

EFFECTIVE SURFACE AREAS OF COALS MEASURED BY DYE ADSORPTION

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INTRODUCTION

Coals are well known to be more or less porous structures, but just how much porosity and surface area is measured depends very much on the measurement technique. For example, even though N_2 and CO_2 molecules are essentially the same size, surface areas measured by CO_2 adsorption are $>100 \text{ m}^2/\text{g}$ for most coals, but less than $10 \text{ m}^2/\text{g}$ when measured by N_2 adsorption. This is attributed to the fact that the N_2 measurements are made at 77°K while the CO_2 measurements are made at much higher temperatures, up to 298°K . That is, most of the pores in coals are so small that rate of diffusion of even such small molecules into the pores becomes a limiting factor. This is clearly because most of the surface area in coals is in micropores, $<2\text{nm}$ diameter, and even in ultra-micropores, $<0.8\text{nm}$ diameter (1).

Similarly, use of other small molecules such as methanol vapor (2, 3), water, or butane (3) at temperatures of $273\text{--}298^\circ\text{K}$ also gives high surface areas of $30\text{--}400 \text{ m}^2/\text{g}$, compared to nitrogen surface areas of only $0.1\text{--}1.5 \text{ m}^2/\text{g}$ for the same coals. This quotation from (2) is relevant: "It is apparent from past work that no absolute method of total surface area measurement exists and that any method will only give the surface area accessible to the adsorbate molecules at the temperature of adsorption." A very similar statement is made by Fuller (4).

Since most coal processing is done in aqueous slurries, adsorption from water is generally of more practical interest than adsorption of vapors. A considerable number of papers dealing with adsorption from aqueous solutions are in print and we can only give some principal conclusions here. The solutes examined include: 1) a variety of surfactants (5-9), which are of interest for dewatering and for coal/water slurries; 2) alcohols which are used as frothers (10-14); 3) polysaccharides such as dextrin and guar, used for coal depression (15, 16); 4) substituted dioxanes (flotation promoters) (17); 5) phenol (10, 18-20); 6) organic acids (14, 21); 7) dyes (22, 23); etc.

In these various publications, establishment of equilibrium adsorption is stated to require anywhere from one hour to >100 hours. One point of agreement is that adsorption of most reagents on most coals is generally within the range $0.1 - 10 \text{ mg}$ of reagent per gram of coal, for a wide variety of types of reagent. Also, it is consistently concluded that nonionic molecules, e.g. alcohols or weak acids, adsorb via their hydrocarbon portion and adsorption therefore decreases as coal is oxidized, although adsorption of stronger acids can occur via the polar end and increase with oxidation. Ionic surfactants apparently adsorb both on fresh and on oxidized surfaces, either via electrostatic or hydrophobic interactions (5, 6).

An extensive study of dye adsorption on coals is given by Nandi and Walker (23). Using 24 hour equilibration times, adsorption for either an anionic dye, metanil yellow, or a cationic dye, methylene blue was found to be approximately related to nitrogen surface areas for most of the coals examined. Two obvious exceptions, however, were lignites, where dye adsorptions were approximately 20-100 times those expected from nitrogen surface areas.

Most studies of adsorption are concerned with "equilibrium" measurements. Since equilibrium, however, usually requires a day or more, such results may have little relevance to most real coal processing problems, where the time that the coal spends in an aqueous slurry is generally less than one hour (an obvious exception is the case of coal/water slurries, where coals are expected to be stably dispersed in aqueous slurries for weeks or months). Our primary interest has been to examine adsorption behavior especially at short contact times, ten minutes to an hour, to determine whether such measurements might give useful data on effective surface areas - i.e., the surface that would be accessible to reagents within times comparable to those typical of most coal processing. Accordingly, most of our emphasis is on the effect of time on adsorption, rather than on traditional adsorption isotherms.

Although most literature on cationic dye adsorption (mostly on carbons) uses methylene blue, it happened that we originally used safranin O instead because this dye was reported to be useful in distinguishing oxidized coals from fresh coals (24). Many of our experiments were repeated using methylene blue (in water), with very similar results. It was noted early that swelling of coals in water was common, especially for more oxidized or lower rank coals, and adsorption experiments were also done in another solvent, namely methanol. This produced quite striking differences for some coals.

EXPERIMENTAL

For the aqueous dye solutions, the amount of mixing during adsorption had a considerable effect on the results. Best mixing appeared to be when bottles containing dye solutions plus coal were placed on rollers. A shaker generally gave lower results, since the coals tended to stay at the bottom of the bottle. On the other hand, more vigorous mixing with a magnetic stirring bar gave some results that were far too high, especially in the case of the oxidized coals, indicating breakup from the combination of swelling by the water and the mechanical agitation. For example, stirring of Coals B or C for only an hour in aqueous solution gave some apparent adsorptions greater than 40 mg/g. Adsorptions from methanol solution were little affected by mixing conditions.

Except for the adsorption isotherms (shown here only for Coal A), adsorptions were done from 100ppm safranin O (Kodak Chemical) solutions at room temperature ($23 \pm 2^\circ \text{C}$), with from 0.1 to 10.0 gm of coal per 100ml of solution, as necessary to give a readily measurable adsorption. Coals were afterwards separated either by centrifuging

or rapidly filtering through a small millipore filter attached to a plastic syringe. Dye concentrations were determined from absorption at 520nm, after appropriate dilution to less than 10ppm.

RESULTS AND DISCUSSION

Adsorption isotherms for Coal A (Fig. 1) are shown from both water and methanol for 16 hour and for one hour adsorptions. From Fig. 2, 16 hours appears adequate to give "equilibrium" adsorption from the aqueous solutions. The one hour curve in Fig. 1 is clearly far from equilibrium, but it is considered significant that a surface area corresponding to just under 0.4 mg/g adsorption is very readily covered by the dye and further adsorption does not take place until high concentrations are reached or longer times are allowed; N_2 area of this coal is 0.4 m^2/g . Isotherms from methanol solutions are nearly independent of time and the maximum adsorption is not too different from that which is quickly attained from water solutions.

The oxidized Coals B and C show the most striking differences between adsorption from water or from methanol. As noted above, such coals are considerably swollen by water; for Coal C, adsorption from water is more than an order of magnitude greater than from methanol. From methanol, there is again nearly a 1:1 correspondence between N_2 surface area and the amount of dye that is quickly adsorbed: for Coal B, S.A. = 1.2 m^2/g , while adsorptions are 1.0 and 2.1 mg/g at ten minutes and one hour, respectively; for Coal C, S.A. = 0.67 m^2/g , and adsorptions are 0.23 and 0.47 mg/g at ten minutes and one hour, respectively.

To demonstrate that the steep initial increase in adsorption on Coals B and C from aqueous solution was due to swelling by the water rather than just slow diffusion of the dye, the following comparison was made: For Coal B, adsorption from 100ppm aqueous safranin for one hour was 13.5±1.5 mg/g; similarly, adsorption from 100ppm aqueous safranin for ten minutes was 5.4±0.5 mg/g; contacting the coal with water for 50 minutes, followed by only ten minutes contact with safranin gave adsorptions of 12.5±1.5 mg/g (i.e., coal plus water for 50 minutes, then an equal volume of 200ppm safranin was quickly mixed in and kept another ten minutes). Contact with the water is clearly more important in determining adsorption on such coals than is diffusion of the dye. Such swelling must also be responsible for the high adsorption on lignites reported by Nandi and Walker (23), as was suggested by them, but not demonstrated.

For the PSOC coals 217 and 315, adsorptions from aqueous solutions at short times again give numbers that are close to the nitrogen surface areas for these coals, 1.6 and 1.4 m^2/g , respectively. For PSOC 217, adsorption from methanol gives much lower values; it may be that the water helps to open up the pores, but in an experiment similar to that done with Coal B above, we found no obvious swelling.

Note that all of the coals discussed above had quite low surface areas. We did have two other coals with somewhat higher surface areas (3.4 and 7.1 m^2/g) and we also examined two pure clay minerals,

kaolin and illite, and two natural coal/clay mixtures. These latter four samples had surface areas from 15 to 61 m²/g; unlike high area coal samples, however, the surfaces of the clay would be all external and readily accessible, and the surface areas of the mixtures were undoubtedly determined mainly by the clay minerals. As expected from non-porous particles, adsorption on these samples was essentially constant after only an hour. Quantities of safranin adsorbed from the aqueous solutions again showed a close correspondence with the nitrogen surface areas. Adsorptions from methanol on these clays or clay-rich samples gave distinctly lower capacities, by factors of four to six.

Short term safranin adsorption data for all samples in Table 1, from aqueous or from methanol solutions, are summarized in Figs. 5 and 6, respectively. In Fig. 5 especially, the correspondence between safranin adsorptions from water and nitrogen surface areas is surprisingly good. The only two points that clearly do not fit in are for the Coals B and C, where anomalously high adsorptions were shown to be related to swelling by water.

Correlation of N₂ area with adsorption from methanol solutions shows the general trend, but is not as good as from water. Many of the samples show significantly less adsorption from methanol. In the case of highly oxidized coals, however, these lower values from methanol were seen to be much closer to the N₂ areas.

From the correlation in Fig. 5, it happens that 1.0 mg/g of adsorbed safranin is essentially equivalent to 1.0 m²/g of N₂ surface area. This would require an area of only 0.58 nm² per safranin molecule, which is considerably less than the 2.2 nm² we estimate for the molecule lying flat. The 0.58 nm² would be consistent with an edge adsorption, or alternatively, may indicate multilayer adsorption (3-4 layers stacked flat). Since there is no apparent reason why a 3-4 multilayer configuration would be particularly stable, an edge adsorption is more likely.

Our coal samples were all of rather low surface areas, 0.2-7 m²/g; the only higher surface areas were for essentially non-porous particles. It is expected that as coal surface areas increase above about ten m²/g, pores are necessarily smaller and less accessible and the ratio of dye adsorbed to N₂ area must decrease. This is essentially what was found in (23) for coals with surface areas of 10-100 m²/g. We expect to extend this present work to also include higher surface area coals. In addition, we have some preliminary results using adsorption of a proprietary reagent that selectively adsorbs only on the coals and not on the ash minerals, permitting a separation of the contributions of the coal and ash to the surface area.

SUMMARY

Coal surfaces that are readily accessible to adsorption by safranin are found to correlate well with N₂ surface areas, with adsorption of 1.0 mg safranin per gram of coal corresponding to essentially a

surface area of $1.0 \text{ m}^2/\text{g}$. Highly oxidized coals were found to swell considerably in water, with correspondingly increased adsorption. Areas of such coals can be estimated by adsorption of safranin from methanol solutions.

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Table 1. Samples Used

Sample	%C	%H	%O	%N	%S	%Ash	N ₂ area m ² /g
Coal A -Virginia	83.0	4.8	10.7	0.9	0.6	7.1	0.4
Coal B -W.V.stockpile	67.4	3.6	27.7	0.9	0.5	16.2	1.2
Coal C -British Columbia surface outcrop	75.4	3.9	19.9	0.6	0.2	18.2	0.67
PSOC 217 -Kentucky	78.9	5.6	8.0	1.8	5.5	17.7	1.6
PSOC 315 -Colorado	76.7	5.8	14.8	2.0	0.8	11.6	1.4
Coal A, oxidized, 200hrs.@150°C	73.7	3.3	21.5	0.9	0.6	6.4	3.4
Coal D -Arizona							7.1
Coal/Ash Mix 1-Kentucky						50.	30.6
Coal/Ash Mix 2-Kentucky						33.	15.1
Kaolin							23.2
Illite							61.2

Figure 1. Adsorption isotherms for safranin on Coal A, from water and from methanol solutions and for 16 hour and one hour contact times.

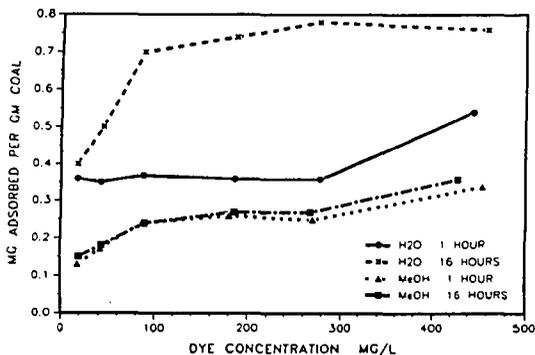
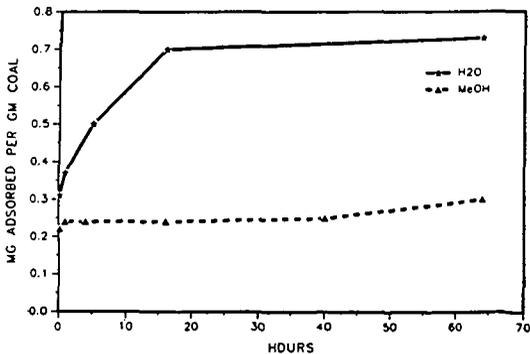


Figure 2. Adsorption on Coal A vs. time, from 100ppm safranin solutions in water and in methanol.



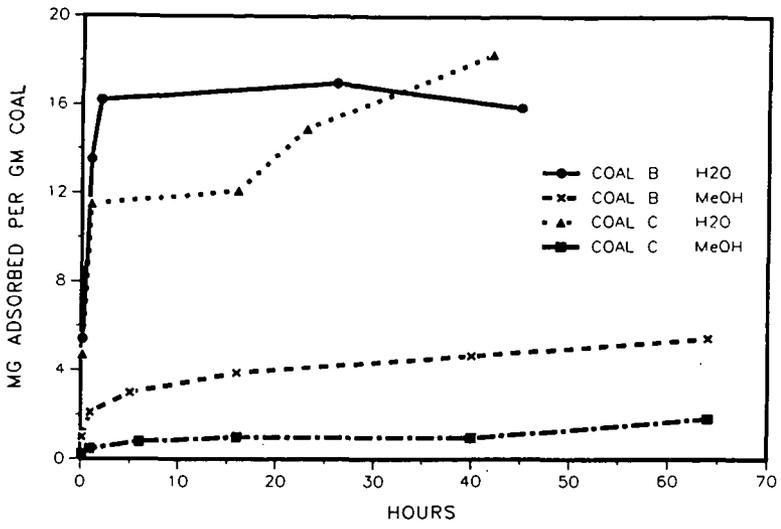


Figure 3. Adsorption on Coal B and Coal C vs. time, from 100ppm safranin solutions in water and in methanol.

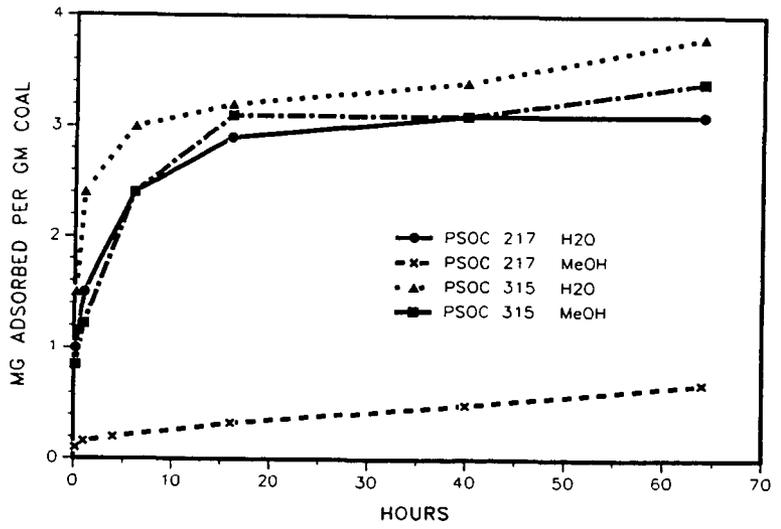


Figure 4. Adsorption on PSOC 217 and PSOC 315 vs. time from 100ppm safranin solutions in water and in methanol.

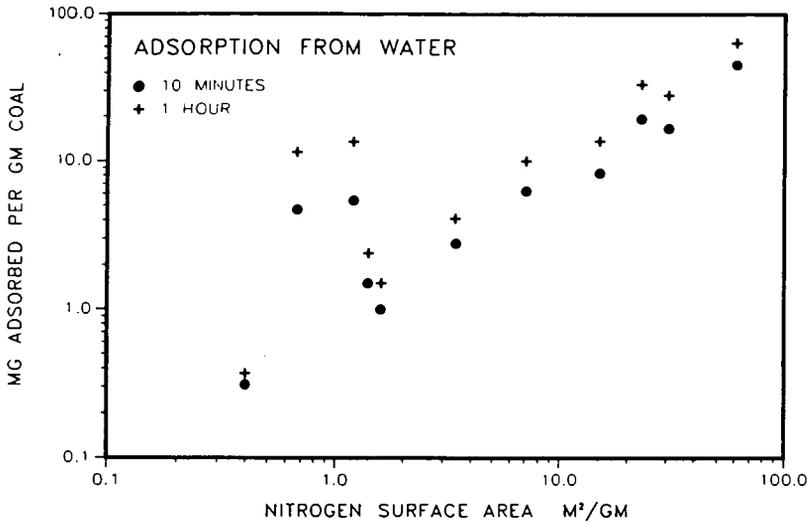


Figure 5. Ten minute and one hour adsorptions of 100ppm safranin from water onto samples of Table 1 vs. nitrogen surface area.

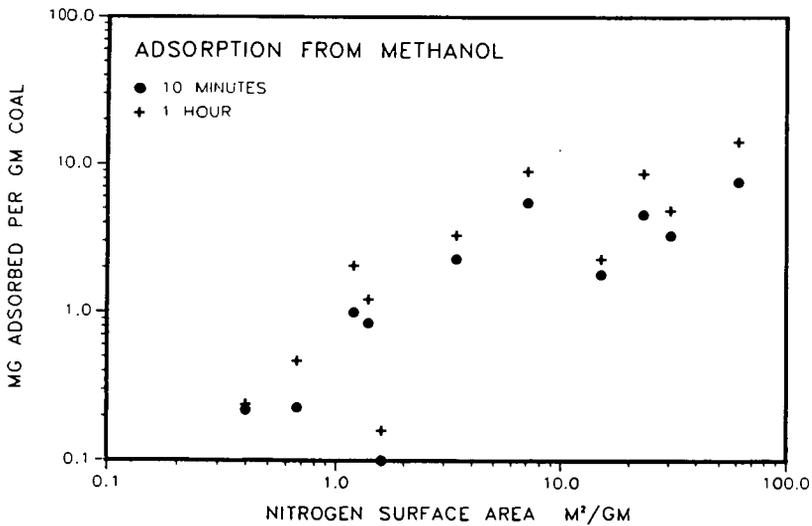


Figure 6. Ten minute and one hour adsorptions of 100ppm safranin from methanol onto samples of Table 1 vs. nitrogen surface area.