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Kinetics of Adsorption with Granular, Powdered, and Fibrous Activated Carbon

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ABSTRACT

The properties of three different types of activated carbon, fibrous, powdered, and granular, were investigated theoretically and experimentally. The adsorption rate of the activated carbon fiber was found to be two orders of magnitude higher than that of the granular activated carbon, and one order of magnitude higher than that of the powdered activated carbon. Diffusion coefficients of methylene blue in the fibrous, powdered, and granular activated carbons were determined experimentally. A new method for estimating the meso- and macropore surface areas in these carbons was proposed.

INTRODUCTION

A large number of industrial applications require adsorbents that can reduce the concentration of organic impurities to a very low level in a short time. Applications include the production of high purity water in electronics manufacturing, hospitals and medical laboratories, industrial wastewater treatment, municipal water filtration, color removal in pharmaceuticals purification, and household tap water purification. Granular activated carbon (GAC) and powdered activated carbon (PAC) are traditionally used in these applications. The relatively slow adsorption rate of commercially available granular adsorbents leads to adsorption devices with a large volume and a slow throughput. Typical sizes of GAC particles vary between 200 and 1000 μm. Powdered adsorbents with typical particle sizes between 20 and 200 μm have faster adsorption rates. However, powdered adsorbents compact under flow, resulting in a strong flow resistance (1–3).

Another technique is to mix powdered carbon with polyethylene. The mixture is then heated up to form a rigid porous carbon matrix. The binding reduces the adsorption capacity, but the rigid porous matrix does not compress under flow. Nevertheless, the speed of adsorption of these carbon blocks is only a few times that of granular adsorbents, while exhibiting a strong flow resistance (1, 4, 5).

Activated carbon fiber (ACF) is a relatively new material for adsorption (7). Conventional ACF is made by carbonizing and activating rayon, polyacrylonitrile, pitch, or phenolic resin. ACF has a very high adsorption rate. However, the manufacturing cost of ACF is high and ACF's adsorption capacity of heavy metals is low (6). A new type of activated carbon fiber (Aqualen) has been developed by Pimenov et al. (7). Aqualen is produced by carbonizing, activating and post treating rayon fibers. The relatively long (over 5 mm) and inherently strong fiber does not compact under flow, resulting in low flow resistance.

The three-dimensional structure of the activated carbon comprises a network of interconnected macropores, mesopores, and micropores. The rate of adsorption of these materials depends on the sizes of the individual micropores, on the tortuosity and the pore-size distribution of the meso- and macropores, and on the size of the adsorbent particle. An important parameter for any carbon is its degree of graphitization. Activated carbon contains graphite layers, often as thin as one atomic layer, twisted at different angles toward each other. The spacing between these twisted layers essentially defines the size of micropores.

The porosity of the carbon depends on the distance between the adjacent graphite layers. Distance between the adjacent graphite layers is defined as d_{002}. d_{002} is 3.354 Å for pure perfectly structured solid graphite. d_{002} for porous graphite carbons varies between 3.354 and 3.44 Å. d_{002} in carbons that do not have long range graphite structure is between 3.44 and 3.7 Å. The last type of carbon is considered amorphous (8).

When an organic molecule diffuses into the adsorbent, it migrates initially through the meso- and macropore network, and subsequently into the micropores where the majority of adsorption takes place. As the organic molecule diffuses from the larger into the smaller pores, its migration velocity decreases due to the increase in the molecule–pore surface interactions. For example, the diffusion coefficient of methylene blue in the micropores of an activated carbon particle is approximately 2×10^{-10} cm^2/s, which is 25,000 times smaller than its free diffusion coefficient (1). The diffusion coefficient in the adsorbent particle as well as surface areas of the macro- and mesopores of the adsorbent particle are important parameters in practical applications, because the rate of adsorption is dependent upon them.

In this paper we report out investigation on the dynamic adsorption properties of fibrous, powdered, and granular activated carbon and on determining the diffusion coefficients of methylene blue, and the macropore surface areas of these different types of carbon.

EXPERIMENTAL STUDY

Aqualen activated carbon fiber (ACF), Calgon granular activated carbon F400 (GAC), and Calgon powdered activated carbon 80 × 325 (PAC) were used for comparison studies. The adsorption capacity of ACF was determined by taking a 500-mL flask containing 400 mL of 200 mg/L of methylene blue (Sigma Corporation) and 100 mg of ACF and shaking it for 24 hours. All methylene blue concentration measurements were done by first filtering the solution through a polyester filter and then measuring the light absorbency at 622 nm. The experiment was repeated with 1 g GAC and 200 mg PAC. The adsorption capacities of ACF, PAC, and GAC were found to be 503, 184, and 51 mg/g, respectively.

The rate of adsorption experiment with ACF was done by taking a 500-mL flask containing 400 mL of 200 mg/L of methylene blue and 100 mg of ACF and shaking it. Experiments with PAC and GAC were done by taking 500 mL flasks containing 400 mL of 200 mg/L of methylene blue and 200 mg of PAC and 1 g of GAC, respectively. The adsorption rate of methylene blue at different times was determined by taking 4 mL samples of solution, filtering through a polyester filter, measuring the methylene blue concentration spectrophotometrically, and returning the sample to the flask.

The average diameters of the PAC and the GAC particles were 88 and 1000 μm, respectively. ACF fiber was 6 μm in diameter (1).

The structure of ACF, PAC, and GAC, in terms of d_{002}, was examined by using an x-ray diffractometer (Model DRF-20, SKB Burevestnik, Orel, Russia) (8). GAC and PAC samples were ground to fine powders with a hand grinder. Powdered samples and a small strand of ACF fibers were attached to acrylic support plates using Vaseline and analyzed with the x-ray diffractometer.

THEORETICAL ANALYSIS

A typical activated carbon particle, whether in a fibrous, powdered, or granular form, has a porous structure consisting of macropores (>500 Å), mespores (20 to 500 Å) and micropores (<20 Å). The particle is permeated with a system of macro- and mesopores that serve as an avenue for the rapid diffusion of adsorbed substances to the internal, smaller pore surfaces. Micropores are formed inside small crystalline structures that are surrounded by the meso- and micropores. The bulk of the adsorption capacity of the activated carbon for low molecular weight substances (MW < 500) is in its micropores. The active carbon micropore structure is formed during activation when an activating agent, typically steam or carbon dioxide, creates pores in the carbonized particle at high temperature, typically between 800 to 1200°C. If the burnout, defined as the weight loss of the carbonized particle due to activation, is less than 30%, then micropores with sizes between 10 to 12 Å prevail. When activation is between 30 to 67%, pores with sizes between 17 to 20 Å prevail (9). Most activated carbons are activated with the burnout between 30 to 60%.

As a first approximation, the migration of species into a spherical adsorbent can be described by the following form of Fick's second law of diffusion,

$$\frac{\partial c}{\partial t} = D\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right)\right] \tag{1}$$

where r is the distance from the center of the particle, D is the diffusion coefficient of the solute in the adsorbent particle, and c is the solute concentration in the adsorbent. The diffusion coefficient in the adsorbent particle is smaller than the diffusion coefficient in free solution.

Since species adsorb onto the adsorbent particle readily, it is assumed that the concentration of species adsorbed onto the surface layer is constant, and that it approaches the surface adsorption capacity. The boundary and initial conditions are therefore

$$c = G, \qquad @\, r = r_0 \tag{2}$$

$$\frac{\partial c}{\partial r} = 0, \qquad @\, r = 0 \tag{3}$$

$$c = 0, \qquad @\, t = 0 \quad \text{and} \quad 0 < r < r_0 \tag{4}$$

where G is the adsorption capacity of the activated carbon and r_0 is the adsorbent radius.

The solution of Eq. (1) subject to these boundary conditions is available in Ruthven (4):

$$\frac{m_t}{m_\infty} = 1 - \frac{6}{\pi^2}\sum_1^\infty \frac{1}{n^2}\exp\left(-\frac{n^2\pi^2 Dt}{r_0^2}\right) \tag{5}$$

where m_t is the amount of species adsorbed by the adsorbent particle at time t, and m_∞ is the amount of species adsorbed by the adsorbent particle at equilibrium.

The migration of species into a cylindrical adsorbent particle can be described by Fick's second law of diffusion in cylindrical form:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r}\right) \tag{6}$$

The boundary and initial conditions are therefore

$$c = G, \qquad @\ r = r_0 \tag{7}$$

$$\frac{\partial c}{\partial r} = 0, \qquad @\ r = 0 \tag{8}$$

$$c = 0, \qquad @\ t = 0 \quad \text{and} \quad 0 < r < r_0 \tag{9}$$

Solution of Eq. (6) subject to these boundary conditions is available in Carslaw and Jaeger (10).

RESULTS AND DISCUSSION

Values of d_{002} for ACF, PAC, and GAC from x-ray diffraction measurements are shown in Table 1. Results of experiments on the kinetics of adsorption of methylene blue are shown in Figs. 1–3. Figure 1 shows the rate of adsorption by ACF, PAC, and GAC during the first 5 minutes of adsorption. Figures 2 and 3 show rates of adsorption by ACF, PAC, and GAC at longer times, during the first 30 minutes and during 24 hours. Figures 1–3 show that even though the amount of ACF was only 100 mg, and there were 200 mg of PAC and 1 g of GAC, the rate of adsorption of methylene blue by ACF is an order of magnitude faster than that by PAC and two orders of magnitude faster than that by GAC. The adsorption capacity of ACF was found to be three times higher than the adsorption capacity of PAC and ten times higher than the adsorption capacity of GAC. The diffusion coefficient was estimated from fitting the solution of

TABLE 1
d_{002} for ACF and PAC

Adsorbent	d_{002} (Å)
ACF	3.51
PAC	3.63
GAC	Amorphous

Eq. (1) and Eq. (6) to experimental data. D was found to be 2×10^{-11} cm^2/s for ACF, 4.6×10^{-10} cm^2/s for PAC, and 3.5×10^{-8} cm^2/s for GAC. Theoretical solutions for these diffusion coefficients are shown as solid lines in these figures. The smaller diffusion coefficient for ACF than for PAC indicates tighter carbon packing in ACF than in PAC. X-ray analysis also shows smaller d_{002} spacing between carbon layers in ACF.

Figures 1–3 indicate good correlation between theory and experiment for granular activated carbon and powdered activated carbon. The theory does not fit the data well for fibrous activated carbon after the initial 5

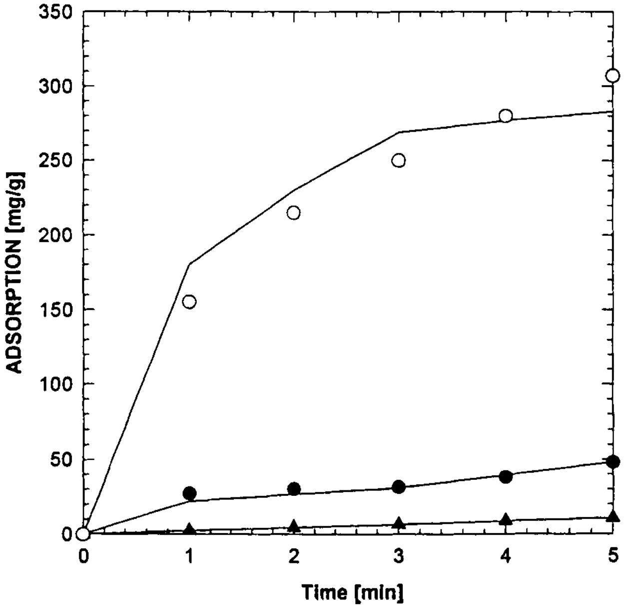

FIG. 1 Methylene blue adsorption during the first 5 minutes. Experimental: (○) ACF, (●) PAC, (▲) GAC. Theoretical: (——).

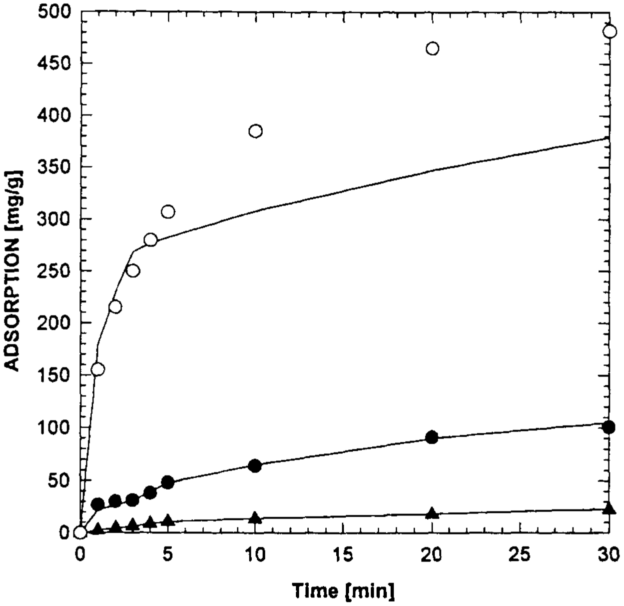

FIG. 2 Methylene blue adsorption during the first 30 minutes. Experimental: (○) ACF, (●) PAC, (▲) GAC. Theoretical: (——).

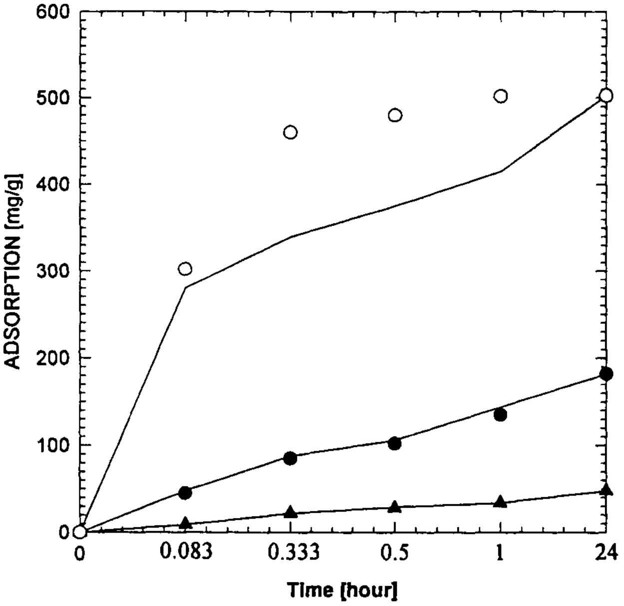

FIG. 3 Methylene blue adsorption during the first 24 hours. Experimental: (○) ACF, (●) PAC, (▲) GAC. Theoretical: (——).

minutes. One possible explanation is because macropores in ACF are relatively large as compared to the diameter of the fiber, thus a single macropore may lead directly into the center of activated carbon fiber (1). Therefore experimental results may show faster adsorption than theoretical predictions for ACF. Macropores in PAC and in GAC are comparable in size to macropores in ACF (1), but macropores in PAC and GAC are much smaller than the diameters of the PAC and GAC particles. Penetration of adsorbate molecules into the center of PAC and GAC is controlled by diffusion through the microporous layers that interconnect individual macropores.

For all three different adsorbents, D was found to be many orders of magnitude smaller than the diffusion coefficient in free solution (1). In reality, when the small species migrate through the macropores of an adsorbent particle, the diffusional resistance approaches that of free solution. When the same species migrate through the micropores in the walls and at the end of the macropore, the diffusional resistance is the same as in a micropore. Tortuosity of the migration path in the adsorbent particle is responsible for additional diffusional resistance.

Diffusion of species into the adsorbent particle can be modeled as migration through consecutive "onion-skin" layers. The thickness of each layer is defined by the length of the macropores in the adsorbent particle. The longer micropore corresponds to a thicker onion-layer. Migration of species through an onion-layer can be modeled as diffusion through a very thin layer with a surface area which is equal to the surface area of all macro- and mesopores in the layer.

As a first approximation, the diffusion coefficient is given by (4)

$$D = fPhD_0 \tag{10}$$

where f is the macroporosity coefficient, which is the proportional increase in the meso- and macropore effective surface area, P is the adsorbent's porosity coefficient, which is equal to the ratio of the adsorbent's particle pore volume to its full volume, h is the tortuosity factor, and D_0 is the diffusion coefficient in the micropores of the activated carbon particle.

The tortuosity factors h generally fall within the 0.15–0.5 range (4). Assuming the porosity coefficient P to be equal to 0.4 for ACF, 0.5 for PAC, and 0.6 for GAC, and the tortuosity factor h to be equal to 1/3 for GAC, PAC, and ACF (1, 4), the macroporosity coefficient f was calculated from Eq. (10) to be equal to 13 for PAC, 834 for GAC, and 1.5 for ACF.

Electron micrographs of ACF, PAC, and GAC show that macropores are correspondingly more penetrating in GAC than in PAC, and in PAC than in ACF (1). This observation is consistent with the changing magnitude of the macroporosity coefficients.

As a first approximation, the thickness of the onion-layers is assumed to be proportional to the size of the adsorbent particle and equal to 0.1 μm for ACF, 1 μm for PAC, and 10 μm for GAC. The effective macropore surface area S_{ms} for a spherical adsorbent particle can be calculated from

$$S_{ms} = 4f\pi \sum_{k=1}^{N} \frac{k^2 r_0^2}{N^2} \tag{11}$$

where N is the number of onion-layers and S_{ms} is the effective macropore surface area. Since the density of all three types of carbon is approximately 0.5 g/cm^3, S_{ms} was calculated from Eq. (11) to be 6.3 m^2/g for ACF, 14 m^2/g for PAC, and 87 m^2/g for GAC.

The macropore surface area of ACF was estimated to be half the macropore surface area of PAC and fourteen times smaller than the effective macropore surface area of GAC. A more important fact is that ACF adsorbs two orders of magnitude faster than GAC and one order of magnitude faster than PAC. The exceptionally fast adsorption rate of ACF is due to its small fiber diameter.

CONCLUSIONS

The total adsorption capacity of ACF exceeds the total adsorption capacity of PAC by threefold and GAC by tenfold. The adsorption rate of ACF is two orders of magnitude higher than the adsorption rate of GAC and one order of magnitude higher than the adsorption rate of PAC. The adsorption rate of activated carbons depends more on the diameter of the adsorbent particles than on the macropore surface area of these adsorbents. Theoretical estimates of the macropore surface area of the adsorbents was confirmed by x-ray diffraction analysis. Results showed that the distance between adjacent carbon layers in ACF is less than that in PAC. X-ray diffraction results and values of the diffusion coefficient of methylene blue showed that GAC has a more porous structure, and ACF has the least porous structure among these three adsorbents.

A new method of estimating the effective macropore surface area of adsorbent from diffusion coefficient data allows one to calculate the macropore surface area from a simple experiment.

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