Adsorption of Eriochrome Black T on polyaniline from aqueous and methanolic solutions

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The adsorption of Eriochrome Black T (EBT) has been studied on acidic and basic forms of polyaniline from aqueous and methanolic solutions. The adsorption has been studied as a function of adsorbate concentration (2-40×10^{-4} M), adsorbent particle size (30 - 140 mesh) and temperature (293.15-313.15 K). The data have been fitted to Langmuir isotherm and its parameters have been obtained. Langmuir parameter b has large magnitude and increases with temperature suggesting that the adsorption is endothermic and entropy dominated. Kinetic studies have been performed to calculate rate constants for adsorption processes. The first order kinetics in the initial stages confirms that the rate controlling step is the diffusion of the dye molecules through a stagnant layer formed around the adsorbent particles. This mechanism is overtaken at later stages by the rearrangement of the dye molecules on the surface of the adsorbent and finally by intraparticle diffusion. The energetics of the adsorption process have been obtained.

Polyaniline (PANI) has been recently reported to be a potentially useful material for rechargeable batteries\(^{1-3}\), electrochemical actuators\(^4\), organic electroluminescent devices\(^{5,4}\), electrochromic devices\(^{5,4}\), photoresist for lithography\(^{11}\), sensor\(^{12-14}\), control of electromagnetic radiation\(^{15-16}\), separation of gases\(^{17,19}\), corrosion inhibition of metals\(^{20}\) and as a semi-conductor in photochemical assemblies\(^{21}\). Literature survey indicates that no studies have been carried out on polyaniline as an adsorbent. As far as we know this is the first study to use polyaniline as an adsorbent to remove dyes from their aqueous and methanolic solutions. Its relatively higher cost compared to other adsorbents is likely to be compensated by its higher adsorption capacity and long-term stability for reuse.

Adsorbents used earlier for adsorption of dyes are activated charcoal, silica, bagasse pitch, fuller earth, clays, aluminium and iron hydroxide\(^{22-35}\). In this class, activated charcoals have been evaluated for waste treatment of different class of dyes. However, adsorption cycles for these adsorbents are limited. We have undertaken systematic study of the adsorption of Eriochrome Black T on polyaniline from aqueous and methanolic solutions. The study in methanol as solvent has been undertaken to extend the range of concentration as the solubility of the dye in water is somewhat low.

Materials and Methods

Preparation of polyaniline

Polyaniline has been synthesised chemically using the method of MacDiarmid \textit{et al}\(^{36}\). Chemical oxidative polymerisation was carried out at 273.15K by adding 0.1 molar ammonium persulphate solution to a 0.1 and 1 molar solution with respect to aniline and hydrochloric acid. Stirring of the reaction mixture was continued for about 2 h to ensure the completion of the reaction. The reaction mixture was allowed to stand for 24 h. It was then filtered, washed with distilled water till free from acid and finally washed with methanol. It was dried at 383.15K for about 6 h. The dried green coloured polymer was ground into
fine powder and sieved to desired particle size such as 30-50, 50-100 and 100-140 mesh and the samples were stored in a vacuum desiccator. Emeraldine (basic polymer) was prepared by dipping acidic polyaniline in 1N ammonium hydroxide solution for 24 h. Blue coloured polymer was filtered, washed with doubly distilled water and methanol, dried at 383.15K for about 6 h, ground and sieved to desired particle size and stored in a vacuum desiccator. The surface area of polyaniline 100-140 mesh was measured to be 25 m$^2$ g$^{-1}$ by BET method. All chemicals used were of AR grade. Stock solution of Eriochrome Black T dye (E. Merck, Germany) was made in distilled water or methanol. Polyaniline has already been characterized by various authors $^{37-40}$ by electronic spectra, FTIR, NMR, X-ray-photoelectron spectroscopy, ESR, magnetic properties and conductivity.

Equilibrium studies

The adsorption of EBT from its aqueous and methanolic solution on polyaniline was studied in the concentration range $2.17 \times 10^{-3}$ to $1.083 \times 10^{-3}$ M and $2.00 \times 10^{-4}$ to $4.00 \times 10^{-4}$ M respectively. Twenty-five ml of the solution of the dye in methanol with concentration varying between $2 \times 10^{-4}$ and $4 \times 10^{-4}$ M was added to 50 ml glass-stoppered flasks, which were thermostated at the desired temperature (293.15-$313.15$ K). A known weight (0.1 g) of adsorbent (100-140 mesh size) was added to each flask and the contents were agitated intermittently for 24 hr. After equilibration, the supernatant solution was centrifuged and uptake of the dye was monitored spectrophotometrically at 500 nm. In aqueous solutions, due to limited solubility, the highest concentration of dye was $12 \times 10^{-4}$ M. Adsorption studies from aqueous solution were carried out using 100 ml glass-stoppered flasks, each containing 50 ml of dye solution of varying concentration; and 0.1 g of polyaniline. After the equilibrium period, the dye concentration was monitored at 520 nm. Adsorption studies of Eriochrome Black T from its aqueous solution were also carried out in a similar way on basic polyaniline (emeraldine) (mesh size 100-140) and on activated charcoal (mesh size 200) at 303.15 K.

Kinetic studies

For kinetic studies 25 ml solution of EBT ($10.8 \times 10^{-3}$ M) at different temperatures with 0.1 g of the adsorbent was taken. At pre-decided intervals of time, the aliquot of supernatant was drawn and amount of the dye was estimated spectrophotometrically. Kinetic studies were also carried out on different amounts of adsorbents and on different particle sizes.

Results and Discussion

From the initial $C_i$ and equilibrium $C_e$ concentration of the Eriochrome Black T the amounts of the dye adsorbed per gram of adsorbent ($q = x/m$) were calculated at different equilibrium concentrations $C_e$ of the dye at three different temperatures.
Typical adsorption isotherms (q versus \( C_e \)) for water and methanol as solvent for dyes are shown in Figs 1a and 2a. It can be seen from the plots that a saturation limit is reached in both cases and also adsorption increases with temperature.

The data have been fitted to Langmuir adsorption isotherm, as applied by Giles et al.\textsuperscript{41} for the adsorption of sulphonated dyes on different types of adsorbents and by others\textsuperscript{42-43}.

The Langmuir equation can be written as:

\[
\left( \frac{q}{Q} \right) = \left( \frac{b}{Q} \right) \left( C_e + \frac{b}{Q} C_e \right) \tag{1}
\]

where \( q = \frac{x}{m} \) and \( Q \) is the limiting value of \( q \) and \( b \) is the equilibrium constant for the process.

\[
D (\text{dye in solution}) + S = DS \tag{2}
\]

\[
k_1
\]

\[
k_2
\]

where \( S \) is the adsorbent and \( DS \) is the dye on the adsorbent. Here \( b \) is equal to \( k_1 / k_2 \). Eq.1 can be rearranged to give,

\[
\left( \frac{C_e}{q} \right) = \left[ \frac{1}{b Q} + \frac{C_e}{Q} \right] \tag{3}
\]

or

\[
\frac{1}{q} = \left[ \frac{1}{Q} + \frac{1}{Q b C_e} \right] \tag{4}
\]

The plots of \( C_e/q \) against \( C_e \) (Figs 1b and 2b) or \( 1/q \) against \( 1/C_e \) at different temperatures were found to be linear indicating the applicability of Langmuir equation. The intercepts in these plots have large

**Table 1—Parameters of Langmuir equation for the adsorption of Eriochrome Black T on acidic polyaniline mesh 100-140**

<table>
<thead>
<tr>
<th>Temp./K</th>
<th>( Q \times 10^3 ) mol g(^{-1} )</th>
<th>( b \times 10^{-2} ) mol(^{-1}) l</th>
<th>( K \times 10^{-5} ) mol(^{-1}) l</th>
<th>( \Delta G^0/ ) kJ mol(^{-1} )</th>
<th>( \Delta H^0/ ) kJ mol(^{-1} )</th>
<th>( \Delta S^0/ ) J mol(^{-1}) K(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>0.298</td>
<td>8.85</td>
<td>4.908</td>
<td>31.94</td>
<td>249.22</td>
<td>41.88</td>
</tr>
<tr>
<td>303.15</td>
<td>0.315</td>
<td>15.60</td>
<td>8.626</td>
<td>34.45</td>
<td>249.25</td>
<td>40.31</td>
</tr>
<tr>
<td>313.15</td>
<td>0.321</td>
<td>26.00</td>
<td>14.332</td>
<td>36.90</td>
<td>249.15</td>
<td>36.36</td>
</tr>
</tbody>
</table>

**Table 2—Thermodynamic Parameters for the adsorption of Eriochrome Black T on acidic Polyaniline mesh 100-140**

<table>
<thead>
<tr>
<th>Temp./K</th>
<th>( -\Delta G^0/ ) kJ mol(^{-1} )</th>
<th>( \Delta S^0/ ) J mol(^{-1}) K(^{-1} )</th>
<th>( \Delta H^0/ ) kJ mol(^{-1} )</th>
<th>( -\Delta G^0/ ) kJ mol(^{-1} )</th>
<th>( \Delta S^0/ ) J mol(^{-1}) K(^{-1} )</th>
<th>( \Delta H^0/ ) kJ mol(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>28.53</td>
<td>394.88</td>
<td>88.88</td>
<td>28.53</td>
<td>394.88</td>
<td>88.88</td>
</tr>
<tr>
<td>303.15</td>
<td>32.50</td>
<td>394.95</td>
<td>85.46</td>
<td>32.50</td>
<td>394.95</td>
<td>85.46</td>
</tr>
<tr>
<td>313.15</td>
<td>36.36</td>
<td>394.66</td>
<td>87.23</td>
<td>36.36</td>
<td>394.66</td>
<td>87.23</td>
</tr>
</tbody>
</table>

Average 41.12
uncertainties and therefore, \( b \) and \( Q \) have been obtained from their slopes and are given in Table 1. The Langmuir parameters \( Q \) and \( b \) increased with temperature, suggesting that the adsorption is endothermic and entropy dominated. From the values of \( b \) at different temperatures various thermodynamic properties have been obtained.

The influence of isotherm shape on favourable or unfavourable adsorption has been carried out by Weber and Chakraborti.\(^4\) For Langmuir type adsorption the isotherm can be classified in terms of correlation coefficient \( r \), a dimension-less constant, where

\[
r = \frac{1}{1 + bC_i}
\]

(5)

where \( b \) is the term appearing in the Langmuir isotherm and \( C_i \) is the initial concentration of dye. The value of \( r \) is less than one in all cases and decreases with increase in temperature indicating favourable adsorption at all temperatures. The adsorption results on emeraldine are almost comparable to those of acidic polyaniline.

**Thermodynamic parameters**

Thermodynamic parameters have been calculated from the temperature dependence of Langmuir parameter \( b \). The standard free energy \( \Delta G^0 \) and enthalpy \( \Delta H^0 \) for adsorption of Eriochrome Black T on polyaniline were determined using the equations:

\[
\Delta G^0 = -RT \ln K
\]

(6)

where \( K = b(1000 \rho / M) \)

\[
\Delta H^0 = \Delta H^0 - T \Delta S^0
\]

(8)

In order to have the same reference state for the dye in the initial (solution) and the final (adsorbed) states, the concentration of the dye has to be taken in mole fraction. For dilute solutions, as in the present case, the molarity can be converted into mole fraction by dividing it with the factor 1000 \( \rho / M \) (number of mole of solvent/litre of dilute solution) where \( \rho \) is the density and \( M \) is the molecular mass. This value of equilibrium constant in dimensionless units can be obtained by multiplying its value \( b \) in mol l\(^{-1}\) by 1000 \( \rho / M \). The values of densities of water and methanol at three temperatures have been taken from the literature and \( \Delta G^0 \) values thus calculated for both the systems are given in Table 1.

The enthalpies of adsorption have been calculated from the temperature dependence of \( K_1 \), i.e., from the equation

\[
\Delta H^0 = (RT_1/T_2 - T_1) \ln \left( K_2 / K_1 \right)
\]

(7)

Values of \( \Delta S^0 \) were determined from the Eq. 8, taking average value of \( \Delta H^0 \) from Table 2 for each system.

**Kinetics of adsorption**

From the kinetic point of view, effects of contact time, amount and particle size of the adsorbent and concentration of the adsorbate solution on uptake of Eriochrome Black T on polyaniline have been studied. The effect of contact time of adsorbents with dye is presented in Figs 3a and 3b. The rate of uptake of Eriochrome Black T on polyaniline (acidic) is initially quite rapid and 50-60\% of the ultimate adsorption occurs within the first 30 min of contact at 303.15 K which then slows down considerably and approaches equilibrium state in about 15 h.

A number of mass transfer models have been discussed in literature for the adsorption of pollutants from aqueous solutions onto various adsorbents\(^4\)\(^5\). These are mass transfers across boundary layer surrounding the adsorbent particle\(^4\)\(^6\), mass transfer within the internal structure of the adsorbent\(^4\)\(^7\) (intraparticle diffusion) and adsorption at a site. In rate determining process, adsorption at a site is quite rapid and is neglected. In our study based on external\(^4\)\(^6\) mass transport, adsorption kinetics parameters have been determined.

The adsorption of Eriochrome Black T on polyaniline can be considered as a reversible reaction with equilibrium established between two phases. The Lagergren\(^4\)\(^8\) first order rate expression as applied by Singh et al.\(^4\)\(^9\) and Periasamy and Namasvayam\(^5\)\(^0\) has been applied for the determination of specific rate constant for aqueous and methanolic system for the adsorption of Eriochrome Black T on polyaniline. Plots of \( \ln (q_e - q_t) \) against \( t \) at different temperatures...
Fig. 3a — Effect of temperature on uptake of Eriochrome Black T from its aqueous solution on polyaniline at (■) 293.15K, (●) 303.15K and (▲) 313.15K and (▼) 320.15K.

Fig. 3b — Effect of temperature on uptake of Eriochrome Black T from its methanolic solution on polyaniline at (■) 293.15K, (●) 303.15K, (▲) 313.15K.

Fig. 4 — Lagergren plots for the adsorption of Eriochrome Black T from its aqueous solution on polyaniline at (■) 306.15K, (●) 313.15K and (▲) 320.15K.

Table 3 — Kinetics parameters for the adsorption of Eriochrome Black T on acidic polyaniline mesh size 100-140.

<table>
<thead>
<tr>
<th>Temp/K</th>
<th>( k_1 \times 10^2 \text{min}^{-1} )</th>
<th>Temp/K</th>
<th>( \tilde{k}_1 \times 10^2 \text{min}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>306.15</td>
<td>1.65</td>
<td>293.15</td>
<td>0.45</td>
</tr>
<tr>
<td>313.15</td>
<td>2.84</td>
<td>304.15</td>
<td>1.70</td>
</tr>
<tr>
<td>320.15</td>
<td>4.85</td>
<td>313.15</td>
<td>5.07</td>
</tr>
</tbody>
</table>

(Fig. 4) give straight lines confirming the applicability of the first order expression of Lagergren during the first 20-30 min of adsorption time. The adsorption rate constant \( k_1 \) has been evaluated from the slope of Fig. 4 and the values of rate constants are given in Table 3. The \( k_1 \) values are comparable to the values reported for adsorption of Chrome dye on mixed adsorbents \( (2.8 \times 10^{-2} \text{min}^{-1}) \) (Gupta et al.\(^{51}\)) and Crystal Violet – Wollastonite \( (2.8 \times 10^{-2} \text{min}^{-1}) \) and are higher than the values obtained for Astrazone Blue on peat \( (3.41 \times 10^{-3} \text{min}^{-1}) \) and Malachite Green \( (7.22 \times 10^{-3} \text{min}^{-1}) \) and activated carbon \( (7.48 \times 10^{-3} \text{min}^{-1}) \). Activation energies have been calculated from the slope of plot of \( \ln k_1 \) against \( 1/T \) and are 63.0 kJ mol\(^{-1}\) for water system and 93.0 kJ mol\(^{-1}\) for methanol system. We find the first order kinetics in the initial stages which confirms that the rate controlling step is the diffusion of the dye molecules through a stagnant layer formed around the adsorbent particles. This mechanism is overtaken at later stages by the rearrangement of the dye molecules on the surface of the adsorbent and finally by intraparticle diffusion.

It has been observed that the rate of uptake of dye on the same amount of adsorbent increases with the decrease in particle size of adsorbent (Fig. 5). As the particle size decreases, surface area increases and time required for total adsorption is also less for particles of smaller size. This relationship indicates the advantage of powdered adsorbent over that with the large particle size.

The rate of removal of adsorbate increases with increase in the adsorbent material. The half-life of the process decreases with increasing amount of adsorbent, confirming that the rate of adsorption is dependent on the amount of polyaniline present in the reaction. The increased mass of polyaniline will result in an increase in the overall rate of dye removal from
solution. This causes a rapid decrease in dye concentration with a corresponding reduction in the driving force for rearrangement of molecules.

**Adsorption mechanism**

It can be seen from the Fig. 6 that EBT has one ionic (-SO$_3^-$) and 3 polar (2-OH and 1-NO$_2$) functional groups. Therefore, in polar solvents like water and methanol, these polar groups will try to remain in contact with polar solvent and be away from the adsorbent surface, which due to conjugation is electron rich and adsorption should be edge-wise or endwise on the adsorbent (Fig. 6 a and b). In doing so it may be partially desolvated leading to endothermic adsorption process. The vertical molecules standing edge-wise or end-wise may stack together. During stacking small water molecules may still hang around the -OH groups with which they interact through hydrogen bonding but the large CH$_3$OH molecule may be squeezed away. This is in agreement with the fact that adsorption from methanol is more endothermic than from aqueous solution. This is further supported by the fact that from the total surface area of the adsorbent per gram and Q in aqueous and methanolic solution the area occupied per molecule is 13.17 Å$^2$/molecule and 11.62Å$^2$/molecule at 303.15K respectively. The endothermic nature of adsorption itself is an indication of barrier and supports the partial desolvation of the dye molecule on adsorption. The desolvation of dye molecule takes place in both the solvents but is much more in methanol leading to higher entropy of adsorption compared to that in water. A slight increase in Q with temperature shows that at higher temperature there is likely to be further increase in desolvation due to lateral aggregation$^{54,55}$ of dye molecules in methanol.

It may be noted that Lagergren plot is a straight line only for short period. During this period molecules may have flat orientation on the surface but as the adsorption increases the molecules acquire

![Figure 5](image1.png)

**Fig. 5** — Effect of particle sizes (■) 100-140 mesh, (•) 50-100 mesh and (▲) 30-50 mesh on uptake of of Eriochrome Black T from its aqueous solution on polyaniline at 313.15K.

![Figure 6](image2.png)

**Fig. 6** — (a) ERT molecule lying horizontally on the surface of polyaniline. All benzene rings lie flat on the surface. (b) ERT molecule lying vertically on the surface of polyaniline. Only one edge of benzene ring touching the surface.
edge-wise or end-wise orientation, and area occupied per molecule of adsorbate changes.

**Desorption studies**

The desorption experiments were carried out from 0.2 g of polyaniline-adsorbed sample with 10 ml of acetone and kept for 45 min. Desorption was found to be about 40% of the adsorbed dye in first step and subsequent treatment with acetone desorbed the dye almost completely. The percentage recovery of the dye was between 85 and 90 percent of the adsorbed dye. After desorption, polyaniline was washed with 50 ml of hot deionised water and re-used for adsorption studies.

**Conclusions**

Our results indicate that polyaniline can be successfully used for removal of Eriochrome Black T from its aqueous as well as methanolic solutions. The extent of removal of Eriochrome Black T on polyaniline (acidic) and emeraldine is almost 100% at lower concentrations. Experimental data closely follow Langmuir adsorption isotherm. The adsorption results have been compared with those for activated charcoal. The adsorption process on activated charcoal is slow and maximum adsorption is almost 50% in comparison to acidic polyaniline. Adsorption isotherms of Eosin, Alizarin red S, Tartrazine Supra (C.I. 640) and Amaranth Supra (Tri sodium 1-(4-sulpho-1-naphthylazo)-2-naphthol 3,6 disulphonic acid) are under study to prove the versatility of polyaniline as an adsorbent but preliminary results indicate nearly similar behaviour as shown by Eriochrome Black T. Polyaniline is conducting material and polyaniline adsorbed with dye shows change in electrical conductivity. Further research work shall be carried out to find if there is any correlation between adsorption and electrical conductance of PANI.

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**References**


