Adsorption of dyes from aqueous solution — the effect of adsorbent pore size distribution and dye aggregation

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Abstract

The removal of acid dyes, Tectilon Blue 4R, Tectilon Red 2B and Tectilon Orange 3G, from single component solution by adsorption on activated carbon and bone char has been investigated in isotherm experiments. Results from these experiments were successfully modelled using Langmuir and Freundlich isotherm analyses. Nitrogen adsorption analysis was also undertaken and indicated that the activated carbon had a much higher specific surface than the bone char. Calculations involving the pore size distribution data indicate that only 14% of the total specific surface of the activated carbon is available for adsorption due to the high molecular area and aggregation of the dye. The equilibrium data indicate that dye aggregation takes place in the solid phase of both adsorbents with higher solid phase aggregation numbers found using the bone char, which is indicative of multilayer adsorption. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Adsorption; Carbon adsorbents; Dye aggregation; Isotherm analysis; Pore structure

1. Introduction

The acid dyes Tectilon Blue 4R, Tectilon Red 2B and Tectilon Orange 3G account for over 75% of coloured components from the aqueous effluent of a carpet printing plant in Northern Ireland, therefore these dyes have been targeted for removal from aqueous solution. The data from this work was used in the selection of an adsorbent in a pilot scale biological activated carbon (BAC) wastewater treatment facility at the plant. Dye removal from wastewater has received considerable attention with several adsorbents and several classes of dye being investigated [1,2]. The successful prediction of adsorption isotherms of dyes on activated carbon has been reported [3]. This work investigates the relatively low adsorption capacity of acid dyes on activated carbon by comparison with adsorption using bone char which possesses a much more open pore structure.

2. Experimental materials and methods

2.1. Adsorbate specifications

Tectilon Blue 4R-01 (TB4R). TB4R is an acid anthraquinone dye manufactured by Ciba-Giegy and is supplied as in 50% liquid solution containing 40% 6-caprolactam. TB4R is miscible in water giving a pH of 6.0–7.5, yielding a royal blue colour in aqueous solution and has the colour index classification CI Acid Blue 277:1. The chemical structure of TB4R is shown in Fig. 1.

Tectilon Red 2B (TR2B). TR2B is an acid monoazo dye manufactured by Ciba-Giegy and is supplied in 50% liquid solution and is miscible in water with a pH of 6.0–7.0. TR2B produces a dull blood red shade in aqueous solution and has the colour index classification CI Acid Red 361. The chemical structure of TR2B is shown in Fig. 2.

Tectilon Orange 3G (TO3G). TO3G is an acid di-azo dye manufactured by Ciba-Giegy and is supplied in 33% liquid solution containing 2% of 2-(2-butoxyethelene)-ethanol and is miscible in water. TO3G which has a neutral pH, produces a dull rusty orange shade in aqueous solution and has the colour index classification CI Acid Orange 156. The chemical structure of TO3G is shown in Fig. 3.

The adsorption of acid dyes in this work has been compared to the adsorption of Methyl Blue on activated carbon. Methyl Blue has the colour index classification CI Basic Blue 9.

2.2. Adsorbent specifications

Two commercially available adsorbents were used in this study namely the granular activated carbon Filtrasorb 400

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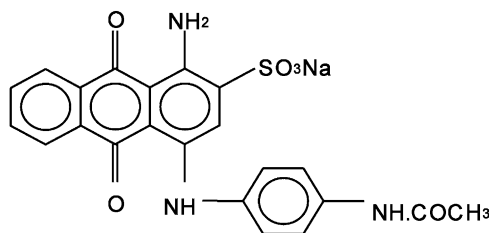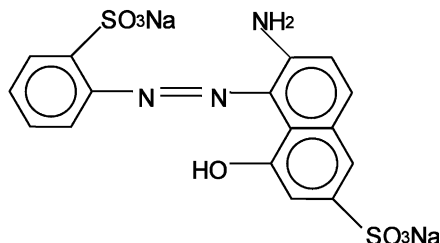
Fig. 1. Chemical structure of TB4R.
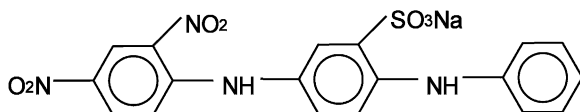

Fig. 2. Chemical structure of TR2B.

Fig. 3. Chemical structure of TO3G.

Table 1
Physical properties of GAC F400 (source: Calgon Carbon)

Total surface area (N_2 BET method) ($m^2 g^{-1}$)	1050–1200
Solid phase density ($kg m^{-3}$)	2100
Particle density (wetted in water) ($kg m^{-3}$)	1300–1400
Porosity	0.4
Iodine No.	1000–1100
Methylene Blue No.	280–300

and the bone char Brimac. The adsorbents were washed in deionised water and sieved into discrete particle size ranges before contacting with the adsorbate solutions. The physical properties of the activated carbon and the bone char are given in Tables 1 and 2, respectively.

Table 2
The physical properties of Brimac (source: Tate and Lyle)

Carbon content	9–11%
Moisture content	5% maximum
Hyroxyapatite	70–76%
Total surface area ($m^2 g^{-1}$)	100
Carbon surface area ($m^2 g^{-1}$)	50
Pore size distribution	7.5–60 000 nm
Pore volume ($cm^3 g^{-1}$)	0.225

2.3. Experimental

Batch equilibrium experiments were undertaken using a series of solutions of consecutively increasing initial dye concentration and of fixed volume which were placed in vessels where they are brought into contact with carbon. The mass of carbon was predetermined to give a constant volume to mass ratio. The jars were sealed and placed in a shaker for 3 weeks until equilibrium was reached. The samples were then analysed using standard spectrophotometry techniques (Perkin Elmer Lambda 12 Spectrophotometer) for the liquid dye concentration, C_s ($mg dm^{-3}$). This was then used to calculate the solid phase dye concentration, q_s ($mg g^{-1}$) by a material balance on the adsorption system. The particle size of the adsorbent was maintained at 355–500 μm. The temperature of the solution was held at 20°C and a pH of 7.

The adsorbent–adsorbate contacting time was determined in a preliminary test with samples having identical initial sorbate concentration and equal volume to mass ratio with each sample then being contacted for a different length of time. The time taken for the equilibrium to reach >99% was 3 weeks, and this was then taken as standard for subsequent equilibrium experiments. The carbon dosage for this work was expressed in terms of the mass to volume ratio, i.e., the mass of adsorbent to volume of solution and was standardised at $M/V = 0.05 g/0.05 l = 1 g/l$. The mass of adsorbate to mass of adsorbent ratio was varied by increasing the initial dye concentration from 100 to 3000 mg/l. Prior to spectrophotometric analysis the adsorbent/dye slurry was separated by passing it through a 0.45 μm filter pad.

Adsorbent surface area investigations were carried out using Sorptomatic 1900 (Fisons Instruments) equipment from which the total surface area was calculated by the Brunauer–Emmett–Teller (BET) method by measuring the adsorbent's adsorption and desorption of nitrogen under varying pressures. The instrument was capable of producing cumulative pore size and pore size distribution data.

3. Results and discussion

3.1. Adsorption isotherms

Fig. 4 illustrates a typical adsorption isotherm for the adsorption of acid dyes (TO3G) onto activated carbon and bone char, as a plot of solid phase equilibrium concentration, q_s, versus liquid phase equilibrium concentration, C_s. Data from the adsorption isotherms were modelled using the Langmuir and Freundlich isotherm models with the resulting isotherm constants correlated in Tables 3 and 4, respectively.

Langmuir isotherm theory is based on the assumption that adsorption on a homogeneous surface, i.e., the surface consists of identical sites, equally available for adsorption and with equal energies of adsorption, and that the adsorbent is saturated after one layer of adsorbate molecules forms
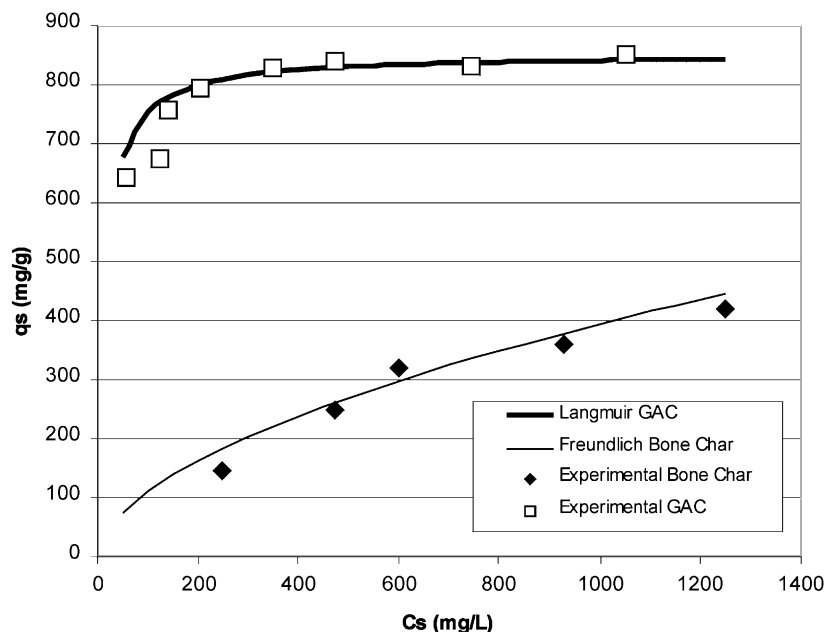
Fig. 4. Equilibrium isotherm adsorption of TO3G on GAC F400 and Brimac at 20°C.

Table 3
Langmuir isotherm constants for acid dye adsorption

Dye	Adsorbent	K_L (dm^3 g^{-1})	a_L (dm^3 mg^{-1})	r^2	Monolayer q_m (mg g^{-1})
TB4R	GAC F400	316	0.588	0.992	537
TB4R	Brimac	2.740	0.00575	0.959	476
TR2B	GAC F400	325.9	0.574	0.987	535
TR2B	Brimac	0.758	0.00149	0.905	508
TO3G	GAC F400	65.6	0.077	0.987	852
TO3G	Brimac	1.002	0.00210	0.931	477

on its surface. The Langmuir equation can be written in the following form:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \tag{1}$$

where q_e is the solid phase equilibrium concentration (mg g^{-1}), C_e the liquid phase equilibrium concentration (mg l^{-1}), K_L the Langmuir constant (l g^{-1}), a_L the Langmuir constant (l mg^{-1}), q_m the mass of adsorbate adsorbed/mass of adsorbent for complete monolayer $= a_L/K_L$ (mg g^{-1}).

The Freundlich isotherm describes adsorption where the adsorbate has a heterogeneous surface with adsorption sites that have different energies of adsorption and which are not always available. The energy of adsorption varies as a function of the surface coverage (q_e) and is represented by the Freundlich constant K_F (l g^{-1}) in Eq. (2).

$$q_e = K_F C_e^n \tag{2}$$

where n (dimensionless) is the heterogeneity factor which has a lower value for more heterogeneous surfaces.

Acid dye adsorption onto the activated carbon was generally well described by the Langmuir isotherm with correlation coefficients of $r^2 = 0.987$ or above. The monolayer capacity of TO3G on GAC F400 was significantly higher

Table 4
Freundlich isotherm constants for acid dye adsorption

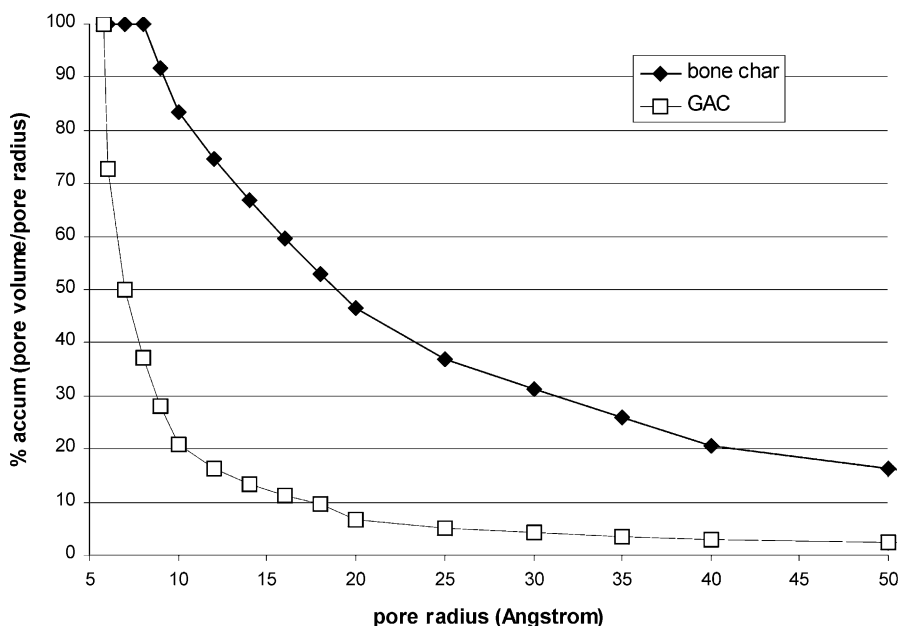| Dye	Adsorbent	K_F (dm^3 g^{-1})	n (dimensionless)	r^2
TB4R	GAC F400	167	0.228	0.905
TB4R	Brimac	44.6	0.3208	0.985
TR2B	GAC F400	515.6	0.01355	0.943
TR2B	Brimac	4.328	0.465	0.988
TO3G	GAC F400	167	0.243	0.930
TO3G	Brimac	8.725	0.552	0.998

Fig. 5. Pore size distribution of adsorbents.

(approximately 60%) than the other two dyes. Fig. 4 illustrates the fit of the Langmuir isotherm to the experimental data for the adsorption of TO3G on the activated carbon. Results from the Freundlich analysis shown in Table 4 indicate that the correlation coefficients are significantly less than the Langmuir analysis in describing the adsorption of acid dyes on the activated carbon.

Fig. 4 also illustrates the fit of the Langmuir isotherm to the experimental data for the adsorption of TO3G on the bone char. Results from the Langmuir and Freundlich analyses of the adsorption of acid dyes on the bone char are also reported in Tables 3 and 4. The monolayer capacity for Brimac calculated from the Langmuir constants was lower than that of the activated carbon at 89, 95 and 56% for TB4R, TR2B and TO3G, respectively. Correlation coefficient values for the adsorption of acid dyes on these adsorbents indicate that the Langmuir model best describes the adsorption onto activated carbon, and that the Freundlich model best describes the adsorption onto bone char.

The Freundlich heterogeneity factor, n, for adsorption of acid dyes on bone char is significantly higher than that of adsorption on activated carbon. This indicates that the activated carbon has a more heterogeneous structure than the bone char, a fact that is at odds with the high regression coefficients found with the adsorption onto bone char. It can be concluded that factors other than the heterogeneity of the adsorbent need to be considered to explain the experimental data.

3.2. Surface area measurement

Results of BET surface area measurements for the activated carbon and the bone char are illustrated in Fig. 5 and

in Table 5. These results indicate that the activated carbon has a specific surface area 10 times than that of the bone char. Furthermore, 80% of the total surface area of the activated carbon is situated in pores having a radius less than 1 nm, compared to 10% for the bone char.

3.3. Effect of dye aggregation on adsorption

Dye ions have a tendency to self-associate (or aggregate) in aqueous solutions [4]. At very low dye concentrations (10^{-4}–10^{-6} M), dyes form dimers (Eq. (3)) with dimerisation essentially complete before further aggregation occurs. The aggregation number, N, of a dimer is 2. Subsequent aggregation will take place initially between dimeric units (Eq. (4)):

$$2(\text{Dye}) \leftrightarrow (\text{Dye})_2 \tag{3}$$

$$n(\text{Dye})_2 \leftrightarrow (\text{Dye})_4 + (n-2)(\text{Dye})_2 \tag{4}$$
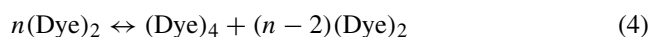
Acid dyes are often referred to as cationic dyes, i.e., the chromophoric system resides in the cation. Cationic dyes are adsorbed as sandwich micelles with an average solid phase aggregation number, N, proportional to the cube of the ionic weight of the dye [4,5]. The ionic weight of the dyes used in this study is relatively high and would have an approximate

Table 5
Specific surface area results for both adsorbents

Adsorbent (355–500 μm)	Specific surface area (m² g⁻¹)	r^2 (BET)
GAC F400	1069.2	0.9998
Brimac	109.4	0.9999

Table 6
Effect of dye agglomeration on adsorption

Dye	Ionic weight	Molecular area flat (nm^2)	End on (nm^2)	N			Capacity	
				Aqueous	Carbon	B. char	Carbon (mg g^{-1})	B. char (mg g^{-1})
TB4R	477	2.8048	0.9	2.5	12	22	537	476
TR2B	469	2.7424	0.9	2.5	12	23.2	535	508
TO3G	452	2.6098	0.9	2.5	19	21.5	852	477
Methylene blue	284	1.2	0.64	1.6	2	–	300	–

molecular area of $0.9\,nm^2$, end on, and $2.70\,nm^2$ flat (see Tables 6 and 7). For dyes molecules of this size and weight, the aggregation numbers up to 10 have been reported for adsorption onto carbon [5]. An aqueous solution aggregation number of 2.5 (typical value) would result in an aggregate having end on dimension of 2.7 nm in the liquid phase. From Fig. 5, it can been seen that only 14.5% of the total available surface area of the activated carbon is available for adsorbates having a dimension of 2.7 nm in the liquid phase (i.e., pores of 13 Å radius or larger). This analysis shows good correlation with the minimum pore radius for adsorbents of 7.5 Å with the cationic Methylene Blue dye as the adsorbate, possessing and end on dimension of 1.5 nm with aggregation [5]. The bone char, however, has 70% of its specific surface available for adsorption of adsorbates of this size.

Considering the molecular size of the aggregated dye molecules in the liquid phase the specific surface available for adsorption is 155 and $76\,m^2/g$ for activated carbon and bone char, respectively. Giles [5] has reported that the micelles of dye appear to be adsorbed flat, so the area that each covers is the same as that of a single dye molecule. An estimation can now be made of the aggregation number in the solid phase, on the basis of this assumption, knowing the adsorbent pore size distribution and the adsorption capacity, i.e.,

$$\frac{\text{surface area available for adsorption (g}^{-1})}{\text{surface area of micelle (flat on)}}$$
$$= \text{no. of micelles (g}^{-1})$$

$$\frac{\text{adsorption capacity for dye (mg/g)}}{\text{no. of micelles (g}^{-1})}$$
$$= \text{average weight of micelle}$$

$$\frac{\text{average weight of micelle}}{\text{molecular weight of dye}}$$
$$= \text{aggregation number}, N$$

The results of this calculation are tabulated in Tables 6 and 7 with solid phase aggregation numbers of 12–19 reported for the adsorption of acid dyes on activated carbon and aggregation numbers of 21–23 reported for the adsorption of acid dyes on bone char. These results are in excess of reported aggregation numbers, up to 10, for cationic dye adsorption on carbon. However, it is noted that a dye aggregation number in the adsorbed phase of approximately 2 is required if the total specific surface of the activated carbon was available. There is no evidence in the literature of such low solid phase N values for high molecular weight dyes. However, Methylene Blue does adsorb on activated carbon as a dimer [5]. The specific surface area available for adsorption of Methylene Blue on the activated carbon has been calculated at 37% of the total available (pore radius > 8 Å) and the adsorption capacity calculated at 300 mg/g, which correlates to a Methylene Blue Number of 280–300 quoted by the carbon manufacturers.

The adsorption of acid dyes on bone char results in relatively high aggregation numbers, $N = 21$–23. Since a high fraction of the specific surface was available for adsorption, it was concluded that these high N values were indeed achieved. However, there is no literature on dye adsorption on bone char with which these data may be compared. Giles described the adsorption of dyes onto the pore structure of cellulose and indicated that at high surface concentrations, i.e., high N numbers, the multilayer adsorption breaks up and non-adsorbed three-dimensional aggregates form within the pore structure [5]. Walker and Weatherley [6] reported the relative ease of desorption of acid dyes from bone char

Table 7

Dye	Capacity				Area			
	Carbon (mmol g^{-1})	B. char (mmol g^{-1})	Carbon (mmol g^{-1})/N	B. char (mmol g^{-1})/N	Carbon (m^{-2} g^{-1})	B. char (m^2 g^{-1})	Carbon (%)	B. char (%)
TB2R	1.126	0.998	0.094	0.045	158.40	76.589	14.818	70.265
TR4B	1.141	1.083	0.095	0.047	156.93	77.078	14.681	70.714
TO3G	1.885	1.055	0.099	0.049	155.86	77.116	14.581	70.749
Methylene blue	1.056	–	0.528	–	381.54	–	35.692	–

as opposed to the irreversible adsorption associated with the adsorption of acid dyes on activated carbon. From these results it is postulated that dye desorption using the bone char is caused by the multilayer break-up at high aggregation numbers.

Although the pore size distribution and the relative size of the adsorbate molecules have a significant effect on adsorption capacity, the chemical nature of both the adsorbate and adsorbent also plays a significant role. This is illustrated in this work in which significant variation of adsorption capacity is shown by three acid dyes having similar molecular weights. The di-azo TO3G dye attained higher levels of solid phase aggregation and of subsequent adsorption capacity on activated carbon when compared with the other dye classes. However, similar levels of solid phase aggregation and adsorption capacities on bone char were found for the three dye classes. The variances in solid phase aggregation of dyes on activated carbon, and between activated carbon and bone char, are probably due to interactions between the cationic groups on the dye molecules and the carboxyl, carbonyl, lactonic and quinone (acidic) and basic functional groups within the activated carbon structure.

4. Conclusions

Study of the adsorption of acid dyes onto solid adsorbent showed that the pore size distribution of the adsorbate was an important parameter in the selection of a cost-effective adsorbent. Much of the specific surface of commercially available activated carbon, especially that surface associated with the micropore structure, was found to be redundant in the adsorption of large molecular weight aggregating compounds such as dyes. Although the total adsorption capacity was lower, adsorption of dyes on relatively inexpensive bone char proved successful in that 70% of the specific surface was utilised, and that high solid phase aggregation, i.e., multilayer adsorption was achieved. Results form the correlation coefficients using the Langmuir and Freundlich analyses for adsorption on activated carbon and bone char also correlated with the solid phase aggregation numbers found in this study.

Acknowledgements

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