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Adsorption of Dyes on Activated Carbon and Graphitic Thermal Carbon Black

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Abstract—The adsorption of a basic dye (Methylene Blue; MB) and an acidic dye (Acid Orange; AO) has been studied on three activated carbons (ACs; FAS, SKD, and BAU) significantly differing in their porous structures and surface concentrations of ion-exchange groups and on graphitic thermal carbon black (GTCB). The effective specific surface area of FAS, SKD, and BAU determined by dye adsorption is, respectively, 60, 50, and 40% of the BET nitrogen adsorption surface area. The MB uptake on ACs and GTCB increases with rising pH, while the AO uptake decreases. Addition of an electrolyte (0.3 M NaCl) virtually does not effect the adsorption of dyes on ACs and GTCB. It is suggested that hydrophobic interactions, and not ionic ones, are the major contributors to the adsorption of dyes on ACs.

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Activated carbons (ACs) [1–3] and other carbon materials (carbon blacks [4] and thermally expanded graphites [5]) are highly efficient in decontamination of water from dyes and other organic contaminants. The effects of the surface geometry and surface chemistry of carbon materials on dye adsorption have been studied in several works [6–9], but the adsorption mechanism remains incompletely clear. In order to ascertain molecular-sieve effects and the character of surface interactions, here we study the adsorption of one basic dye and one acidic dye on three activated carbons that strongly differ in their porosity characteristics and concentrations of ion-exchange groups. For comparison, we study graphitic thermal carbon black (GTCB), which is a nonporous carbon adsorbent with a homogeneous nonpolar surface. We study adsorption as a function of the solution pH and the concentration of a neutral electrolyte (sodium chloride) in order to ascertain the contributions of ionic and hydrophobic interactions to the adsorption of dyes on ACs.

EXPERIMENTAL

Three ACs (FAS-E, SKD-515, and BAU-A) and Sterling MT GTCB were milled to obtained the fraction with particle sizes of 40–100 μm. The adsorbents were dried at 180°C for 6 h. Their specific surface areas *S* were measured by thermal nitrogen adsorption [10]. The reference used was GTCB with the BET specific surface area of 11.5 m^2/g. The total specific micro- and mesopore volume *V* of the ACs was derived from capillary benzene condensation after 10-day exposure to benzene vapor in a desiccator.

The concentration of anion- and cation-exchange groups in the ACs was determined by back-titration with 0.01 N solutions of hydrochloric acid and sodium hydroxide, respectively, after weighed AC samples were exposed to aqueous acid or base for 5 days until equilibration. Methyl Red indicator was used to titrate equilibrated solutions.

The zero-charge-point (pH_{zcp}) of the ACs was measured, as described in [11], as follows. To an AC sample (100 mg), 5 mL of 0.1 N NaCl (pH 7.0) was first added until a constant pH was acquired; then, the following aliquot of the solution was added. The procedure was repeated six times. The zero-charge point was set to be the pH of the plateau on the pH versus solution volume plot.

The dyes used were Acid Orange (an acidic dye containing one sulfo group) and Methylene Blue (a basic dye containing two alkylamino groups).

The adsorption was measured as follows. Weighed samples of a sorbent were periodically shaken in vials with 5–10 mL of solutions during 10–30 days until equilibration. The dye concentration was determined spectrophotometrically after centrifuging.

Dye adsorption isotherms were calculated for solutions in distilled water and in 0.01 M phosphate buffer solutions with pH ranging from 2 to 10. From these isotherms, the maximum adsorption A_m was calculated using the Langmuir equation. The dye uptake was measured as a function of pH in 0.01 M phosphate buffer solutions and in the same solutions after adding sodium chloride and adjusting its concentration to 0.3 N.

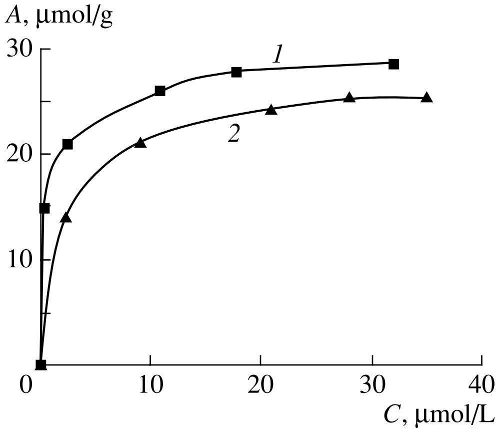

Fig. 1. Dye adsorption isotherms on GTCB from a 0.01 M phosphate-buffered solution with pH 6.0 for (*1*) AO and (*2*) MB.

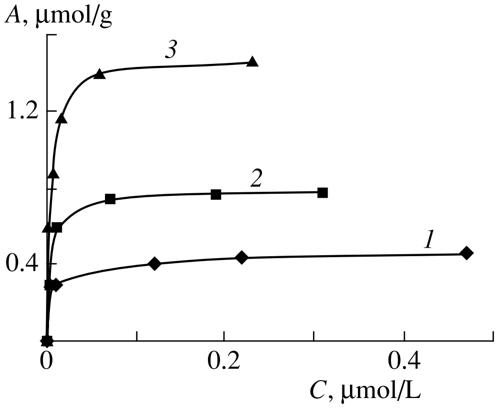

Fig. 2. Acid Orange adsorption isotherms on ACs from a 0.01 M phosphate buffer solution with pH 6.0 on (*1*) BAU-A, (*2*) SKD-515, and (*3*) FAS-E.

RESULTS AND DISCUSSION

The AC surface is used only partially for dye adsorption because of the molecular-sieve effect [7]. In order to ascertain this effect, we compared the adsorption of dyes on GTCB and ACs.

Figure 1 shows isotherms of AO and MB adsorption on GTCB from phosphate buffer solution (pH 6). The adsorption of AO in the initial concentration region is slightly higher than that of MB.

Table 1 displays the maximum uptakes per unit surface calculated from these isotherms and the molecular areas in the monolayer. These quantities for both dyes are quite similar.

The isotherms of AO on ACs adsorption from a pH-6 phosphate buffer solution are shown in Fig. 2. The adsorption isotherms for this dye on ACs and GTCB have approximately identical shapes. There is a rapid rise in adsorption in the initial concentration region followed by a plateau in the range 0.1–0.5 mmol/L. This type of isotherm was also obtained for MB on ACs.

Assuming that the molecular areas for the adsorbate dye on ACs and GTCB are identical, the accessibility of the AC surface to dye molecules can be ascertained from these adsorption isotherms. Table 2 lists the effective specific surface areas of ACs calculated from the dye adsorption isotherms and those determined by thermal nitrogen desorption. The specific pore volumes derived from capillary benzene condensation are also listed in Table 2. One can see that the specific pore volume of FAS-E ($V = 1.07$ cm^3/g) is about three times that of either of the other two ACs; the BET effective specific surface area of FAS-E is about 1.6 and 1.8 times that of SKD-515 and BAU-A, respectively. The effective specific surface areas of ACs determined with AO and MB are quite similar. These specific surface areas are about 60, 50, and 40% for FAS-E, SKD-515, and BAU-A, respectively. Therefore, the exclusion of AO and MB molecules from pores is the highest on BAU-A and the lowest on FAS-E.

Table 3 lists the maximum adsorptions of dyes on ACs from phosphate buffer solutions with pH 2, 6, and 10. On all ACs, the maximum adsorption of the acidic dye increases noticeably with rising solution pH; that of the basic dye decreases. This behavior of the dye uptake as dependent on pH in [8] was related to the ζ potential and the zero-charge point of AC.

In order to elucidate the types of interactions between dye molecules and the surface, we determined the following parameters of ACs (Table 4): N_A, the anion-exchange-group concentration; N_C, the cation-exchange-group concentration; N_Σ (mequiv/g), the overall concentration of ion-exchange groups; N_A/N_C, the ratio between the concentrations of anion- and cation-exchange-groups; and pH$_{zcp}$. On all three ACs, the anion-exchange-group concentration is noticeably higher than the cation-exchange-group concentration (Table 4). The highest N_A/N_C ratio (17.6) is observed on SKD. On FAS and BAU, this ratio is the same and is one-fifth that on SKD. Accordingly, the zero charge point on SKD is the highest (pH$_{zcp}$ 8.66); on FAS and BAU, the zero charge points are far lower and roughly equal (pH$_{zcp}$ 7.93 and 7.95, respectively). In BAU (the most hydrophilic AC), the ion-exchange-group concentration N_Σ is 0.71 mequiv/g, i.e., 1.5 times that in SKD ($N_\Sigma = 0.47$ mequiv/g). FAS is the least hydrophilic AC

Table 1. Adsorption of dyes on GTCB: maximum adsorption A_m (µmol/g), a_m (µmol/m^2), and molecular area ω_m (nm^2)

Parameter	Acid Orange	Methylene Blue
A_m, µmol/g	29	27
a_m, µmol/m^2	2.5	2.4
ω_m, nm^2	0.64	0.69

Table 2. Structural parameters of ACs

AC type	S_{nitrogen}, m^2/g	S_{AO}, m^2/g	S_{MB}, m^2/g	V_{benzene}, cm^3/g
FAS-E	880	580	520	1.07
SKD-515	560	290	270	0.43
BAU-A	480	180	190	0.37

Table 3. Maximum adsorption A_m (mmol/g) of dyes as a function of pH

Dye	Acid Orange			Methylene Blue		
pH	2	6	10	2	6	10
FAS-E	1.71	1.43	1.40	1.06	1.25	1.91
SKD-515	1.12	0.77	0.68	0.88	0.88	1.42
BAU-A	0.62	0.48	0.38	0.45	0.46	0.60

Table 4. Zero-charge point and concentrations of anion-exchange N_A (mequiv/g) and cation-exchange N_C (mequiv/g) groups in ACs

AC type	N_A	N_C	N_Σ	N_A/N_C	pH_{zcp}
FAS-E	0.23	0.063	0.29	3.65	7.93
SKD-515	0.44	0.025	0.47	17.6	8.66
BAU-A	0.55	0.16	0.71	3.55	7.95

(N_Σ = 0.29 mequiv/g). Comparing the adsorption on ACs with that on a nonpolar carbon material (GTCB) as functions of solution pH and ionic strength offers a means for ascertaining the character of adsorption interactions between the dye and the AC surface.

Figure 3 illustrates the adsorption of AO and MB on GTCB as a function of pH in low-ionic-strength solutions (in 0.01 M phosphate buffer solutions) and the adsorption of AO in the same buffer solutions that contain 0.3 N NaCl. Both on ACs (Table 3) and on GTCB, the highest adsorption of the acidic dye is observed for the lowest pH (pH 2) and that of the basic dye is observed for the highest pH (pH 10). The fraction of the molecular species of the dye increases and that of the ionic species decreases with decreasing pH in the acidic dye solutions and with increasing pH in the basic dye solutions. An electrolyte (0.3 N NaCl) virtually does not affect the adsorption. The adsorption of dyes on the nonpolar GTCB surface is controlled by hydrophobic interactions. Figure 4 shows similar dye adsorption curves on BAU (the most hydrophilic AC with the highest total concentration of ion-exchange groups, equal to 0.71 mequiv/g). One can see that the trend of dye adsorption on BAU as dependent on the pH and electrolyte concentration is the same as on GTCB. The adsorption of the acidic dye increases with decreasing pH, while that of the basic dye increases with increasing pH. Addition of an electrolyte to the solution influences the adsorption of AO on BAU as insignificantly as on GTCB. However, an electrolyte, as a rule, dramatically decreases the ion-exchange sorption of organic compounds [12]. All the aforesaid implies that hydrophobic interactions, and not ionic ones, are the main contributors to dye adsorption on ACs.

In summary, our comparative experiments on the adsorption of dyes on GTCB and ACs resulted in the determination of effective specific surface areas for ACs and ascertained the character of adsorption interactions between dyes and the AC surface.

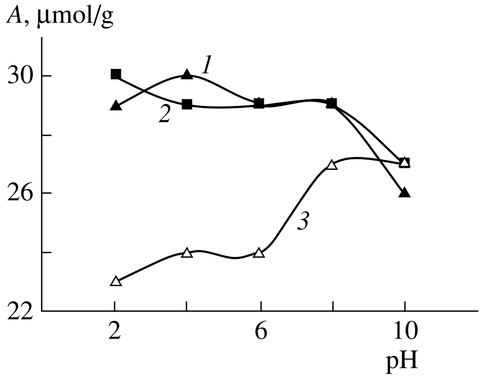

Fig. 3. Maximum adsorption on GTCB vs. solution pH: (*1*, *2*) adsorption of AO (*1*) from 0.01 M phosphate buffer solutions and (*2*) from the same solutions containing 0.3 N NaCl, and (*3*) adsorption of MB from 0.01 M phosphate buffer solutions.

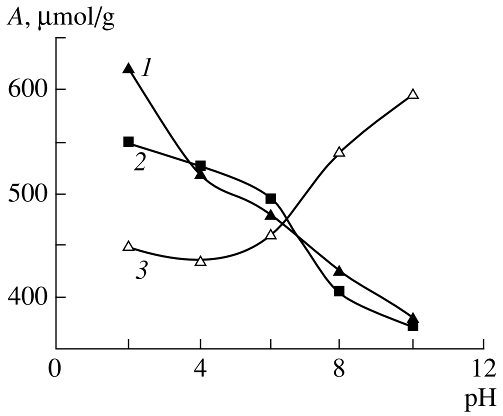

Fig. 4. Maximum adsorption on BAU-A vs. solution pH: (*1*, *2*) adsorption of AO (*1*) from 0.01 M phosphate buffer solutions and (*2*) from the same solutions containing 0.3 N NaCl, and (*3*) adsorption of MB from 0.01 M phosphate buffer solutions.

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