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The Effect of Surface Acidity upon the Adsorption Capacities of Activated Carbons

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TECHNICAL NOTE

The Effect of Surface Acidity upon the Adsorption Capacities of Activated Carbons

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ABSTRACT

In this study the effects of the surface acidity of adsorbents on adsorption from solution are investigated. For this purpose, methylene blue (cationic) and metanil yellow (anionic) adsorbates, which have opposite ionic characters, are used. At 298 K, the values of surface acidity indicate that methylene blue molecules occur on the surface at a greater probability than those of metanil yellow. That is, metanil yellow molecules are repulsed from the surface and methylene blue molecules are attracted to the surface.

Key Words. Activated carbon; Dyestuff adsorption; Surface acidity

INTRODUCTION

The surface area of solids can be determined from gas adsorption or from adsorption from aqueous solutions. Although the solution method is simpler experimentally, it is more difficult to interpret the experimental data. In addition to solute properties, some other factors such as the adsorption of solvent, the molecular dimensions of the adsorbate and its orientation to the surface, the chemical properties of the adsorbate and adsorbent, the pore structure of the adsorbent, etc., affect adsorption from the solution. The most important factor is the concentration of acidic groups formed on the surface during the preparation (by oxidation during or following activation) of the porous activated carbons.

In a previous study we investigated the effect of the molecular dimension of the adsorbate and the pore structure of the adsorbent on adsorption from solution (1). In this study the effects of the properties of the adsorbent surface on adsorption from the solution are investigated. To do this, methylene blue (MB) and metanil yellow (MY), which have opposite ionic characters but whose molecular dimensions are the same (2), are used as adsorbates. Methylene blue is a cationic (basic) dyestuff and metanil yellow is an anionic (acid) one.

EXPERIMENTAL

The activated carbon in this study was obtained from almond shells (B-8) as in the previous investigation. The shells were carbonized/activated in CO_2 for 4 hours at 1073 K followed by chemical activation with 1:1 w/w H_2SO_4 for 6 hours. The commercial activated carbons Merck-2514 (M-2514) and Merck-2184 (M-2184) were used as adsorbents (1, 3). In addition, we also used Spheron-6 (S-6) in this study.

In previous studies (1, 3) we measured nitrogen adsorption by B-8 which is carbonized (or activated) for 4 hours in a CO_2 gas medium, after which the almond shells were brought to a size of 2 mm as an adsorbent with a 1:1 w/w sulfuric acid solution for 6 hours, M-2514 and M-2184 at 77 K (1), and the methylene blue (MB) adsorptions from aqueous solution at 298 K (3). In this study the nitrogen adsorption of S-6 at 77 K, the MB adsorption from aqueous solution at 298 K, and the metanil yellow (MY) adsorptions from aqueous solution at 298 K were determined. For this purpose, 0.1 g of each adsorbent and 50 mL of 10^{-2} M solutions were stirred and maintained at 298 K. The stirring period was 55 hours for MB and 60 hours for MY. The postadsorption equilibrium concentrations were determined by using a visible-field spectrophotometer (Shimadzu UV-160) at wavelengths of 662 and 442 nm for MB and MY, respectively. In this study the concentrations of acidic substituent groups on the carbon's surface were also determined by titration. One gram of each carbon type and 100 mL of 0.01 N NaOH solution were contacted at 298 K for 48 hours. The clear portion of the mixture was sampled and then backtitrated to the pH of a 0.01 N NaOH solution with a 0.1 N NaOH solution. The results were given in milliequivalents per gram.

RESULTS

The values of the nitrogen surface area (S_{N_2}) and the MB surface area (S_{MB}) for B-8, M-2514, and M-2184 are shown in Table 1 (1, 3).

TABLE 1
The Values of the Surface Area Obtained from the Adsorption Results and Surface Acidity Related to the Various Carbons

Carbon	S_{N_2} ($m^2 \cdot g^{-1}$)	S_{MB} ($m^2 \cdot g^{-1}$)	S_{MY} ($m^2 \cdot g^{-1}$)	Acidity of carbon surface ($meg \cdot g^{-1}$)	S_{MB}/S_{N_2} (%)	S_{MY}/S_{N_2} (%)	S_{MY}/S_{MB} (%)
S-6	86.0	85.5	85.0	0.00	99.4	98.8	99.4
B-8	869.0[a]	221.1[b]	176.8	0.22	25.4	20.3	80.0
M-2184	974.4[a]	382.1[b]	271.2	0.27	39.2	27.8	71.0
M-2514	1160.3[a]	208.9[b]	179.6	0.18	18.0	15.5	86.0

[a] From Ref. 1.
[b] From Ref. 3.

Figure 1 shows the adsorption and Langmuir (linear form) isotherms of nitrogen on the S-6. From the reciprocal value of the slope of the Langmuir isotherm, the monolayer capacity, V_m, was found for nitrogen gas adsorption. The S_{N_2} relationship to S-6 and to other samples (1, 3) (Table 1) was calculated from the following equation (4):

$$S_{N_2}(m^2 \cdot g^{-1}) = \frac{V_m(\text{STP cm}^3 \cdot g^{-1})\sigma \times 10^{-20}(m^2)N_A(\text{mol}^{-1})}{22415(\text{STP cm}^3 \cdot \text{mol}^{-1})} \tag{1}$$

where N_A is Avogadro's number and σ is the cross-sectional area occupied by a molecule of the adsorbate (this is 16.2 Å^2 for nitrogen at 77 K) (4).

Figure 2 shows the adsorption and Langmuir (linear form) isotherms of MY from aqueous solution at 298 K on all the adsorbents. Figure 3 shows the adsorption and Langmuir (linear form) isotherms of MB from aqueous solution at 298 K on S-6. From the reciprocal values of the slopes of the Langmuir linear isotherms, the monolayer capacities, C_m, were found for adsorption from the solution. The specific surface area values related to the adsorbates (S_{MB} and S_{MY}) (Table 1) were calculated from the following equation (5):

$$S(m^2 \cdot g^{-1}) = \frac{C_m(\text{mol} \cdot g^{-1})\sigma \times 10^{-20}(m^2)N_A(\text{mol}^{-1})}{n} \tag{2}$$

In this study, the calculation of the specific surface area related to S-6 from the MB adsorption aqueous solution at 298 K, σ, was taken as 120 Å^2 (5). In Eq. (2) n is the average number of dye ions in a micelle, or the aggregation number since the dyestuffs were adsorbed in the form of ionic micelles from the aqueous solution. A value of 2 was used for MB at 298 K (5). This is the value for MY used in this study. In other studies (2, 6) the investigators observed different values for C_m at different tempera-

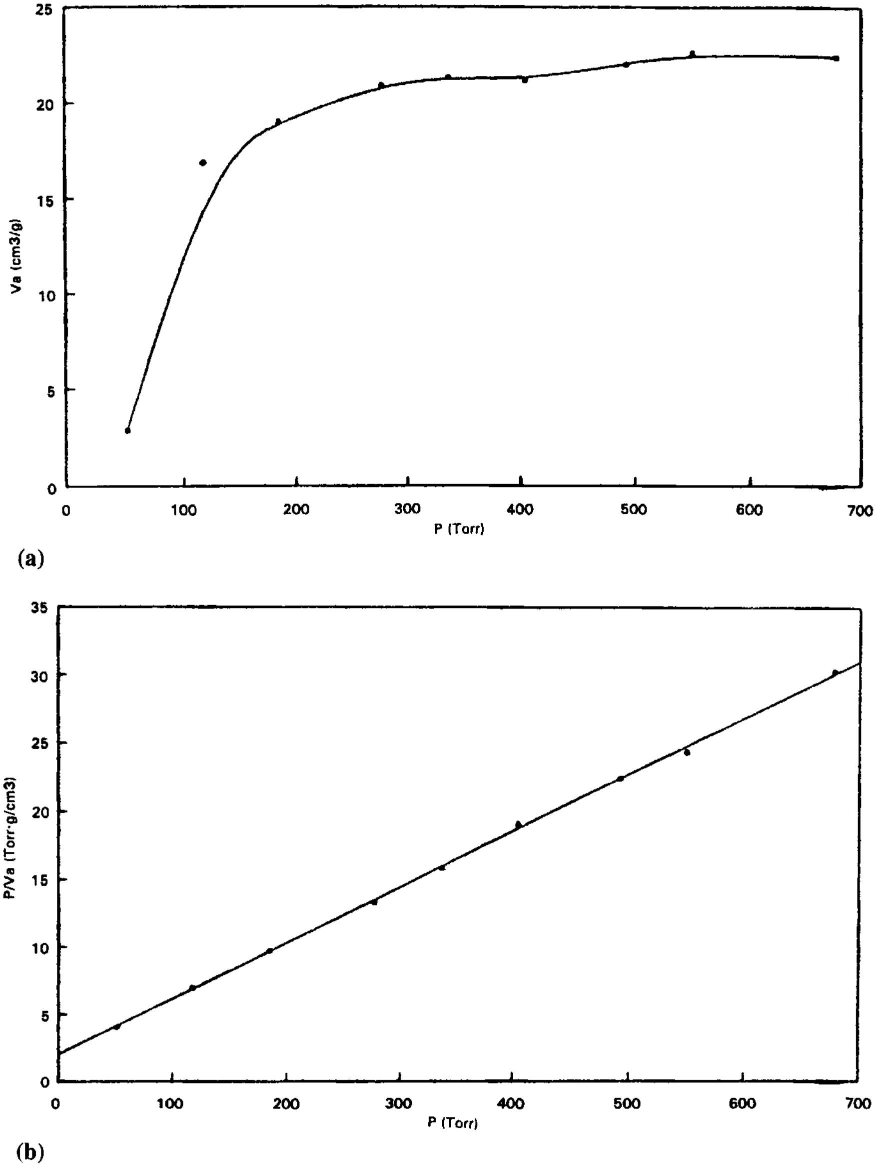

FIG. 1 The nitrogen (77 K) gas (a) adsorption and (b) Langmuir linear isotherms related to Spheron-6.

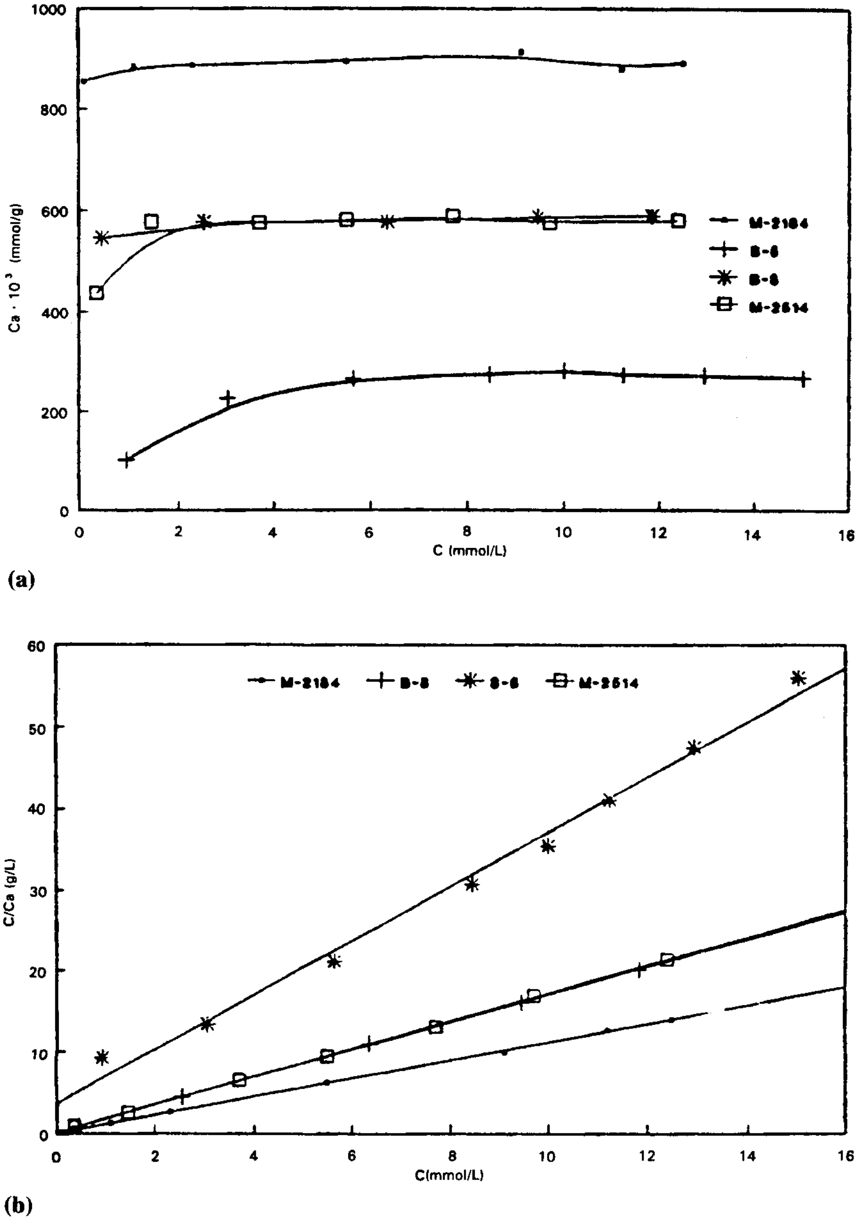

FIG. 2 (a) Adsorption and (b) Langmuir linear isotherms (298 K) of metanil yellow from the aqueous solution related to the activated carbons.

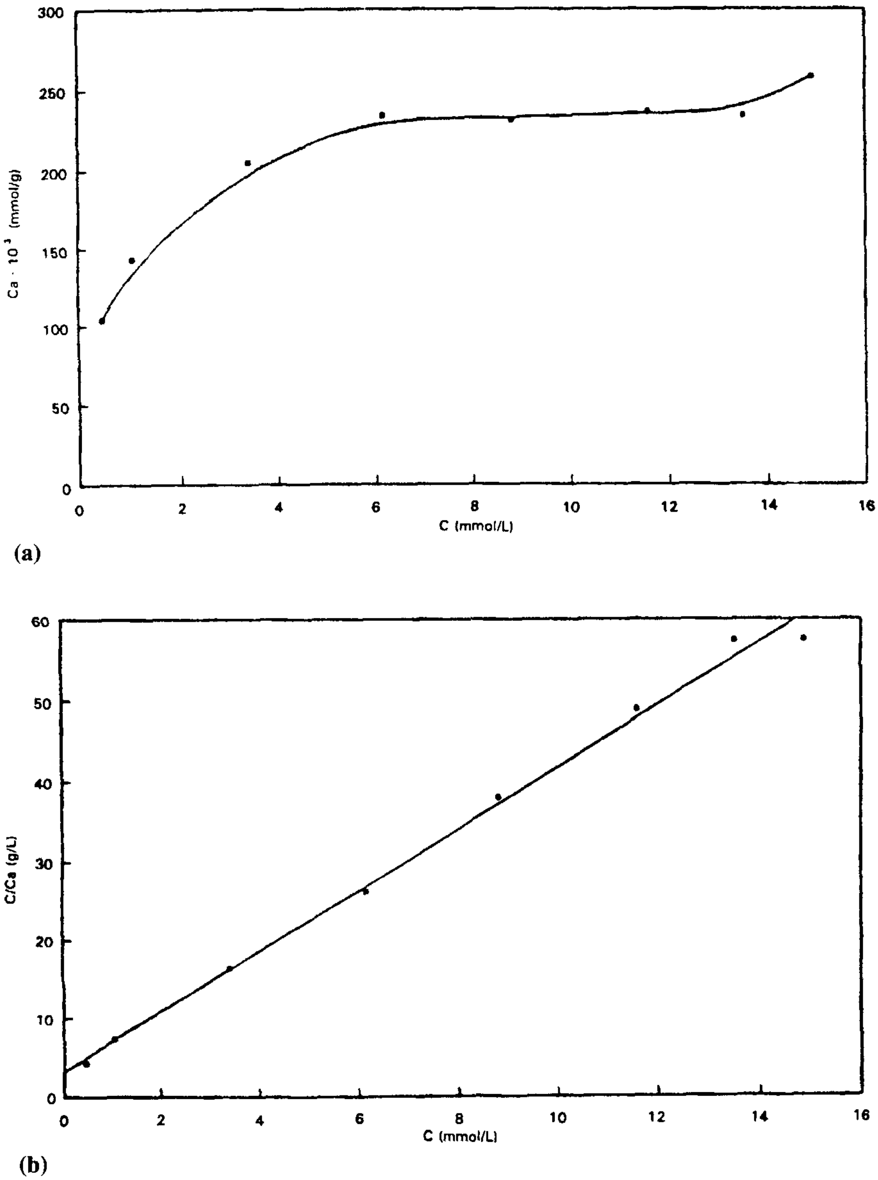

FIG. 3 (a) Adsorption and b) Langmuir linear isotherms (298 K) of methylene blue from the aqueous solution related to Spheron-6.

tures. The adsorption was carried out in a nonporous carbon at 293 and 353 K, with MB as a monomer at 353 K and as a dimer at 293 K. In the present study, MY adsorption on S-6 from aqueous solution at 298 and 353 K was carried out in a similar way, and the C_m values (2.79×10^{-4} mol·g^{-1} at 298 K and 1.49×10^{-4} mol·g^{-1} at 353 K) were found. As in previous studies (2, 6), the difference between the C_m values at different temperatures was found to be twofold. For this reason, the value of n for MY was taken as 2. If these C_m values, the S_{N_2} value (Table 1), and an n value of 2 for the evaluation of S-6 are used, a value of 102.1 is found for Å^2 at 298 K and 191.5 for Å^2 at 353 K for MY. In this study the value used in the calculation of the specific surface area of the adsorbents from MY adsorption from aqueous solution at 298 K, σ, was 102.1 Å^2.

Table 1 also includes values of the accessible surface area ratios (S_{MB}/S_{N_2} and S_{MY}/S_{N_2}) for MB and MY relative to nitrogen, the values of the accessible surface area ratios (S_{MY}/S_{MB}) of MY relative to MB, and the values of the surface acidity (meq·g^{-1}) for the tested adsorbents.

DISCUSSION

To examine the pore-sieving effect of adsorbents, methylene blue (MB), which is a cationic (basic) dye, is generally used. In this study metanil yellow (MY), which is an anionic (acidic) dye and whose length is 18 Å and width is 9 Å and has the same molecular dimension as MB (2), was also used. From the data in Table 1 it is clear that S_{N_2}, S_{MB}, and S_{MY} values, and S_{MB}/S_{N_2} and S_{MY}/S_{N_2} values of S-6 are about the same. This result indicates that S-6 is a nonporous material and that there are no surface functional groups affecting MB and MY adsorptions which are carried out at higher temperatures than nitrogen adsorption. In the case of the other adsorbents, the values of S_{N_2}, S_{MB}, and S_{MY} are significantly different. This results from the pore-sieving effect, i.e., the MB and MY molecules are larger than those of nitrogen, and from the absence of any interaction between the adsorbate and adsorbent at the temperature of N_2 adsorption (77 K). However, for the same adsorbents, S_{MB} values are larger than those of S_{MY} although their molecular dimensions are the same (Table 1). This is due to the acidic groups formed on the surface during the preparation of the adsorbent. MB molecules are basic and are attracted by the acidic groups on the surface. In the other words, MY molecules attach to a smaller area of the surface than MB molecules during adsorption. If the data in Table 1 are examined for all the adsorbents, it is seen that while the acidity concentration on the surface of the adsorbent is decreasing, the ratio S_{MY}/S_{MB} is increasing. Consequently, we can say that it is possible to obtain information about the acidity concentration of a carbon by this method from data on MB and MY adsorption from an aqueous solution.

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