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Adsorption of dyes from aqueous solution by coals, chars, and active carbons

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Adsorption of two acidic dyes (amaranth red and metanil yellow) and a basic dye (methylene blue) from aqueous solution has been studied using a wide range of American coals and chars. The adsorption capacity of coals and chars has been compared with commercially available active carbons. The amount of dye removed from solution by raw coals is made up of two parts, one due to interaction with some mineral constituents and the other due to adsorption on the porous surface. There are some indications that pyrite and soluble alkali salts are the reactive minerals. When the coals are washed by refluxing in distilled water for 8 h, reproducible adsorption capacity is obtained. With washed coals, good correlation between the nitrogen BET surface area and dye adsorption capacity is observed. Except for lignites, adsorption of dyes is not influenced by the oxygen groups on the surface. Chars show enhanced capacity over coals, where under the most favourable conditions adsorption approached 25% of the active carbon capacity. The initial rate of adsorption of dye from solution by coals, chars and active carbons has been found to be dependent on the square root of time.

INTRODUCTION

THE PROBLEM of removing pollutants from water is important and becoming more so with the increase of industrial activity. Because the soluble organic impurities in water are so numerous and diverse in character, only a non-specific process like adsorption seems to be ideal for their removal. Active carbons have been suggested as adsorbents and are being used in some cases at present. Carlton et al (Rand Development Corporation)[1] have suggested the use of coal as a filter bed as well as an adsorbent for the removal of pollutants.

From a study of the sorption of amaranth red by a number of coals, it was reported that the high volatile (HVC) coals show the best promise. McClung et al[2], from a study of amaranth red adsorption by a number of West Virginia coals, have found correlations of dye adsorption with the mineral matter content and, more specifically, with the pyrite content of coals. A detailed study of the adsorption capacity of coals (as measured by dye adsorption) of different rank from different geographical locations in the United States has been completed. The results are expected to furnish basic data for any water treatment process involving coals. The chars obtained in different Office of Coal Research processes might be used for water treatment; and, consequently, their adsorption capacity has also been measured. To put the data on coals in perspective, adsorption of dyes on three granular active carbons has also been included.

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EXPERIMENTAL

Samples

A total of forty coals, four OCR process chars, one active carbon obtained by flue-gas/anthracite reaction, and three commercially available granular active carbons have been used in this study. The analytical data of the coals are given in *Table 1*. Of the three granular active carbons, two are derived from coal and the other from coconut shell. The surface area and ash yield data of these are given in *Table 2*.

Table 1 Analyses of coals

| Sample No. | State | ASTM rank | Ultimate analysis (% d.a.f.) | | | | |
			C	H	N	S	O (by diff)
PSOC–108	Pa	HVA	82·9	5·6	1·2	3·5	6·8
PSOC–110	Pa	HVA	84·8	5·6	1·3	1·3	7·0
PSOC–124	Pa	HVA	83·6	7·0	1·4	1·1	6·9
PSOC–127	Pa	LV	89·6	5·0	1·0	0·8	3·6
PSOC–135	Alabama	MV	88·4	4·9	0·3	0·7	5·7
PSOC–168	W Va	HVA	81·5	6·0	0·2	4·3	8·0
PSOC–169	W Va	HVA	82·2	5·6	1·5	3·6	7·1
PSOC–170	W Va	HVA	81·7	5·7	0·1	3·3	9·2
PSOC–171	W Va	HVA	82·3	5·7	1·3	3·3	7·4
PSOC–172	W Va	HVA	81·6	5·4	0·7	3·5	8·8
PSOC–181	Indiana	HVC	77·3	5·2	1·0	0·6	15·9
PSOC–185	Indiana	HVC	80·9	5·9	1·1	3·7	8·4
Rand Enos	Indiana	HVC	79·9	5·3	1·6	3·5	9·7
PSOC–190	Illinois	HVC	75·6	5·3	1·1	3·3	14·7
PSOC–191	Illinois	HVC	77·9	5·5	1·0	3·3	12·3
PSOC–192	Illinois	HVC	78·3	5·8	1·0	3·3	11·6
POC–102	W Va	HVA	79·9	5·8	0·6	5·1	8·6
POC–105	W Va	HVA	84·6	5·6	1·5	0·8	7·5
POC–107	W Va	HVA	82·7	5·6	1·9	2·5	7·3
POC–109	W Va	HVA	84·4	5·5	1·6	0·7	7·8
POC–116	W Va	HVA	80·9	5·8	1·4	2·2	9·7
POC–148	W Va	HVA	79·9	5·7	1·3	5·0	8·1
POC–188	Indiana	HVC	76·7	5·7	1·6	3·2	12·8
POC–196	Kentucky	HVA	79·5	5·7	1·3	5·4	8·1
POC–197	Pa	HVB	76·5	5·6	1·2	4·5	12·2
POC–199	W Va	HVA	81·3	5·3	0·3	5·6	7·5
POC–4	Kentucky	HVA	83·8	5·8	1·6	0·9	7·9
PSOC–12	Kentucky	HVA	85·2	5·7	1·4	0·6	7·1
PSOC–22	Illinois	HVC	78·8	5·8	1·5	2·9	11·0
PSOC–24	Illinois	HVB	80·2	5·5	1·1	4·5	8·7
PSOC–26	Illinois	HVC	77·3	5·6	1·1	7·5	8·5
PSOC–67	Utah	HVB	80·4	6·1	1·2	1·5	10·8
PSOC–80	Pa	Anthracite	90·8	2·6	0·8	0·6	5·2
PSOC–87	N Dakota	L	71·2	5·3	0·6	0·7	22·2
PSOC–88	N Dakota	L	71·9	5·2	0·8	0·9	21·2
PSOC–89	N Dakota	L	63·3	4·7	0·5	1·6	29·9
PSOC–98	Wyoming	Sbb A	74·3	5·8	1·2	1·3	17·4
PSOC–100	Wyoming	Sbb C	72·1	5·3	0·8	0·6	21·2
PSOC–105A	Indiana	HVC	80·3	5·7	1·1	1·8	11·1

Dyes

Analysed-grade amaranth red, metanil yellow and methylene blue (supplied by J. T. Baker) have been used without any further purification. The first two dyes are sodium salts of sulphonic acid and the blue dye is a hydrochloride salt. The dyes were dried to remove moisture, and solutions of known concentrations were made with distilled water. A calibration curve of the optical density of the known standards was made for each dye. A Bausch and Lomb Spectronic 20 instrument was used for optical density measurements. The wavelengths used were 525, 435 and 610 nm for amaranth red, metanil yellow and methylene blue respectively.

Surface area

A volumetric sorption apparatus has been used. Areas have been calculated from nitrogen adsorption isotherms at 77 K, using the BET equation.

Isotherms and rate measurements

A sample (dried for 2 h at 105°C) of known weight was added to each of a number of stoppered conical flasks containing different amounts of dye. The flasks were then kept in a thermostated shaker bath; and after a certain period, varying from one hour to six days for equilibration, the concentrations of the dye solutions were measured. All the experiments were carried out at 25°C. The adsorption of the dye by a sample was obtained from the difference of the initial amount of dye added and that remaining in solution after adsorption. The adsorption data have been presented as milligrams of dye per gram of the dry sample. In the cases of amaranth red and metanil yellow adsorption, the coals or carbons were separated by filtration through Whatman 42 filter paper. In the case of methylene blue adsorption, the solids were separated by centrifuging, as there was preferential adsorption of the dye on the filter paper.

In the rate measurements, known weights of the solid were added to a number of flasks containing the same amount of dye. Flasks were withdrawn from the shaker bath at different times and the concentration of the unadsorbed dye was measured.

RESULTS AND DISCUSSION

The effective adsorbent surface of an active carbon or coal is limited by pore screening and by the effects of impurities and substituent groups on the carbon surface. Of possible substituents, acidic groups are the most important. In the case of coals, the mineral matter affects its sorption in a manner that will be discussed later.

Dye molecules have been used as analogues for the organic pollutants in water. From the standpoint of molecular size, the pollutant molecules are expected to be smaller than the dye molecules used in this study, at least in the case where the polluted water has undergone a biochemical degradation stage. Therefore, the effect of pore screening is expected to place the dye

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molecules at a disadvantage compared to organic pollutants in water. If the average size of the pollutant molecule is taken to be comparable to the size of the phenol molecule, the dye adsorption capacity would rather give a lower limit of anticipated adsorption capacity for the pollutants by the particular carbon or coal. Both acidic and basic dyes have been used to study the effect of substituent groups on the surface of carbon on adsorption capacity.

The dyes selected were amaranth red, metanil yellow and methylene blue. The first two are acidic dyes. Amaranth red was used by Rand Development workers[1]. Adsorption of methylene blue (a basic dye) has been used as a standard test for decolourizing carbons for many years[3]. Metanil yellow has been used by Graham[4] for active carbons. The structures of the dyes are given in *Figure 1*. It is believed that these are planar molecules[5]. The minimum

Amaranth red (acidic)

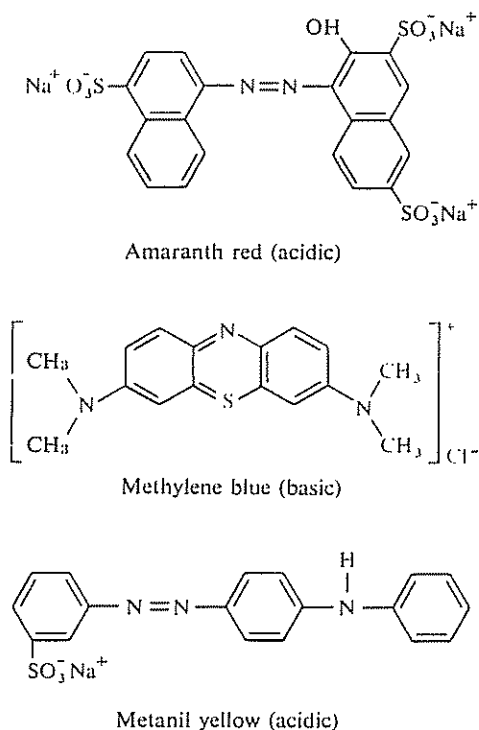Methylene blue (basic)

Metanil yellow (acidic)

Figure 1 Structure of the dye molecules

thickness of the two acidic dyes may be assumed to be equal to the size of sulphonic acid group, which is estimated to be about 6Å in diameter (1 Å = 0·1nm). The estimation of the thickness of the methylene blue molecule is rather difficult. The thickness of the adsorbing species becomes important in the case of active carbons where slit shaped pores have been reported[6]. The area occupied by the dyes on carbon surfaces has been estimated by the following approach.

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Estimation of the size of the dye molecules

It is of interest to obtain an idea of the area occupied by a dye molecule on adsorption. For this purpose, adsorption of the dyes at 25°C has been measured on Graphon, a graphitized carbon black. It was chosen as a reference because it is non-porous and free from impurities and substituent groups on its surface. The isotherms are shown in *Figure 2*. It was observed that the rate
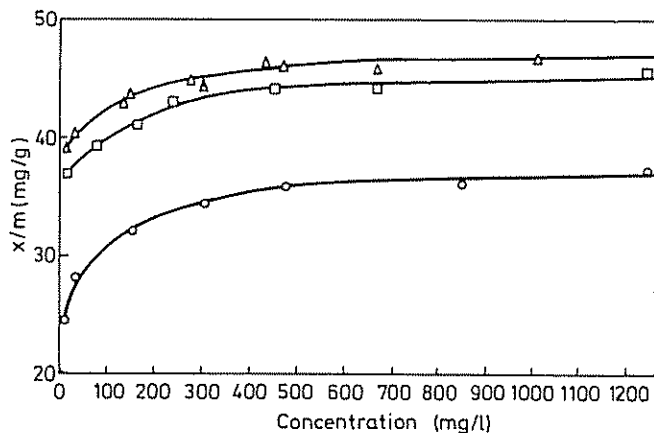
Figure 2 Isotherms on Graphon at 25°C
○ Amaranth red △ Metanil yellow
□ Methylene blue Equilibrium time 6 days

of attainment of equilibrium was rather slow; and, consequently, a time of six days was allowed for equilibration. The isotherms are of Type 1, according to Brunauer's classification[7]. Adsorption was followed for all the three dyes up to a maximum equilibrium dye concentration of 2500 mg/l (not shown in *Figure 2*), but the adsorption points show a scatter in the higher concentration range. This scatter could be expected as the amount of dye adsorbed is obtained as a difference of two large numbers. It might be added, however, that no definite deviation from the constant sorption value was observed in the concentration range studied. It can be seen from *Figure 2* that adsorption remained practically constant from and above 500 mg/l equilibrium concentration in all three cases. The plateau region of the isotherm has been assumed to be due to the completion of a monolayer of the dye on the geometrically flat surface of Graphon.

The nitrogen surface area of the Graphon sample was 89 m²/g. From this figure and the adsorption in the plateau region, the areas occupied by 1 mg of amaranth red, metanil yellow and methylene blue were found to be 2·41, 1·89 and 1·96 m² respectively. These factors have been used in the present work to convert the limiting dye adsorption values to the surface area covered by a dye for a particular coal or carbon. It is probable that the area covered by a dye molecule would depend on the nature of the solid surface, but the conversion factors obtained by the above procedure are expected to furnish a basis for comparing the adsorption capacity of different carbonaceous substances.

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Adsorption of dyes by granular active carbons

All the carbons were washed three times with distilled water (at room temperature), dried overnight at 105°C and stored in screw capped bottles. All the isotherms were determined at 25°C, and an equilibrium time of six days in the shaker bath was allowed in all cases.

Sample 1. The carbon is derived from bituminous coal. The stock sample (original) has an ash content of 6·1 %. In order to study the effect of mineral matter removal on dye adsorption, this sample was first treated with 5% hydrochloric acid and then with hydrochloric acid/hydrofluoric acid at 90°C. The acid treated samples were first batch-washed with hot (≃90°C) distilled water. The sample was kept for 30 min in contact with a large quantity of water which was stirred until virtually acid free. Subsequently, the samples were taken in a small column, where washing with hot water was continued until the effluent was chloride free.

The adsorption isotherms of the dyes on the original, hydrochloric acid-treated and hydrochloric acid/hydrofluoric acid-treated activated carbon were determined. The isotherms for the original carbon are shown in *Figure 3*. The
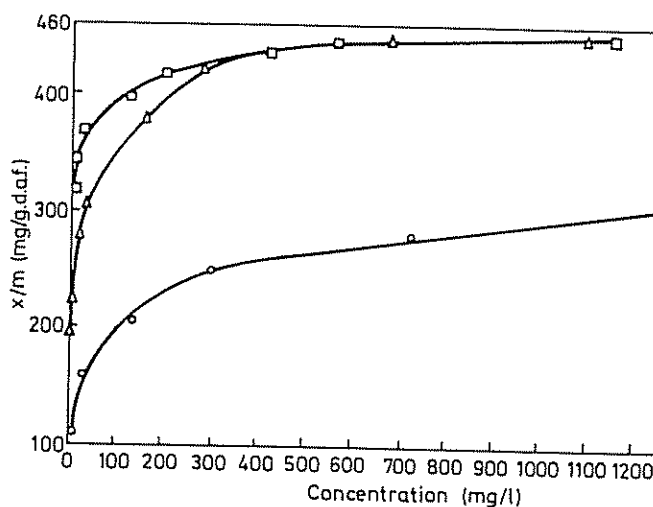

Figure 3 Isotherms of dyes at 25°C on Pittsburgh activated carbon (original), (28 × 65) mesh
○ Amaranth red   △ Metanil yellow   ◻ Methylene blue

isotherms for the dyes for the hydrochloric acid and hydrochloric acid/ hydrofluoric acid-treated carbons were very similar in shape and extent to those in *Figure 3*. From *Figure 3* it can be seen that the adsorption of methylene blue and metanil yellow approaches the same limiting value of 448 mg/g d.a.f., whereas the sorption of amaranth red is about 292 mg/g d.a.f., at an equilibrium concentration of 1000 mg/l. Further, the sorption in the latter case is still increasing. It is of interest to compare the methylene blue and metanil yellow isotherms in *Figure 3*. The adsorption of methylene blue at low equilibrium concentrations is greater; but, at higher concen-

trations, the isotherm merges with that of metanil yellow. In the cases of hydrochloric acid-treated and hydrochloric acid/hydrofluoric acid-treated samples, it was observed that the methylene blue isotherm, at higher concentrations, falls below that of metanil yellow. As the groups on the surface of the active carbon are expected to be acidic in nature and as the adsorption of the acid dye is equal to or greater than that of the basic dye, it is highly probable that the effect of the oxygen groups on adsorption was not significant in the case of this particular carbon.

Sample 4. The isotherms of the three dyes are shown in *Figure 4.* For this
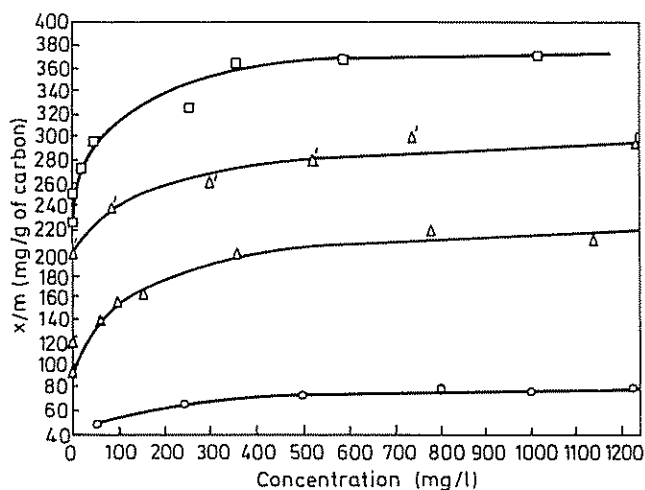

Figure 4 Isotherms of dyes on coconut shell activated carbon at 25°C, (12 × 16) mesh

☐ Methylene blue △' Carbon heated to 800°C in N_2—Metanil yellow △ Metanil yellow ○ Amaranth red

carbon, the adsorption of methylene blue is much higher compared to that of metanil yellow. Also the adsorption of metanil yellow increases if the sample is heat treated at 800°C under a nitrogen stream. This increase may be attributed to the removal of some acidic groups on heat treatment. Consequently, for this carbon the chemical nature of the surface groups does influence dye adsorption. It is probable that this carbon has seen a lower temperature in its preparation, compared to that of Sample 1. As a result, more oxygen groups remain on its surface; and these oxygen groups might be more reactive in nature.

Sample 6. This active carbon is also obtained from coal and has an ash content of 7%. The metanil yellow isotherm on this carbon was determined. The adsorption capacity was very similar to that of Sample 1.

The results of the dye adsorption on carbons are summarized in *Table 2.* It can be seen that the removal of mineral matter from Sample 1 has no effect on the fraction of area available to the dye molecules. Amaranth red covers about 60% of the nitrogen area and the other two dyes cover about 75%.

Table 2 Dye adsorption data on carbons*

Sample no.	Description	Ash yield (%)	Nitrogen BET area (m²/g, d.a.f.)	Limiting value of dye adsorption† (mg/g, d.a.f.)			Nitrogen area covered (%)		
				Amaranth red	Methylene blue	Metanil yellow	Amaranth red	Methylene blue	Metanil yellow
1	Coal-based activated carbon original	6·1	1145	292	448	448	61	77	74
2	Coal-based activated carbon, HCl treated	5·0	1124	296	437	454	63	76	76
3	Coal-based activated carbon, HCl-HF treated	0·2	1132	293	430	472	62	74	78
4	Coconut shell activated carbon	0·7	1180	78	368	212	16	61	34
5	Coconut shell activated carbon, heat treated at 800°C	0·8	1120	–	–	290	–	–	49
6	Coal-based activated carbon	7·0	1100	–	–	422	–	–	72

* Granular active carbons ground and 28 × 65 mesh fraction taken
† Adsorption at an equilibrium concentration of 1000 mg/l has been taken to be the limiting value

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For the Sample 6, the area available to metanil yellow is 72%, which indicates that its pore structure might be similar in nature to that of Sample 1. On the other hand, a relatively small fraction (16%) of the total area of the coconut shell activated carbon is open to amaranth red. This would indicate that the porous structure of this carbon is quite different from those of the two other carbons.

Adsorption of dyes by original coals

Adsorption of amaranth red: standard amaranth red test. As suggested[1], the standard amaranth red adsorption test was conducted with a number of coal samples. The sieve size of all coal samples was (40 × 70) mesh. Two grams of dry coal were placed in a beaker and 20 cm^3 of 50 mg/l amaranth red solution was added to it. After allowing 15 min with stirring, the solution was filtered through Whatman 42 filter paper and the concentration of the unadsorbed dye measured. The results are summarized in *Table 3*. All the

Table 3 Standard amaranth red adsorption test on original coals

Sample No.	Equilibrium concentration of filtrate (mg/l)	Dye adsorbed (mg/g dry)	Adsorption (%)
POC–102	30·9	0·197	39·6
POC–105	26·9	0·231	46·2
POC–107	39·2	0·108	21·6
POC–109	48·2	0·018	3·6
POC–116	38·1	0·119	23·8
POC–148	41·5	0·085	17·0
POC–188	27·2	0·227	45·4
POC–199	35·8	0·141	28·2
PSOC–124	42·6	0·074	14·8
PSOC–167	46·8	0·032	6·4
PSOC–168	45·4	0·046	9·1
PSOC–170	46·7	0·033	6·6
PSOC–171	46·2	0·037	7·5
PSOC–172	46·2	0·037	7·5

samples, except POC–188, were of HVA rank; but their adsorption capacity, as indicated by 'percent adsorption', varied widely between 3% and 45%. It is evident that this simple test would not be suitable for measuring adsorption capacity of coals and it was decided to obtain adsorption isotherms of the dyes on coals.

Amaranth red isotherms. Adsorption isotherms of amaranth red were measured with a number of coal samples. An equilibrium time of 1 h in the shaker bath was allowed. Adsorption isotherms for four samples are shown in *Figure 5*. Adsorption data for nineteen other samples are given in *Table 4*.

Adsorption capacities do not show any correlation with rank. The HVC samples, however, have higher capacities compared to HVA coals. One sample of lignite (PSOC–89) shows adsorption comparable to HVC coals, whereas two others (PSOC–87 and –88) had lower capacities, even below that of the HVA coals. The isotherms do not belong to any well defined type. They might be analysed with the help of the Freundlich[7] equation, as has been done
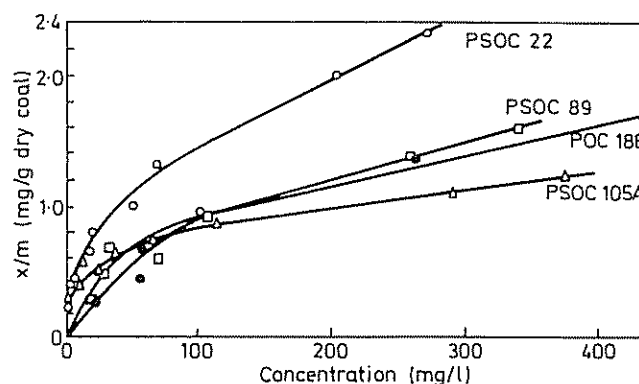
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Figure 5 Isotherms of amaranth red at 25°C on (40 × 70) mesh
coals. Equilibrium time 1 h

Table 4 Amaranth red adsorption data on additional original coals
(one hour equilibrium time)

Sample no.	Adsorption at an equilibrium concentration of 400 mg/l (mg/g dry)
PSOC–80	0·04
PSOC–4	0·04
PSOC–12	0·12
PSOC–108	0·32
PSOC–110	0·15
PSOC–24	0·41
PSOC–26	3·80
Rand Enos	0·66
PSOC–98	0·23
PSOC–87	0·02
PSOC–88	0·02
POC–197	1·10
PSOC–67	0·89
PSOC–100	0·37
PSOC–98	0·21
POC–102	0·91
POC–199	0·73
POC–196	0·58
POC–105	0·52

in the Rand Report,[1] but the treatment is not expected to yield any further
information. It was thought that the equilibrium time allowed for the isotherms
was too small and, consequently, the effect of equilibrium time on adsorption
was studied. In *Figures 6* and *7* are shown isotherms of amaranth red on
Rand Enos and PSOC–26 samples for different equilibrium times. The
amaranth red isotherm for a Rand Enos sample, with 48 h equilibrium time,
shows a plateau region above 500 mg/l equilibrium dye concentration. It
is evident that for amaranth red adsorption on coals an equilibrium time
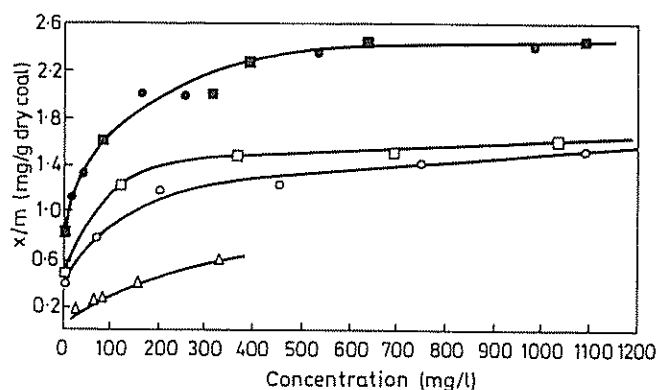of 48 h, or more, would be necessary.

Figure 6 Amaranth red and methylene blue isotherms on Rand Enos coal at 25°C

△ 1 h ⎫
○ 24 h ⎬ Amaranth red
□ 48 h ⎭

● 24 h ⎫
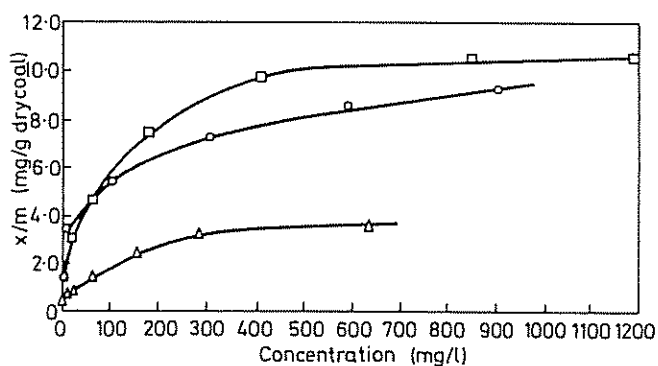▨ 48 h ⎬ Methylene blue

Figure 7 Isotherms of dyes on PSOC–26 at 25°C

△ 1 h ⎫
○ 24 h ⎬ Amaranth red   □ 24 h Methylene blue

From the studies with active carbons, it has been shown that, because of the larger molecular size, the fraction of the area available to amaranth red was lower compared to the other two dyes. It would be of interest to probe the porous structure of coals with other molecules as has been done in the case of active carbons. From this consideration, isotherms of methylene blue and metanil yellow on coals have been measured.

Methylene blue isotherms. In *Figure 6* is shown the methylene blue isotherm of the Rand Enos sample. It may be noted that the 24 h and 48 h equilibrium points fall on the same curve. Therefore, it may be concluded that in 24 h equilibrium is essentially attained for coals with methylene blue. In *Figure 7* the methylene blue isotherm (24 h equilibrium time) of PSOC–26 is shown. The adsorption of the blue dye is higher compared to that of the red dye, as could be expected from the sizes of the respective molecules. Methylene blue

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isotherms, with 24 h equilibrium time, for POC–196, POC–105, PSOC–4, PSOC–80, PSOC–87 and PSOC–89 were determined and some isotherms are shown in *Figures 8* and *9*. It was observed that for POC–105 and POC–196 the
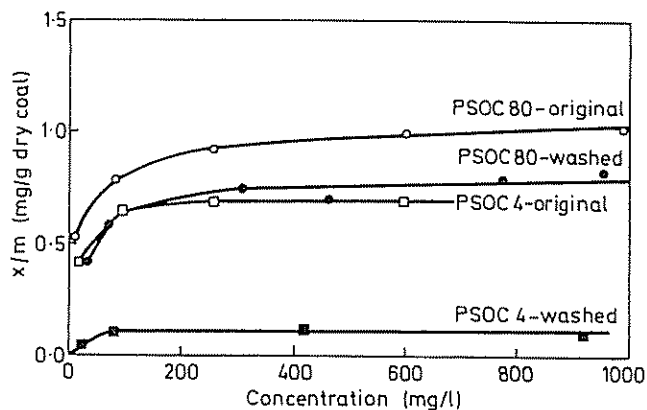

Figure 8 Methylene blue isotherms on PSOC–4 and PSOC–80 at 25°C. Equilibrium time 24 h

amaranth red adsorption is somewhat higher compared to that of methylene blue which is unusual. The two lignites have very high capacity for methylene blue (*Figure 9*) compared to that for amaranth red. The probable cause of this very high methylene blue adsorption will be discussed later.
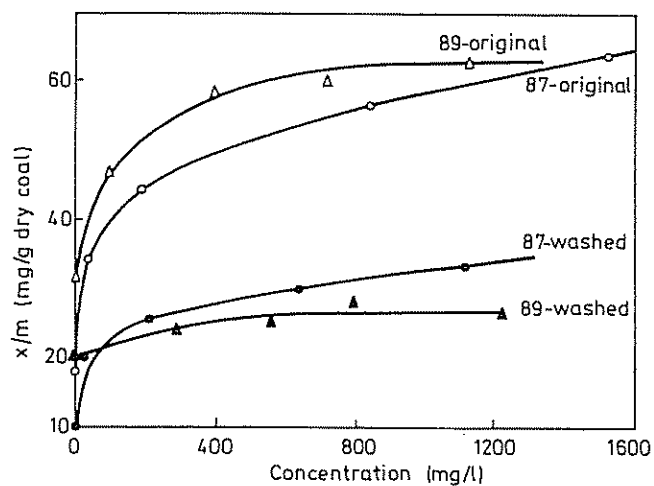

Figure 9 Methylene blue isotherms on PSOC–87 and PSOC–89 at 25°C. Equilibrium time 24 h
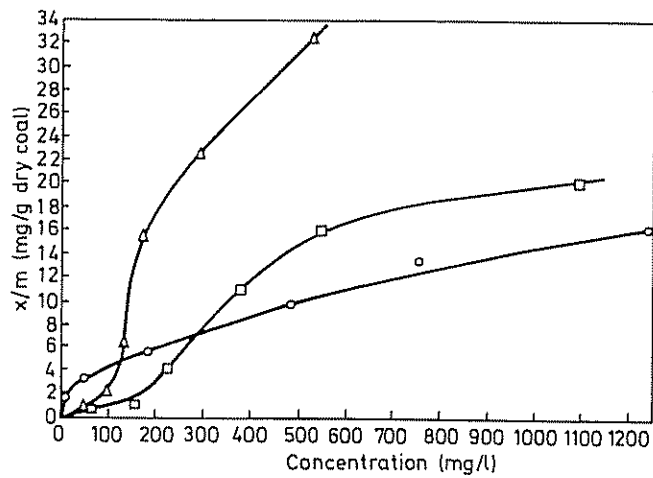
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Figure 10 Metanil yellow isotherms at 25°C
O Rand Enos △ POC–196
□ POC–105 Equilibrium time 24 h

Metanil yellow isotherms. This acidic dye molecule is slightly smaller in size than is methylene blue. It was thought that its adsorption might be hindered by the presence of acidic groups on the surface of coal in comparison to that of the blue dye. Isotherms of metanil yellow, with 24 h equilibrium time, are presented in *Figures 10* and *11*. The effect of equilibrium time on adsorption was not studied for this dye, but the 24 h time was selected by
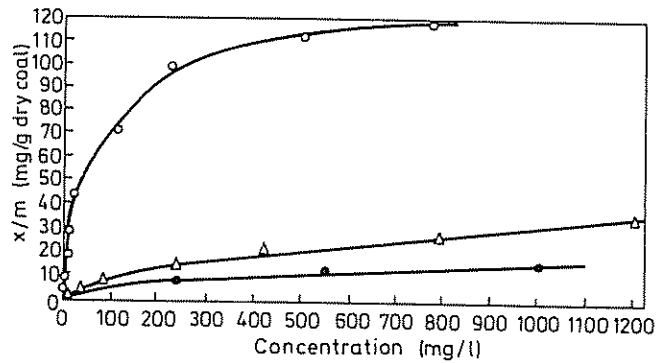

Figure 11 Metanil yellow isotherms at 25°C
O PSOC–26 △ PSOC–87
● PSOC–26 Water washed Equilibrium time 24 h

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analogy with methylene blue. Metanil yellow adsorption at an equilibrium concentration of 1000 mg/l for the PSOC–80 (anthracite)and PSOC–4 (HVA) samples were 0·95 and 0·59 mg/g respectively. Compared to the methylene blue values (*Figure 8*), the capacity for the yellow dye is higher for the PSOC–4 sample; whereas for the anthracite, the metanil yellow capacity is slightly lower.

Coming to *Figure 10*, it may be noted that the isotherms for POC–105 and POC–196 have a peculiar shape. The methylene blue adsorption capacities of these two samples are only 0·58 and 0·62 mg/g at their limit. The Rand Enos sample has a higher capacity for the yellow dye compared to that for methylene blue (*Figure 6*). Further, dye adsorption on the Rand Enos sample does not attain a limiting value in the range of concentration studied.

Isotherms of metanil yellow for PSOC–26 and PSOC–87 are shown in *Figure 11*. The isotherm of the lignite sample (PSOC–87) shows a continuous rise with increased concentration. Further, the amount of dye adsorbed is much too high compared to that of amaranth red (0·2 mg/g dry), but is still lower than that of the blue dye (*Figure 9*). The adsorption of metanil yellow by PSOC–26 is very high indeed. In this case the total adsorption cannot be accounted for by the surface area available for adsorption (nitrogen area of 42 m²/g dry). A considerable fraction of the sorption has to be assigned to some specific interaction. In the organic matter of coal, the presence of large amounts of basic functional groups is not indicated. As a result, specific interaction with the mineral matter is a distinct possibility. The behaviour of PSOC–26 is not an isolated case, as the data on POC–105 and POC–196 indicate.

Adsorption of dyes by treated coals

Effect of mineral matter on dye adsorption. It was shown with activated carbon Sample 1 that the presence of minerals had no effect on the adsorption of dyes. This was probably because the mineral matter present in the starting coal had undergone thermal and oxidative treatments during activation, which might have rendered them inactive. Two relatively mild treatments, (1) refluxing with distilled water for 8 h and (2) refluxing with 5% hydrochloric acid solution for the same period, were given to five samples of coal. The samples were filtered and washed free of acid by the same procedure as used for Sample 1. They were then dried in a current of nitrogen and their adsorption capacity was determined. The results with amaranth red as adsorbate are shown in *Table 5*. The coals after treatment (1) are designated hereafter as 'water washed' and those after treatment (2) are reported as 'acid washed'. The removal of the mineral matter by the treatments, as measured by the ash yields of the treated and original sample, are given in *Table 6*.

It can be seen from *Table 5* that refluxing the coals with water lowers their adsorption capacity. Acid treatment, however, does not produce any further change, though there is considerable ash reduction, as can be seen from *Table 6*. It is hypothesized that only a part of the mineral matter of coals is reactive as far as dye adsorption is concerned. The sorption capacity of the washed samples may be attributed to the organic matter of coals. As acid

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Table 5 Adsorption of amaranth red by original and treated coals*

	Sorption by original		Sorption by water washed		Sorption by acid washed	
Sample no.	Equilibrium concentration of filtrate (mg/l)	Adsorption (mg/g dry)	Equilibrium concentration of filtrate (mg/l)	Adsorption (mg/g dry)	Equilibrium concentration of filtrate (mg/l)	Adsorption (mg/g dry)
POC–196	84·4	0·78	93·7	0·31	93·7	0·31
POC–197	79·2	1·04	96·4	0·18	97·0	0·15
Rand Enos	82·6	0·87	89·2	0·54	88·8	0·56
POC–188	62·0	1·90	89·2	0·54	89·2	0·54
PSOC–89	84·8	0·76	98·2	0·09	98·8	0·06

* 50 cc of 100 mg/l amaranth red solution for 1 g of coal in shakerbath for 24 h

Table 6 Removal of mineral matter from coals by different treatments

	Ash (%)		
Sample no.	Original	Water washed	Acid washed
PSOC–80	15·4	15·3	–
PSOC–127	5·5	5·3	–
PSOC–135	4·1	3·5	–
PSOC–4	1·9	1·8	–
POC–196	11·9	10·9	7·5
POC–197	16·1	10·1	7·6
PSOC–67	3·9	3·9	–
PSOC–26	10·8	6·5	–
PSOC–105A	7·7	7·3	–
POC–188	10·2	9·1	5·9
Rand Enos	8·0	6·8	6·0
PSOC–181	7·2	6·3	–
PSOC–185	13·1	10·2	–
PSOC–190	7·1	5·8	–
PSOC–191	6·7	5·3	–
PSOC–192	6·5	5·0	–
PSOC–87	6·6	6·3	–
PSOC–89	12·0	9·2	2·5

treatment does not bring about any further change in adsorption capacity, work in this line was discontinued. It might be added that the treatment with water is not solely a solution process. There is a possibility of mechanical separation. In the case of high-pyrite-containing coals[8], such as PSOC–26, it was observed that a brownish precipitate separated from the coal during refluxing and settled at the bottom of the flask. This precipitate remained attached to the glass and so the coal could be separated from it.

It is important here to comment on a few aspects of dye adsorption by original coals. Adsorption capacities of original coals are comparatively higher, which is desirable. The adsorption capacity shows no correlation with

rank. The total dye adsorption appears to be made up of two contributions; (1) that due to the available surface and (2) that due to the interaction with a part of the mineral matter. In the course of this study, it has not been possible to determine precisely the particular mineral responsible; but there are some indications that pyrite and soluble alkali-metal salts may be responsible.

Isotherms of dyes on water washed coals. In the case of water washed samples, isotherms of methylene blue and metanil yellow at 25°C with an equilibrium time of 24 h have been determined for a number of coal samples. Some of the metanil yellow isotherms are shown in *Figure 12* and some of the methylene blue isotherms are shown in *Figure 13.* Not all the isotherms show a well defined plateau region. For the purpose of comparing the adsorption capacity of different coals, the adsorption at the equilibrium concentration of 1000 mg/l of the dye has been reported as the 'limiting dye adsorption'.
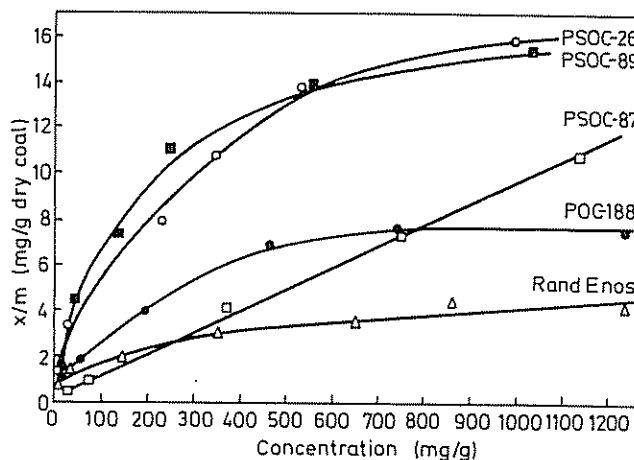

Figure 12 Metanil yellow isotherms at 25°C on water washed samples. Equilibrium time 24 h

The results of metanil yellow and methylene blue adsorption are summarized in *Table 7.* The nitrogen surface area values of the coals are also included. It can be seen that the amount of dye adsorbed is related to the nitrogen area of the coal. From the rank consideration, coals of HVC or lower have relatively high adsorption capacities. From about 30% to 70% of the nitrogen area is available to metanil yellow and about 40% of the area to methylene blue for these coals. The sample PSOC–181 seems to be an exception, where 90% of the nitrogen area is available to methylene blue. The correlation with nitrogen area implies that the sorption of the dyes is a physical process. Indirectly, it is confirmed that the sorption capacity of the water washed coals is primarily due to adsorption on the porous structure of the organic matter of coals.

The two lignite samples have very low nitrogen areas but rather high dye pick-up. In their case, in the presence of water, considerable swelling of the porous structure is possible, which increases the accessibility of the dye
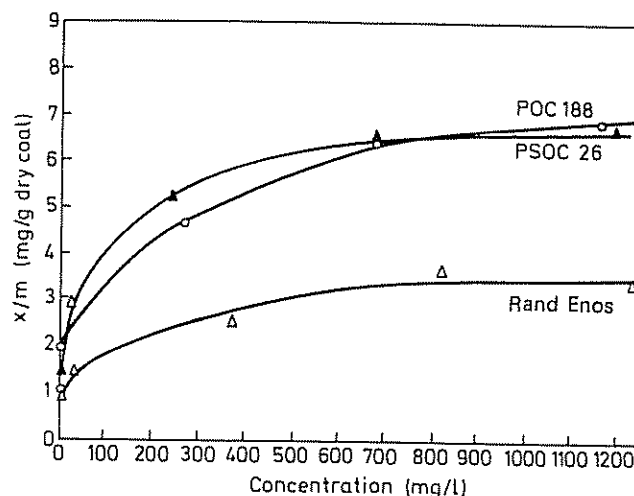
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Figure 13 Methylene blue isotherms at 25°C on water washed samples. Equilibrium time 24 h

molecules. For these two samples, adsorption of methylene blue is much higher compared to that of metanil yellow. Lignites have a rather high proportion of their oxygen content present as carboxyl groups. These groups might prevent the complete coverage of the surface by the acid dye by electrostatic repulsion, whereas the adsorption of the basic dye may be enhanced by specific interaction. It can be seen from *Table 7* that the adsorption of dyes in excess of that which could be accounted by their nitrogen surface area does not occur for any coal except for the lignites. Also specific interaction becomes important only with lignites.

Effect of particle size on equilibrium adsorption

The effect of particle size on adsorption of metanil yellow has been studied with three particle sizes of two samples. The isotherms for PSOC–181 are shown in *Figure 14*. The results with the other sample are very similar. In the case of PSOC–181, the -200 mesh sample adsorbs about 28% more dye than that by the (40 × 70) mesh sample, whereas the corresponding figure for PSOC–191 is 14%. This increased capacity is probably due to increased accessibility brought about by decreased diffusion distance but the advantage may be negated by the difficulty of working with very fine particles in fixed bed operations.

Adsorption of metanil yellow by chars

In some of the OCR processes, chars are obtained as a by-product. It was thought worthwhile to measure the dye adsorption capacity for some of them. Char POC–131 was derived from multistage pyrolysis of HVC coal at temperatures between 32°C and 870°C and partial combustion in the high temperature stage. Chars HT–131 and HT–144 were derived from reaction of

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Table 7 Results of dye adsorption by water washed coals

Coal	N₂ area (m²/g dry)	Metanil yellow adsorption (mg/g dry coal) Limiting value*	Area covered by metanil yellow (m²/g dry)	Percent N₂ area covered by metanil	Methylene blue adsorption (mg/g dry coal) Limiting value*	Area covered by methylene blue (m²/g dry)	Percent N₂ area covered by methylene blue
PSOC–80	7·1	0·14	0·26	3·6	0·80	1·5	22·0
PSOC–127	<1·0	none	–	–	0·10	0·19	–
PSOC–135	<1·0	none	–	–	0·03	0·06	–
PSOC–4	<1·0	0·05	–	–	0·10	0·19	–
PSOC–67	–	0·58	1·0	–	0·30	0·59	–
POC–105	<1·0	1·2	2·2	–	–	–	–
POC–196	<1·0	0·45	0·8	–	0·60	1·1	–
POC–197	9·8	1·7	3·2	33·3	–	–	–
POC–188	29·6	7·5	14·1	47·8	6·7	13·2	44·7
Rand Enos	18·5	4·0	7·5	40·8	3·5	6·8	37·1
PSOC–26	42·0	15·2	28·7	68·4	6·6	13·0	31·0
PSOC–105A	33·4	8·7	16·5	49·5	7·0	13·7	40·1
PSOC–181	45·2	17·1	32·3	71·5	20·8	41·7	90·1
PSOC–185	41·2	8·1	15·3	37·2	–	–	–
PSOC–190	104·0	28·7	54·2	52·2	21·2	41·5	40·0
PSOC–191	67·8	22·0	41·5	61·3	–	–	–
PSOC–192	67·9	16·8	31·7	46·8	–	–	–
PSOC–87	<1·0	10·7	20·2	>100	32·4	63·5	>100
PSOC–89	<1·0	15·0	28·3	>100	26·5	51·9	>100

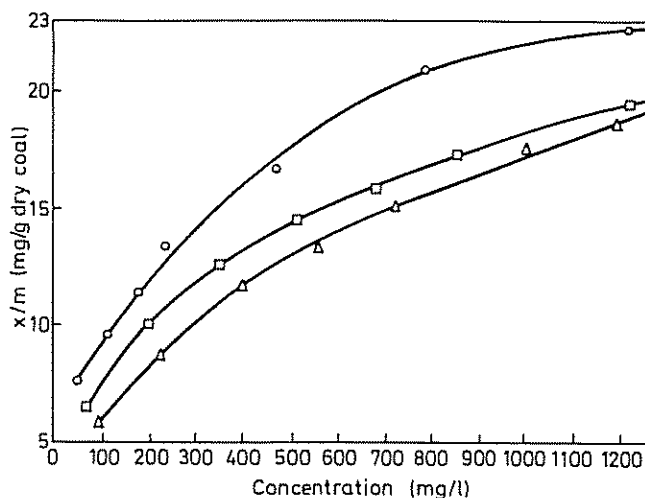* Adsorption at an equilibrium concentration of 1000 mg/l

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Figure 14 Metanil yellow isotherms at 25°C (24h points) on PSOC-181 water washed
O −200 mesh □ (150 × 200) mesh △ (40 × 70) mesh

Table 8 Results of metanil yellow adsorption on chars

Sample	F.C. loss, % of F.C. in pretreated coal feed	Particle size Tyler mesh	N₂ area (m²/g dry)	Adsorption of dye at 1000 mg/l equilibrium dye concentration (mg/g dry)	Area covered by dye (m²/g)	Percent N₂ area covered by dye
POC-131	9	(40 × 70)	84	31·0	58·6	69·7
HT-131	23	(40 × 70)	272	24·8	46·8	17·2
HT-144	33	(40 × 70)	429	100·5	189	44·2
532-D-2	36	(40 × 70)	485	120·0	226	46·7
Active carbon from flue-gas/anthracite reaction	50	(~100)	800	228·0	430	53·8

HVA coal and lignite respectively, with steam and hydrogen at temperatures up to 930°C. Char 532-D-2 was derived from reaction of sub-bituminous coal with steam. Also included in the study was an active carbon obtained from flue-gas/anthracite interaction at 800°C, in this laboratory. An equilibrium time of six days, as was allowed for active carbons, was used. The adsorption data on the chars are given in *Table 8*. The sample HT-131 has only 17% of the pore area available to the dye. The others have about 50% of their nitrogen area available and might be suitable for a liquid phase adsorption process.

Kinetics of adsorption of metanil yellow by coals and carbons
It has been shown that the metanil yellow molecule is the smallest in size amongst the three dyes. It has also been shown that among coals, except for

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lignites, the adsorption of the dye does not appear to be hindered by the presence of acidic groups. Consequently, this dye was selected for studies on the rate of adsorption at 25°C by active carbon No. 3 (28 × 65 mesh), char HT–144 (40 × 70 mesh), and coal PSOC–181 (40 × 70 mesh). All the samples were water washed and dried in a manner described earlier, before rate measurements were undertaken. The data are presented in *Figure 15*. During a period of about 100 min the adsorption varied rectilinearly with the square root of time. Also the adsorption rate increased, not proportionately however, with an increase in starting concentration (C_0) of the dye. As *Table 9* shows, the ratio of the slope (K) of the line (x/m vs $t^{\frac{1}{2}}$) to the square

Table 9 Effect of initial concentration of metanil yellow on rate of adsorption

C_0 (mg/l)	K (mg/g min$^{1/2}$)	$K/C_0^{1/2}$
PSOC–181		
100	0·119	0·012
200	0·160	0·011
HT–144		
100	1·20	0·120
200	1·66	0·117
Carbon No. 3		
100	3·80	0·380
200	5·37	0·379
500	7·35	0·329
2500	14·1	0·282

root of the initial concentration (C_0) is nearly constant for these data. The same dependence of rate on initial concentration has been reported earlier by Carrell and Weber[9] in the case of the dodecylbenzene-sulphonate/active-carbon system. The parameter $K/C_0^{\frac{1}{2}}$ does not appear to have any theoretical significance. It is nearly constant if the change of C_0 is within a factor of two for the three materials studied. In the case of carbon No. 3, where C_0 was varied over a greater range, $K/C_0^{\frac{1}{2}}$ clearly decreased with increasing concentration, however. It can, nevertheless, be accepted as a useful rate parameter, characteristic of the adsorbent, under comparable experimental conditions. On this basis, it can be concluded that coal PSOC–181 performs about one thirtieth as efficiently as the active carbon; whereas the efficiency of the char is about one third that of the active carbon.

SUMMARY

There is definite evidence to indicate that a portion of the mineral matter of coals interacts with dye molecules. The adsorption by coals which have been refluxed with distilled water can be correlated with the surface area available to the dye molecules. Except for the lignites, adsorption of dyes is not influenced by oxygen groups on the surface of coals. From the equilibrium studies, the adsorption capacity of the more promising coals is about one fifteenth to one twentyfifth that of typical commercial granular active carbons. From kinetics studies, the rate of initial dye uptake on the better coals is about one thirtieth that on active carbons.
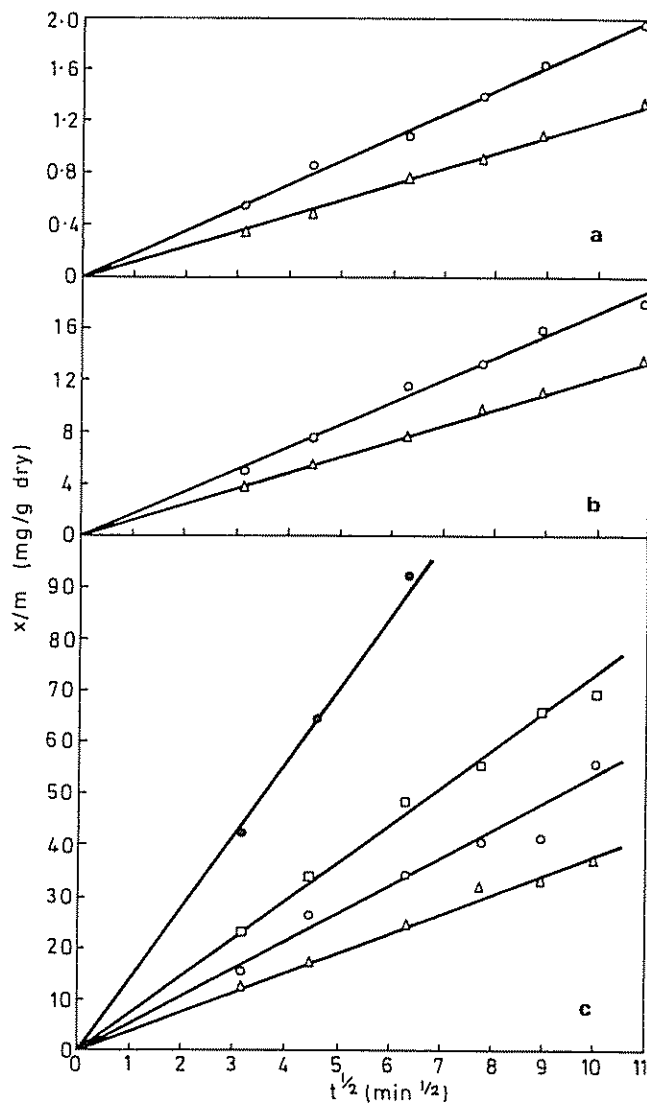
Figure 15 Kinetics of metanil yellow adsorption a PSOC–181
(4 × 70 mesh) b HT–144 (40 × 70 mesh) c Carbon 3 (28 × 65 mesh)
  ○ $C_0 = 2700$ mg/l   △ $C_0 = 100$ mg/l
  ● $C_0 = 2500$ mg/l   □ $C_0 = 500$ mg/l

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REFERENCES

1 Carlton, S. S., Marr, Jr., C. M., Foye, C. W., Owens, C. K., Chiancone, R. A., and Raynes, B. C., U.S. Department of the Interior, Office of Coal Research, Research and Development Report No. 12, 1965
2 Donahue, B. A., Bucklen, O. B., and McClung, J. D., Technical Report No. 33, Coal Research Bureau, West Virginia University, 1968
3 Hassler, J. W., 'Active carbon', Brooklyn Chemical Publishing Co., 1951
4 Graham, D., *J. Phys. Chem.*, 1955 59, 896
5 Fieser, F. L., and Fieser, M., 'Organic chemistry', Reinhold, New York, 1956
6 Metcalfe, III, J. E., Ph.D. Thesis, Pennsylvania State University, 1965
7 Brunauer, S., 'The adsorption of gases and vapors', Princeton University Press, New Jersey, 1943
8 O'Gorman, J. V., and Walker, Jr., P. L., Office of Coal Research Report SROCR–5, 1 July, 1969
9 Carrell, M. J., and Weber, Jr., W. J., PHS Publication No. 999–WP–11, 1964