

## CHARACTERIZATION OF MINERAL AND COAL SURFACES BY ADSORPTION OF DYES

Bogdan J. Slomka, M. Robert Dawson and William H. Buttermore,

Ames Laboratory, Iowa State University, Ames, Iowa 50011

### ABSTRACT

A dynamic method is described for dye adsorption measurements to characterize mineral and coal surfaces for the evaluation of coal cleaning processes. Samples of increasing mineral content were prepared by density separation of a narrowly sized (300 to 425  $\mu\text{m}$ ) wet-sieved coal. The rates and extents of the adsorption of ionic dyes on Illinois No. 6 coal were observed to be highly dependent on mineral content and particle size of ground coal samples. A linear correlation was observed between the adsorbed quantity of dye and the total mineral content of coal samples. Dry-sieved coals were found to be coated by fine material of high mineral ash content which adsorbed greater than 20 times more methylene blue per gram than wet-sieved particles. In preliminary experiments with methylene blue dye, clay was found to adsorb significantly more dye than quartz, pyrite, calcite or low-ash specific gravity fractions of coal.

### INTRODUCTION

Adsorption of dyes from solutions has been extensively used for the determination of surface areas and examining the accessibility of porous structures to dye molecules; and has become a standard practice in the qualitative evaluation of active carbons in industry (1, 2, 3). It is well known that surface properties of solid adsorbents govern the adsorption of molecules from liquid solutions. Generally, increasing the surface polarity of active carbons (e.g., by oxidation) causes an increase in adsorption of the more polar component in binary liquid mixtures (4). For instance, adsorption of stearic acid by nonporous carbons, free from surface oxygen complexes, results in a closely-packed monolayer, whereas on surfaces bearing oxygen complexes, the formation of a complete monolayer is not accomplished, even at the highest possible concentrations of the acid solution (5). Similarly, surface acidity of active carbons strongly influences adsorption of aromatic amines and phenol derivatives from organic solutions (6).

For coals, it has been argued that a portion of the mineral matter of coal, predominantly pyrite and alkali metal compounds, interacts with dye molecules, affecting adsorption results. However, adsorption of dyes is not influenced by surface oxygen groups, except in the case of lignites (7).

Literature references dealing specifically with the use of adsorption methods to evaluate either cleanability of coals or the effects of coal-cleaning processes on coal surface properties have not been found. However, adsorption of surfactants has been used for predicting how easily a stable slurry can be made using a given coal (8). With careful selection of an adsorbate (with respect to polarity, acidity, surface activity, molecular area in the adsorbed state, etc.), adsorption from solutions could become a sensitive 'molecular probe' for investigating coal and mineral surfaces. In particular, adsorption from liquid phases appears to

have the potential to become a useful tool for detecting changes in surface properties (e.g., hydrophobicity) which are important for coal preparation processes.

The primary goal of this study was to develop a practical method for quantifying the selective adsorption of dye on coal and mineral surfaces. In these preliminary tests, adsorption profiles were obtained for: coal samples of different total mineral content, specific mineral species, and coal samples of different particle size.

## EXPERIMENTAL

### Materials

Non-buffered 64.0 mg/l aqueous solutions of methylene blue were prepared by drying the dye under nitrogen at 110°C for 2 hours and dissolving in deionized distilled water.

A bulk sample of coal with a narrow range of particle size was obtained by dry-sieving Illinois No. 6 coal to obtain 330 to 425  $\mu\text{m}$  coal particles. Test samples were then prepared by wet-sieving to remove undersize material from the particle surfaces. Samples of increasing mineral content were prepared by density separation of the wet-sieved particles using aqueous solutions of CsCl at several specific gravities between 1.30 and 1.80 g/cc. Mineral samples for analysis included a single pyrite cube from Ward's Natural Science Establishment; kaolinite flint-clay from A. P. Green quarries of Mexico, Missouri; and single crystals of calcite and quartz obtained from the Department of Earth Sciences at Iowa State University. Mineral samples were ground using a mortar and pestle, and 330 to 425  $\mu\text{m}$  particles were obtained by wet-sieving. Preliminary tests were performed to determine the applicability of the dynamic adsorption technique to fine particle sizes. Illinois No. 6 coal was pulverized and dry-sieved to obtain samples smaller than 150  $\mu\text{m}$  and 44  $\mu\text{m}$ .

### Procedures and Analysis

A continuous-flow apparatus was developed for dynamic measurements of adsorption from liquid phases on solids. Figure 1 shows the configuration of the main components. In a typical experiment, a pre-weighed sample of coal is placed in a sample cell and fixed between two 0.5- $\mu\text{m}$  stainless steel frits. The sample cell is then connected to a six-port switch valve and evacuated to remove air. The valve is set initially to direct the solution of dye to by-pass the cell containing the sample, causing it to flow directly through the ultraviolet/visible detector (Varian UV-50). As soon as a baseline is established for the dye solution, the flowing solution is directed through the sample of coal to the UV/Vis detector. The absorbance measured for the effluent leaving the sample cell is due only to dye not adsorbed by the coal sample. The apparent absorbance is recorded at a fixed wavelength as a function of time using an A/D converter at a sampling rate of 2  $\text{sec}^{-1}$ . This dynamic method of adsorption measurement allows for continuous replacement of the fluid phase in contact with the coal sample, which is not possible in a closed, static system. The rates of adsorption can be continuously measured as a function of time, giving characteristic profiles of adsorption rate, while the total adsorbate uptakes are obtained by integration of the rate profiles over the

time of adsorption. The detector response to dye concentration was linear for the concentrations and wavelengths used in the experiments. The detector was operated in the visible range at 610 nm. Based on preliminary results, two flow rates of solutions were selected, 1 and 0.5 ml/minute, according to the sample size of the materials tested.

To evaluate the adsorptive components of coal and mineral surfaces, coal samples of uniform particle size and increasing mineral content were analyzed. Total mineral content was determined by standard ash analysis. Samples with very low ash content were used to approximate a non-mineral coal surface. To evaluate specific mineral adsorptive characteristics, mineral samples of uniform particle size and composition were analyzed. Ground coal samples of different mean particle size were analyzed to determine the effect of particle surface area.

## RESULTS AND DISCUSSION

Figure 2 shows the correlation between dye uptake and available mineral surface (measured as total ash content) for several coal samples. Quantitative data is presented in Table 1. As shown in Figure 2 and Table 1, increased dye uptakes and adsorption rates are observed for coals with higher mineral content. This implies that methylene blue dye is preferentially adsorbed on mineral surfaces. Figure 3 presents adsorption profiles for samples of different specific gravity (3a), different mineral species (3b), and different particle size (3c). In each graph, the adsorption curve for the head sample of wet-sieved, 300 to 425  $\mu\text{m}$  Illinois No. 6 coal is provided for reference. Data presented in Figure 3a suggest that specific gravity fractions heavier than 1.55 g/cc contain highly adsorbing constituents. Tests are currently underway to identify these constituents from known components of coal mineral matter by testing their behavior during dye adsorption. Figure 3b presents the results of methylene blue adsorption on several common coal mineral species compared to the adsorption pattern for the 300 to 425  $\mu\text{m}$  wet-sieved Illinois No. 6 coal head sample. Based on these data, clay minerals are the most probable single constituent responsible for the high adsorption values reported. Contrary to suggestions by Nandi and Walker (7), pyrite showed the smallest adsorption per gram of sample. In our experiments, pyrite was found to adsorb less methylene blue (Figure 3b) than the coal fraction of 1.30-1.35 specific gravity (Figure 3a).

Early attempts to correlate the extent of adsorption with total coal mineral content using dry-sieved coal samples were unsuccessful. It was later determined that fine-sized material high in mineral content adhered to larger particles and very strongly adsorbed the dye. Figure 3c shows the methylene blue adsorption profiles for dry-sieved and wet-sieved samples of the 300 to 425  $\mu\text{m}$  Illinois No. 6 coal. The integrated uptakes of the dye (Table 1) indicate that the coating of fine material, constituting 20.2% by weight of the dry-sieved sample, adsorbs about 20 times more dye than the wet-sieved coal. Consequently, for later experiments only wet-sieved coals were used.

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Table 1. Adsorption of Methylene Blue Dye on Minerals and Illinois No. 6 Coal (adsorption time: 10 minutes)

<u>Sample</u>	<u>Adsorption, mg/g</u>
<b><u>Minerals</u></b>	
Pyrite	0.017
Quartz	0.030
Calcite	0.135
Clay	0.577
<b><u>Coal</u></b>	
- 45 um, dry grind	4.07
-150 um, dry grind	3.09
-425 + 300 um	
dry-sieved	2.50
wet-sieved	0.51
<b><u>Specific Gravity Fractions of Coal</u></b>	
> 1.80	1.15
-1.80 + 1.65	0.671
-1.65 + 1.55	0.585
-1.55 + 1.50	0.535
-1.50 + 1.45	0.462
-1.45 + 1.40	0.357
-1.40 + 1.35	0.291
-1.35 + 1.30	0.185
< 1.30	0.142

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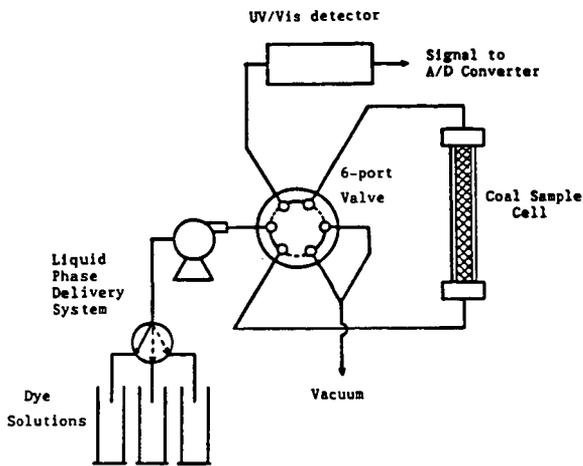


Figure 1. Continuous Flow Dye Adsorption Apparatus

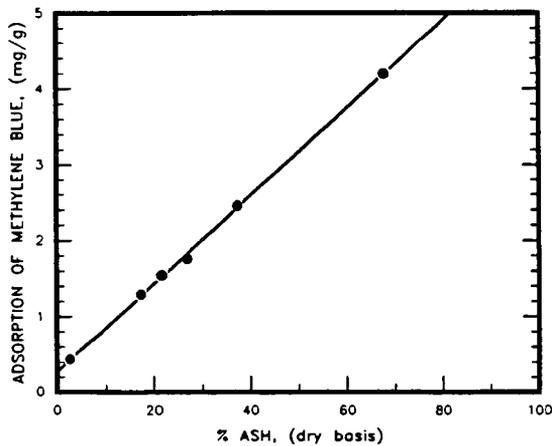
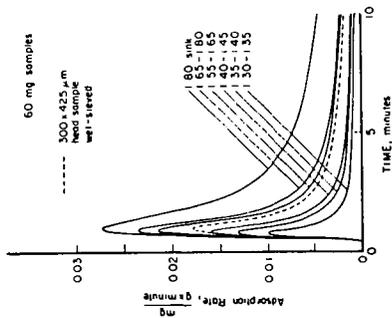
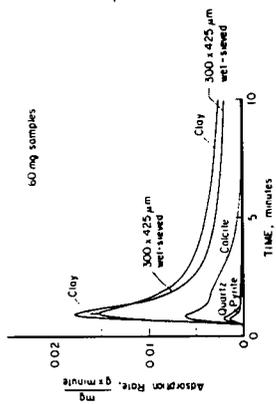


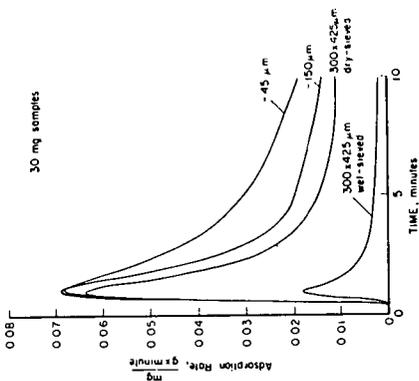
Figure 2. Dye Uptake vs Coal Ash Content (Adsorption time: 6 hours, Flow Rate: 1. ml/min.)



3a. Specific Gravity



3b. Mineral Species



3c. Particle Size

Figure 3. The Effects of Sample Characteristics on Methylene Blue Dye Adsorption.