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Uptake of Cationic Dyes by Sulfonated Coal: Sorption Mechanism

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Mechanistic aspects of sorption of Rhodamine B and Methylene Blue by sulfonated coal have been investigated. The coal surface before and after sulfonation has been characterized with the help of cation-exchange capacity measurements and infrared (IR) spectroscopy. These studies indicate that sulfuric acid treatment not only incorporates a SO₃H group on the coal surface but also oxidizes both aliphatic and aromatic fractions. The IR spectroscopy has been extensively applied to locate the active sites on the surface of the sorbent and the participating functional groups of the dye molecule. Graphical models of the sorbate–sorbent interaction have been proposed. These models are applied to explain the variation in the uptake potential of these dyes by sulfonated coal.

Introduction

Of the physicochemical processes, adsorption is gaining attraction in colored effluent management (Nassar and El-Geundi, 1991). Partly, it can be due to the limitations of chemical coagulation and flocculation to yield good-quality effluent besides causing sludge handling problems. Adsorption offers a cleaner technology, free from sludge handling problems and producing a high-quality effluent after treatment. However, economical nonviability of conventionally used activated carbon has restricted its use particularly in developing countries. It warrants a need to investigate new materials as a replacement for activated carbon.

Mittal and Venkobachar (1989) identified sulfonated coal as a potential sorbent for the uptake of Sandolan Rhodine, an acidic dye, and Methylene Blue, a basic dye. A simple mathematical model was proposed (Mittal and Venkobachar, 1993) to determine the reversibility of sorption of dyes onto the sulfonated coal. However, in the case of colored wastewaters, the dyes present are of varying chemical characteristics and, accordingly, interact differently with sorbent. Thus, delineation of the mechanistic aspects of sorbent–sorbate interaction can lead to the better prediction and modeling of the dye sorption system. Besides, the mechanistic knowledge can assist in modifying the sorbent surface by employing suitable chemical treatment, leading to its enhanced dye sorption potential.

The aim of this paper is to report the results of study carried out to delineate the interaction between the dye molecule and sulfonated coal and to highlight the use of infrared spectroscopy in such investigations.

Experimental Section

Giridih bituminous coal (GBC) from Giridih (India) was sulfonated as per the procedure given by Michelson et al. (1975). The treatment was carried out by adding 600 mL of concentrated sulfuric acid/100 g of GBC. The mixture was treated in a water bath at 90 ± 2 °C for 12

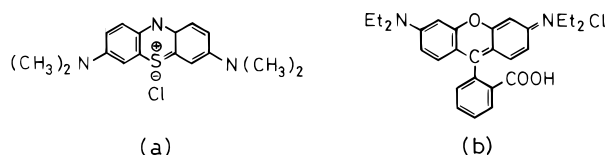


Figure 1. Structural formula of (a) Methylene Blue and (b) Rhodamine B.

h with intermittent stirring. After this, the sulfonated coal was washed with distilled water to remove any loosely bound acid. The dried sulfonated coal (s. coal) was again sieved to 270 μm (geometric mean size).

Two cationic dyes, Methylene Blue (MB; basic blue 9, CI 52015) and Rhodamine B (RB; basic violet 10, CI 45170), were selected. The structures of these dyes are shown in Figure 1.

Batch isotherm experiments were conducted, first, to establish the dye removal potential of s. coal and, second, to determine the dosage of sorbent required to fully saturate the sorbent for subsequent infrared spectroscopy (IR). These experiments were conducted by taking 50 mL of a dye solution (100 mg/L) in (125 mL capacity) glass bottles, and different sorbent doses were added to each bottle. The residual dye concentrations were determined after contacting the sorbate–sorbent mixture for a predetermined equilibrium time, i.e., 14 h.

The cation-exchange capacity (CEC) of the sorbent was determined as per the Salmon and Hale (1959) method. A Na₂SO₄ solution (0.25 M) was passed through a column containing 1.0 g of sorbent at the prescribed rate of 100 mL/h, and the collected effluent, which contained H⁺ replaced from the sorbent, was titrated with 0.1 N NaOH until the phenolphthalein end point.

Results and Discussion

Adsorption is a surface phenomenon. Hence, to understand sorbent–sorbate interaction, it is imperative to characterize the sorbent surface. Infrared (IR) spectroscopy can be profitably used to identify the surface functional groups of the sorbent. The IR spectra

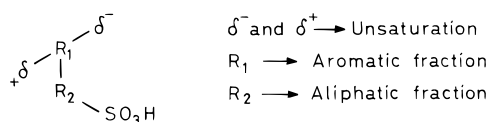
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of GBC and s. coal were analyzed to study the surface modifications after sulfonation.

Characterization of the Coal Surface after Sulfonation. IR spectra of GBC and s. coal are shown in Figure 2. The presence of characteristic SO_3H absorption bands at 1215, 1050, and 605 cm^{-1} (E1, G1, H1) in the infrared (IR) spectra of s. coal in Figure 2b and the absence of these bands in the IR spectra of GBC in Figure 2a indicate the incorporation of a SO_3H group on sulfuric acid treated coal. Besides, the following observations are also made from these figures (Figure 2a,b): (a) increased intensity of the OH^- absorption band for s. coal as compared to coal at 3440 cm^{-1} ; (b) decreased intensity of the saturated aliphatic CH_x for s. coal as compared to GBC at 2950 cm^{-1} and increased intensity of the unsaturated aliphatic CH_x band at 1370 cm^{-1} for s. coal, indicating an increase in the degree of unsaturation on the coal surface after sulfonation; (c) absorption band at 1615 cm^{-1} for GBC, which can be assigned for aromatic ring vibrations has decreased in intensity in the IR of s. coal, indicating oxidation of the aromatic fraction by sulfuric acid treatment; (d) appearance of a shoulder at 1720 cm^{-1} and increase in the intensity of the 1115 cm^{-1} absorption band for s. coal, indicating the oxidation of phenoxycarbonyl after sulfonation. The above observations indicate that sulfuric acid treatment has oxidized CH_x in the aliphatic chain of GBC besides sulfonating its aromatic fraction.

The quantification of the SO_3H group, the cation exchanger of s. coal, could be done by estimating the increase in sulfur content of GBC after sulfonation. The sulfur content was estimated by the Eschka method (ASTM, 1989). It is 14.5 and 32.5 mg/g for GBC and s. coal, respectively. This corresponds to an increase in CEC of coal by 0.57 mequiv/g of coal. However, the observed increase in the CEC is 0.79 mequiv/g of coal. Therefore, the sulfonation process appears to result in oxidation of aliphatic groups on the coal surface as indicated by the increased CEC, in addition to imparting a SO_3H group onto the surface. This further supports the inferences drawn from the analysis of IR spectra of GBC and s. coal; i.e., sulfuric acid treatment of GBC results in sulfonation of the aromatic fraction besides the oxidation of aliphatic groups, which finally leads to a higher degree of unsaturation of the coal surface. On the basis of the above-mentioned observations, the GBC surface after sulfonation can be chemically depicted as shown:



Mechanism of Dye Sorption. It is postulated that the surface functional groups of sorbent interacting with the sorbate will have either a shift or change in the intensity of their corresponding IR absorption bands. The IR spectra of MB, s. coal, and s. coal loaded with MB are presented in Figure 3.

The SO_3H absorption bands at 605 (B1) and 1220 cm^{-1} (A1) have been shifted to 550 (B2) and 1180 cm^{-1} (A2) after sorption, indicating possible electrostatic interaction between SO_3H and the dye cation. Further, the intensity of the C-S absorption band (C1) at 485 cm^{-1} increases after sorption (C2), indicating interaction between the thiazene group (MB chromophore) and the aliphatic cation chain and an increased fraction

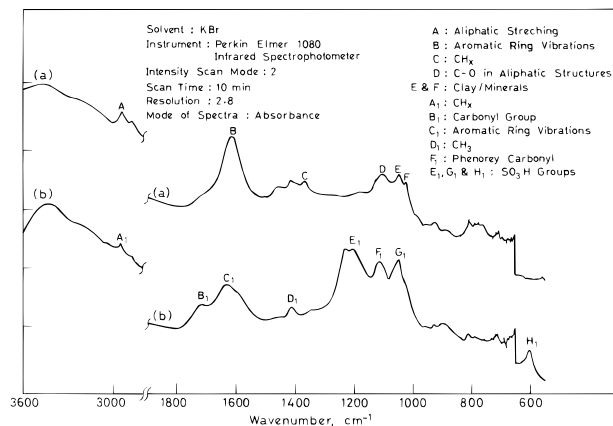


Figure 2. Infrared spectra of (a) coal and (b) s. coal.

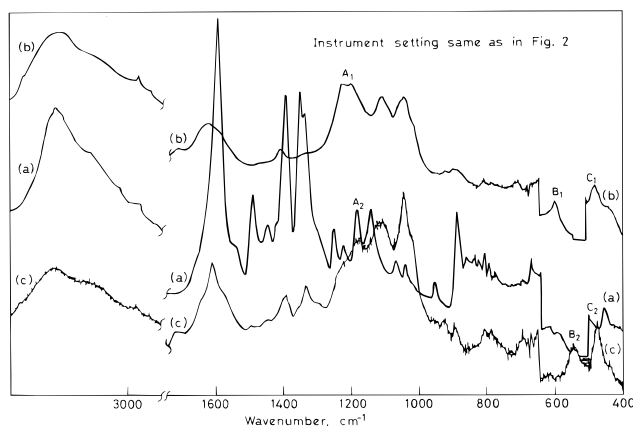


Figure 3. IR spectra of (a) Methylene Blue, (b) s. coal, and (c) Methylene Blue + s. coal.

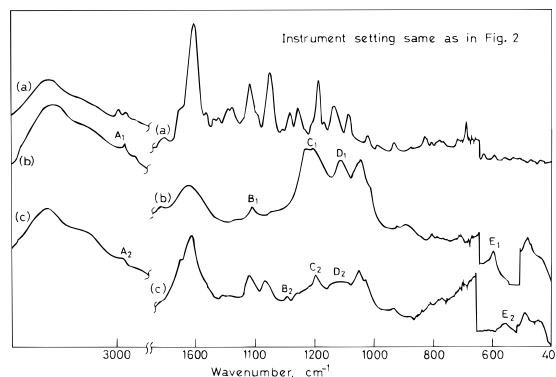


Figure 4. IR spectra of (a) Rhodamine B, (b) s. coal, and (c) Rhodamine B + s. coal.

of the C-S group on s. coal loaded with sorbate. It can be depicted as shown:

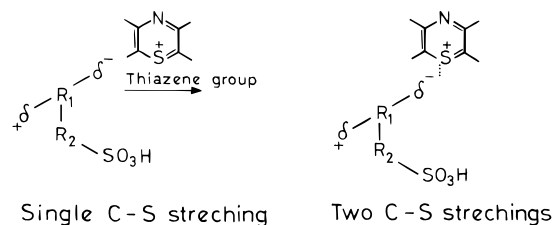


Figure 4 presents the IR spectra for the RB, s. coal, and s. coal loaded with RB. The following observations can be made:

(a) The absorption band E1 at 605 cm^{-1} corresponds to C-S stretching (CSO_3H); it has been shifted to E3

Table 1. Freundlich Isotherm Parameters

dye	K	1/n	equation	saturation capacity, mg/g
RB	6.7	0.50	$\ln(x/m) = 1.90 + 0.501 \ln C_e$	66.69
MB	85.6	0.06	$\ln(x/m) = 4.45 + 0.061 \ln C_e$	113.30

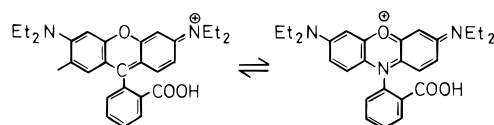
at 559 cm^{-1} after RB sorption, indicating a lowering in bond energy and loosening of C–S stretching. This is because of an interaction between this bond and the chromophore (cationic) of RB.

(b) The absorption band C1 at 1215 cm^{-1} due to a $-\text{SO}_3-$ group has shifted and decreased in intensity to C2 at 1200 cm^{-1} , indicating its interaction with the dye cation.

(c) The absorption band D1 at 1115 cm^{-1} in Figure 4b can be assigned to a phenoxycarbonyl group which is absent at D2, indicating the absence of this group after RB uptake.

(d) C–H stretching at A1 (2950 cm^{-1}) has diminished at A2 in Figure 4c.

On the basis of these observations, it can be presumed that besides the $-\text{SO}_3\text{H}$ group other unsaturated sites are also interacting with the dye. However, this interaction does not appear to be as simple as in the case of MB. There may be two reasons for this. First, the RB chromophore is associated with the resonance hybrid of ammonium and oxinium structures as shown:



Second, this chromophore corresponds to high-energy levels as is evident from its lower λ_{max} (545 nm) as compared to the chromophore of MB (655 nm). If this is true, then the s. coal should have less affinity for RB than MB. The relative affinities can be determined by comparing the saturation capacity of sorbent for the respective dyes. So, the equilibrium data were fitted to the Freundlich isotherm, and the saturation capacities corresponding to the initial equilibrium concentration were determined. These values are 66.69 and 113.30 mg/g for RB and MB, respectively (Table 1). This further confirms that the sulfonation not only transforms the GBC into a cation exchanger but also creates unsaturated sites on the surface. The nonreversibility of the sorption by mineral acids as shown elsewhere (Mittal and Venkobachar, 1993) also supports this.

Conclusions

On the basis of this study, the following conclusions can be drawn:

1. Sulfuric acid treatment of GBC causes oxidation of both aliphatic and aromatic chains besides the incorporation of a $-\text{SO}_3\text{H}$ group.
2. Unsaturation of the coal surface increases after sulfonation.
3. Increased unsaturation and oxidation of the coal surface after sulfuric acid treatment appears to play a major role in enhancing the dye sorption of s. coal, rather than the incorporation of a $-\text{SO}_3\text{H}$ group.
4. Different mechanisms are operative for the uptake of MB and RB.
5. The lower uptake of RB can be attributed to the resonance hybrid of its ammonium and oxinium structures.
6. Infrared spectroscopy could be satisfactorily used in such investigations.

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Nomenclature

C_e = equilibrium dye concentration (mg/L)

K = Freundlich isotherm constant, representing sorption capacity

m = sorbent dose (g/L)

n = Freundlich isotherm constant ($x/m = KC_e^{1/n}$), representing sorption intensity

x = quantity of dye sorbed (mg/L)

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