}$) is the mass transfer coefficient; $m$ (g l$^{-1}$) and $S_s$ (cm$^{-2}$) are the mass and the specific surface of adsorbent per unit volume of particle free slurry respectively. The values of $m$ and $S_s$ were calculated from the equations:

$$m = \frac{W}{V}$$

and

$$S_s = \frac{m}{d_p \rho_p (1 - \varepsilon_p)}$$

where, $W$ is the weight of adsorbent (g); $V$, the volume of solution; $d_p$, the particle diameter (cm); $\rho_p$, the density of adsorbent (g l$^{-1}$) and $\varepsilon_p$ is the porosity of adsorbent.

The plot of $\ln (C/C_e - 1/(1 + mk))$ against time gives a straight line (Figure 2) and the value of mass-transfer coefficient was calculated from the slope and intercept of the plot and found to be $2.73 \times 10^{-5}$ cm sec$^{-1}$ at 30°C. This value indicates that the velocity of mass transfer of victoria blue from solution onto fly ash-wollastonite is rapid enough (McKay et al., 1981) to suggest the use of this adsorbent for the treatment of wastewaters enriched in victoria blue.

Adsorption Isotherm

The equilibrium results at different concentrations and temperatures were analysed in the light of the following rearranged Langmuir equation:

$$\frac{1}{C q_e} = \frac{1}{Q^o b} + \frac{C}{Q^o}$$

where, $C$ is the equilibrium concentration of victoria blue in solution (mg l$^{-1}$) and $Q^o$ and $b$ are constants signifying the adsorptive capacity and energy of adsorption respectively. The values of $Q^o$ and $b$ were calculated from slopes and intercepts of the straight line plots of $C/q_e$ Vs $C$ (Figure 4) and are given in Table 3. The validity

![Fig. 4: Langmuir isotherm at different temperatures 30°C, (0) 40°C and (0) 50°C](image)
of the Langmuir isotherm for the present system was further confirmed by the regression analysis of the equilibrium data at different temperatures. The regression equations relating \( C/q_e \) and \( C \) are found as:

\[
\frac{C}{q_e} = 1.24186 C + 16.55820 \text{ at } 30°C \quad (7) \\
\frac{C}{q_e} = 1.10125 C + 12.80525 \text{ at } 40°C \quad (8) \\
\frac{C}{q_e} = 0.98619 C + 10.38098 \text{ at } 50°C \quad (9)
\]

The values of \( Q^o \) and \( b \) were calculated (Table 3) by comparing equation (6), (7), (8) and (9) and found to be almost equal to the graphical values. This confirms the applicability of Langmuir isotherm at different temperatures in the present system.

**Effect of Temperature**

The effect of temperature on the removal of victoria blue may be described in terms of variations of adsorption capacity, \( Q^o \) of adsorbent with temperature of the systems. The removal capacity of mixed adsorbent increases from 0.801 to 1.002 mg g\(^{-1}\) (Table 3) by increasing the temperature of victoria blue solution from 30 to 50°C at pH 8.5. The increase in uptake of dye with temperature may be explained by the enhanced rate of intraparticle diffusion of dye, within the pores of adsorbent as the diffusion is an endothermic process (Bye et al., 1982). The isosteric heat of adsorption, calculated with the help of Gibb's Helmholtz equation, is always a function of the surface coverage and its value was found to be 4.305 kcal mol\(^{-1}\) for the surface coverage of 0.248 mg g\(^{-1}\) of adsorbent.

The thermodynamic parameters for the adsorption of victoria blue on fly ash-wollastonite, have been calculated at different temperatures using the following relationships (Jain et al., 1979):

\[
\Delta G^o = -RT \ln K_e \\
\Delta H^o = R \left( \frac{T^2}{T^o} - \frac{1}{T^o} \right) \ln K'_e \\
\Delta G^o = \Delta H^o - T \Delta S^o
\]

where, \( K_e, K'_e \) and \( K''_e \) are the equilibrium constants, obtained from the limiting slopes of the adsorption isotherm at zero concentration at different temperatures (Kipling, 1965). Other terms have their usual significance.

The values of \( \Delta G^o \) at 30, 40 and 50°C were found to be -0.747, -0.966 and -1.782 kcal mol\(^{-1}\) respectively, indicating that the interaction of dye with adsorbent is spontaneous and feasible with a high preference of victoria blue for fly ash-wollastonite (Panday et al., 1985). The positive value of \( \Delta H^o \) (+5.877 kcal mol\(^{-1}\) at 30°C) further indicates the endothermic nature of the process and possibility of chemical bonding between the adsorbate and the adsorbent (Panday et al., 1985). The positive entropy change (+21.86 e.u. at 30°C) indicates some structural changes at the solid-solution interface.

**Effect of pH**

With an increase in solution pH from 3.0 to 8.5, the extent of removal increased from 0.0032 mg g\(^{-1}\) (12.99%) to 0.0246 mg g\(^{-1}\) (98.66%) at 1.0 \times 10^{-6} M dye concentration and 30°C (Figure 5a). Similar results were reported earlier in the case of cationic adsorption (Pandav et al., 1985; Khare et al., 1987).

The oxides of silicon, calcium and aluminium of the mixed adsorbent develop electrical
charge on their surface in contact with water according to the pH of the solution which is as follows:

\[
\text{Basic dissociation: } M^{0} + \text{OH} \rightarrow M^{+} \text{OH} \\
\text{Acidic dissociation: } M^{+} \text{OH} \rightarrow M^{0} + \text{OH}^{-}
\]

where, \(M\) stands for Si, Ca and Al. Except silica, all other oxides will possess positive charge for a pH range of interest (Panday, et al., 1986) because the zero point charge (pH\(_{zpc}\)) of SiO\(_2\), CaO and Al\(_2\)O\(_3\) are 2.2, 11.0 and 8.3 respectively. Thus, most of the dye cations at pH 8.5 will be adsorbed by negatively charged silica at surface site of adsorbent. However, a little contribution of alumina for victoria blue adsorption at lower pH cannot be ruled out.

The uptake of dye cations with negatively charged oxide surface may also be explained in terms of ion-exchange mechanism in the following manner:

\[
\text{H}^+ + \text{Mo}^+ + \text{Na}^+ \rightarrow \text{H}^+ + \text{Dye}^+ + \text{Cl}^-
\]

As the solution pH decreases, the negative charge density on the surface decreases which results in an unfavourable condition for the cationic adsorption, consequently decreasing the extent of removal of victoria blue at lower pH of the solution.

**Desorption Studies**

Maximum desorption of 0.3653mg (61.93%) was observed (Figure 5b) from the surface fly ash-wollastonite (1.0g) containing 0.5898mg victoria blue per gram of adsorbent at pH 3.0 and 30°C. As the pH of the aqueous suspension was further increased, the desorption of dye was decreased. The difference in the extent of desorption at pH 3.0 and 10.5 (Figure 5b) clearly suggests strong bonding between the adsorbate species and the active surface sites of adsorbent. The weakly bonded dye cations were detached from the surface at neutral pH while they were mostly desorbed in acidic pH while they were mostly desorbed in acidic medium due to the exchange with H\(^+\) ions.

**CONCLUSION**

A homogenous mixture of fly ash and wollastonite (1:1) has been found quite effective in victoria blue removal from aqueous solution and therefore may be considered as potential adsorbent for colour removal from water and wastewaters. The efficiency of the removal process is enhanced by decreasing the concentration and increasing temperature and pH of the solution. The results of desorption studies show that a considerable amount of dye may be recovered from the surface of adsorbent particularly at low pH. The data thus obtained are useful for colour removal from water and wastewater using batch or stirred tank flow reactor, where head-loss through bed column reactor would be prohibitive.

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