INTRODUCTION

Effluents from dye manufacturing industries, textiles and pulp and paper industries are highly coloured because of the presence of residual dyes. The presence of colour inhibits the growth of aquatic flora and fauna by reducing light penetration. Besides, the presence of dyes has toxic effects on aquatic organism. Furthermore, coloured water is undesirable for domestic and municipal supplies.

Mittal and Venkobachar [1] studied the adsorption of Rhodamine-B (basic violet 10) and Sondolan Rhodine (acid red 1) and found that sulphonated coal exhibited moderate removal potential for both dyes. Desorption and regeneration studies using 1N H₂SO₄, CH₃COOH and HCOOH indicated that the adsorption of Rhodamine-B appeared to be chemical rather than physical or ion exchange whereas adsorption of Rhodine was physical to some extent with the absence of ion exchange mechanism.

Dai and coworkers [2-3] examined the effect of zeta potential on the adsorption of anionic (carmine) and cationic (methyl green and methyl violet) dyes from aqueous solutions. The results showed that the adsorption of anionic dye increases on increasing zeta potential of the carbon surface making the carbon surface positive, whereas decreasing zeta potential (lower than -30 mV) enhances the adsorption of cationic dyes by electrostatic attraction between cationic dyes and carbon surface.
Viraraghavan and Mihial [4] investigated adsorption of one basic and one acidic dye on peat and found that adsorption followed Langmuir and Freundlich adsorption isotherms. The adsorption of the basic dye was better, being 99% compared with 48% of acidic dye. Lin [5-6] studied the effect of powdered activated carbon particle size on the removal of colour of disperse dye and found that multilayer BET isotherm was better fit than the monolayer Langmuir or Freundlich models. He also carried out the adsorption of a disperse dye Red 60 on various adsorbents like molecular sieves, activated alumina, granular activated carbon, sawdust and powdered activated carbon. Activated alumina, molecular sieves and powdered activated carbon were found to be better adsorbents for colour removal than granular activated carbon and sawdust.

Lisitskaya et al. [7] found that the pH effect on the adsorption of anionic azo dyes on carbon adsorbents depended on the molecular form of the dye and its tendency of micelle formation in the solution. The pH effect was not much prominent when there is a tendency for micelle formation.

McKay and Al-Duri [8] examined the mechanism of adsorption of two basic dyes - Soframine Red T and Deorlene Yellow from aqueous solutions on activated carbons. The monolayer capacities for the two dyes were 390 and 1240 mg/g respectively and adsorption data indicated that intrapartical diffusion played an important role in the removal of the dyes. These workers [9-11] in later investigations, studied the adsorption of three basic dyes - Basic Red 22, Basic Yellow 21 and Basic Blue 69 on filtrasorb-400 using single, double and triple component systems. Carbon doses and dye concentrations were varied for kinetic studies. When using agitated batch adsorption technique, these workers calculated an intrapartical diffusion rate parameter which was related to dye concentration and carbon particle size.
Dusart et al. [12] reported the adsorption of cationic and anionic dyes from waste water on peat and charcoal using a dynamic adsorption system. The breakthrough curves showed that peat columns were more effective for removal of basic red dye than the pure charcoal. Graham [13] investigated the adsorption of two dyes of opposite charges but of approximately same molecular dimensions (methylene blue and metanil yellow) on a number of active carbons and studied the influence of pore size and the acidic surface groups on adsorption. He observed that the adsorption of dyes depended more on the chemical structures i.e. acidic groups present on the activated carbon surface rather than on physical nature i.e. pore size of the active carbons. The adsorption of metanil yellow showed linear relationship with the amount of acidic surface groups. Puri and Arora [14-15] studied the adsorption isotherms of methylene blue and Rhodamine-B on graphon and on a number of other commercially available activated carbons. The adsorption isotherms were of Type I of BET classification showing completion of monolayer. Surface areas covered by these dyes were calculated, the values agreed with the BET area for graphon but were very less for other carbons showing inaccessibility of dye molecules to some of the micropores.

RESULTS AND DISCUSSION

ADSORPTION OF METANIL YELLOW

Adsorption isotherms of metanil yellow on the four samples of activated carbons from aqueous solutions in the concentration range 20 to 1000 mg/L are shown in Fig. 1. All the carbons adsorb appreciable amounts of the dye although the amounts adsorbed are different for different carbons. Activated carbon ACF-310 which has the largest surface area adsorbs the largest amount of the dye while ACF-307 which has smallest surface area adsorbs the smallest amount of the dye (cf. Table I). However, there is no linear
FIG. 1 ADSORPTION ISOTHERMS OF METANIL-YELLOW ON DIFFERENT AS-RECEIVED ACTIVATED CARBONS.
Table 1
Surface area and maximum amount of dye metanil yellow adsorbed by different as-received activated carbons

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m²/g)</th>
<th>Maximum amount of dye adsorbed (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACF-310</td>
<td>1284</td>
<td>297</td>
</tr>
<tr>
<td>ACF-307</td>
<td>910</td>
<td>111</td>
</tr>
<tr>
<td>GAC-S</td>
<td>1156</td>
<td>185</td>
</tr>
<tr>
<td>GAC-E</td>
<td>1113</td>
<td>142</td>
</tr>
</tbody>
</table>
relationship between the amount adsorbed and the surface area. This indicates that the adsorption of metanil yellow is not determined by surface area alone. This is probably due to the fact that these carbons are associated with appreciable amounts of carbon-oxygen surface groups (Table I of Chapter V), which may also influence the adsorption of the anionic dye. Puri [15] has shown that the adsorption of dyes can be used as a measure of surface area but only for those carbons which are completely free from chemisorbed oxygen.

It is also known that the adsorption of dyes depends upon the pH of the solution which, in turn, will depend upon the acidity of the carbon surface. The adsorption isotherms were, therefore, determined after oxidation of two samples of carbons ACF-307 and GAC-E with nitric acid and with oxygen gas. The adsorption isotherms on the oxidised samples along with the as-received samples are presented in Figs. 2 & 3. It is evident that the adsorption of metanil yellow decreases on oxidation. The decrease in adsorption is much larger (40%) in case of the oxidation with nitric acid compared to the oxidation with oxygen gas (26%) in case of ACF-307. This can be attributed to the fact that the treatment with nitric acid results in the fixation of larger amount of oxygen as surface oxygen groups (cf. Table II of Chapter V).

In order to examine the influence of carbon-oxygen surface groups on the adsorption of metanil yellow more clearly, the oxidised carbon samples were degassed at 400°, 650° and 950°C to eliminate varying amounts of the carbon oxygen surface groups. The adsorption isotherms on the degassed samples are shown in Figs. 4-7. It is seen that the adsorption of the metanil yellow increases on degassing and that the increase in adsorption increases with increase in the temperature of degassing. The increase in adsorption is only slight in case of the sample degassed at 400°C because this sample had lost only small amounts of the associated oxygen on degassing. The increase in adsorption
FIG. 2 ADSORPTION ISOTHERMS OF METANIL-YELLOW ON ACF-307 BEFORE AND AFTER OXIDATION.
FIG. 3 ADSORPTION ISOTHERMS OF METANIL-YELLOW ON GAC-E BEFORE AND AFTER OXIDATION.

- O As-received
- • Oxidised with HNO₃
- X Oxidised with O₂

Amount adsorbed (mg/g)

Concentration (mg/L)
FIG. 4 ADSORPTION ISOTHERMS OF METANIL-YELLOW ON OXIDISED GAC-E BEFORE AND AFTER DEGASSING.

- Oxidised with HNO₃
- Degassed at 400°
- Degassed at 550°
- Degassed at 950°
FIG. 5 ADSORPTION ISOTHERMS OF METANIL-YELLOW ON OXIDISED GAC-E BEFORE AND AFTER DEGASSING.

- Oxidised with O₂
- Degassed at 400°
- Degassed at 650°
- Degassed at 950°

Amount adsorbed (mg/g) vs Concentration (mg/L)
FIG. 6 ADSORPTION ISOTHERMS OF METANIL-YELLOW ON OXIDISED ACF-307 BEFORE AND AFTER DEGASSING.

- Oxidised with HNO₃
- Degassed at 400°C
- Degassed at 650°C
- Degassed at 950°C

Concentration (mg/L)

Amount adsorbed (mg/g)
FIG. 7 ADSORPTION ISOTHERMS OF METANIL-YELLOW ON OXIDISED ACF-307 BEFORE AND AFTER DEGASSING.

- Oxidised with O₂
- Degassed at 400°
- Degassed at 650°
- Degassed at 950°

Amount adsorbed (mg/g)

Concentration (mg/L)
is however much larger in case of the sample degassed at 650°C. The 650°-degassed samples have lost most of their acidic carbon-oxygen surface groups, while they retain a larger portion of their non-acidic carbon-oxygen surface groups (cf. Tables II and III of Chapter V).

The presence of carbon-oxygen groups on the carbon surface renders the carbon surface negative in character. This causes repulsive interactions between the negatively charged carbon surface and the anions of metanil yellow. Thus the adsorption of metanil yellow decreases on the oxidation of the carbons. When these acidic carbon-oxygen surface groups are gradually eliminated on degassing at 400 and 650°C, the carbon surface becomes lesser and lesser negative thus decreasing the repulsive interactions. The 400°-degassed carbon samples have a larger portion of their surface oxygen groups intact and thus the decrease in adsorption is only slight. In the case of the 650°-degassed samples, the acidic surface groups are eliminated almost completely. The surface, therefore, tends to become positively charged causing an increase in the adsorption of the dye.

The increase in the adsorption of metanil yellow on the 950°-degassed sample cannot be attributed to the interaction of the dye anion with the carbon-oxygen surface groups because these samples are almost completely free of any associated oxygen. This increase in adsorption may be attributed to the availability of a large number of pores for adsorption due to the removal of chemisorbed oxygen.

** ADSORPTION OF RHODAMINE -B **

Adsorption isotherms of Rhodamine-B from aqueous solution in the concentration range 20-3000 mg/L on the four activated carbons are shown in Fig. 8. It is seen that the fibrous activated carbons ACF-307 and ACF-310 adsorb much smaller amounts of the dye.
FIG. 8 ADSORPTION ISOTHERMS OF RHODAMINE-B ON DIFFERENT AS-RECEIVED ACTIVATED CARBONS.

- ACF-307
- ACF-310
- GAC-S
- GAC-E

Amount adsorbed (mg/g)

Concentration (mg/L)
compared to the granulated activated carbons. This is probably due to the fact that the granulated carbons GAC-S and GAC-E have larger amounts of the acidic carbon oxygen surface groups compared to the fibrous activated carbons (cf. Table I).

The adsorption increases on oxidation with nitric acid and oxygen gas (cf. Figs. 9 and 10). The increase in adsorption is from 9.5% to 22% for oxidation with nitric acid and from 9.5% to 19.5% for oxidation with oxygen gas in the case of ACF-307. When the oxidised carbon samples are degassed at 400°, 650° and 950°C, the adsorption decreases (Figs. 11-14) for the 400° and 650°-degassed samples. The adsorption on the 950°-degassed samples is however, larger than either of the other two degassed samples. The decrease in adsorption is only slight for the 400°-degassed samples but much larger for the 650°-degassed samples.

The increase in adsorption on oxidation and decrease in adsorption on degassing can be explained on the basis of the amount of acidic carbon oxygen surface groups as in the case of adsorption of Cr (III) and Co (II) discussed in Chapters II and III. As the dye molecule involves the adsorption of a cation, the adsorption is expected to be more in case of the samples which are associated with larger amounts of the acidic surface groups. The presence of acidic surface groups gives the carbon surface a negative charge and hence enhances the adsorption of cationic dye Rhodamine-B. When these acidic groups are eliminated by degassing at 400° and 650°C, the adsorption of the dye shows a decrease. The larger adsorption in case of the 950°-degassed samples compared to the 650°-degassed samples is due to the availability of a large number of micropores due to the removal of associated oxygen.

It is thus apparent that while the adsorption of an anionic dye is suppressed by the presence of acidic carbon-oxygen surface groups, the adsorption of a cationic dye is enhanced by the presence of these surface groups.
FIG. 9 ADSORPTION ISOTHERMS OF RHODAMINE-B ON ACF-307 BEFORE AND AFTER OXIDATION.
FIG. 10 ADSORPTION ISOTHERMS OF RHODAMINE-B ON GAC-E BEFORE AND AFTER OXIDATION.

- ○ As-received
- ● Oxidised with HNO₃
- × Oxidised with O₂
FIG. 11 ADSORPTION ISOTHERMS OF RHODAMINE-B ON OXIDISED ACF-307 BEFORE AND AFTER DEGASSING.

- As-received
- Oxidised with HNO₃
- Degassed at 400°
- Degassed at 650°
- Degassed at 950°

Concentration (mg/L)

Amount adsorbed (mg/g)
FIG. 12 ADSORPTION ISOTHERMS OF RHODAMINE-B ON OXIDISED ACF-307 BEFORE AND AFTER DEGASSING.

- As-received
- Oxidised with O₂
- Degassed at 400°
- Degassed at 650°
- Degassed at 950°

Concentration (mg/L) vs. Amount adsorbed (mg/g)

[Graph showing isotherms with different degassing temperatures]
FIG. 13 ADSORPTION ISOTHERMS OF RHODAMINE-B ON OXIDISED GAC-E BEFORE AND AFTER DEGASSING.
FIG. 14 ADSORPTION ISOTHERMS OF RHODAMINE–B ON OXIDISED GAC–E BEFORE AND AFTER DEGASSING.
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