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A. V. Pimenov[a]; A. I. Lieberman[a]; J. L. Shmidt[b]; H. Y. Cheh[c]
[a] A DIVISION OF ELECTROPHOR, INC., AQUAPHOR CORPORATION, ST. PETERSBURG, RUSSIA [b] ELECTROPHOR, INC., DOBBS FERRY, NEW YORK, USA [c] DEPARTMENT OF CHEMICAL ENGINEERING AND APPLIED CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK, NEW YORK, USA

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Accelerated Adsorption with Activated Carbon Fiber

A. V. PIMENOV and A. I. LIEBERMAN
AQUAPHOR CORPORATION
A DIVISION OF ELECTROPHOR, INC.
ST. PETERSBURG, RUSSIA

J. L. SHMIDT
ELECTROPHOR, INC.
DOBBS FERRY, NEW YORK 10522, USA

H. Y. CHEH
DEPARTMENT OF CHEMICAL ENGINEERING AND APPLIED CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK, NEW YORK 10027, USA

ABSTRACT

The properties of a new type of polyamphoteric activated carbon fiber (ACF) were investigated theoretically and experimentally. Results are compared with those from granular activated carbon (GAC) and ion-exchange resin (IER) materials. The adsorption rate of ACF was found to be two orders of magnitude higher than that of the GAC and one order of magnitude higher than that of the IER.

INTRODUCTION

A large number of industrial and medical applications require adsorbents which can reduce the impurity concentration to a very low level in a short time. These applications include household drinking water filtration, production of high purity water for laboratories, pharmaceutical and electronics manufacturing, industrial wastewater treatment, plasma and hemo-perfusion. Granular activated carbon (GAC), ion-exchange resin (IER), and chelating resins are traditionally used in these applications. GAC is used usually for removing organic impurities and IER is used for removing ions of heavy metals. Also, both GAC and IER are used in systems where organic and inorganic impurities need to be removed. The relatively slow adsorption rate of commercially available granular and powdered adsorbents leads to adsorption devices with a large volume and a slow throughput. Typical sizes of GAC vary between 200 to 1000 μm. Powdered adsorbents with typical sizes between 50 to 200 μm have fast adsorption rates as compared to the granular materials. However, powdered adsorbents compact under flow, resulting in a strong flow resistance (1–4).

Another technique is to bind powdered activated carbon into a rigid porous matrix. Binding reduces the adsorption capacity, but the rigid porous matrix does not compact under flow. Nevertheless, powdered activated carbon adsorbents have, at best, only a fewfold advantage in speed of adsorption over granular adsorbents of the same type (5).

Activated carbon fiber (ACF) is a relatively new material for adsorption. Conventional ACF is made by carbonizing and activating polyacrylonitrile, phenol resin, pitch, or rayon fibers. ACF has a higher adsorption rate

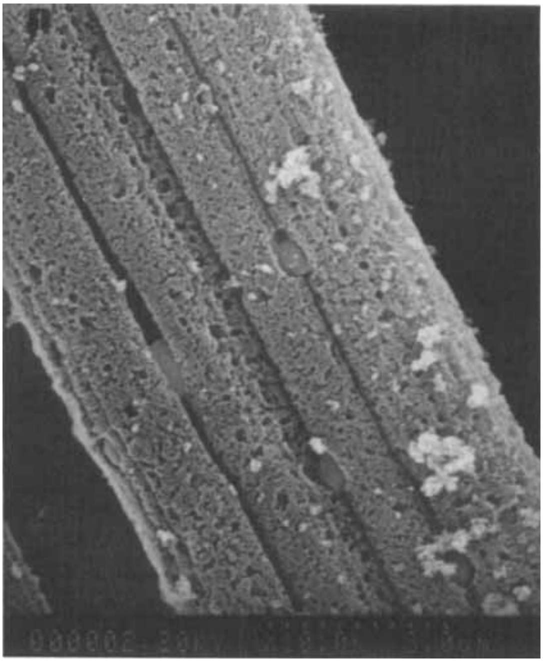

FIG. 1 Electron micrograph of Aqualen activated carbon fiber (1:10,000).

than GAC. However, ACF's manufacturing cost is high and its adsorption capacity is low for heavy metal ions (6, 7).

A new type of activated carbon fiber (Aqualen) has been developed (8). Aqualen is an ACF approximately 6 μm in diameter. Aqualen has a highly developed pore structure. An electron micrograph of Aqualen fiber is shown in Fig. 1. The relatively long (over 5 mm) and inherently strong fibers do not compact under flow, leading to small flow resistance. Aqualen is produced by carbonizing, activating, and posttreating rayon fibers, which gives Aqualen a significant quantity of ion-exchange and complex-forming groups on its surface. Aqualen has a high and irreversible adsorption capacity of organic substances. Aqualen is also significantly selective in adsorbing heavy metals as well as other ions.

In this paper we report our investigation on the dynamic adsorption properties of Aqualen in comparison with GAC and IER's.

THEORETICAL ANALYSIS

Activated carbon particle (in a granular or powdered form) has a porous structure comprising macropores (width > 500 Å), mesopores (widths 20 to 500 Å) and micropores (widths < 20 Å). Each granule is permeated with a system of large macropores which serve as an avenue for the rapid diffusion of adsorbed substances to the internal pore surfaces. Micropores are formed inside small crystalline structures which are surrounded by the meso- and macropores. The bulk of the adsorption capacity of the activated carbon for the lower molecular weight substances (MW < 500) is in its micropores. Smaller sized species migrate from the fluid which surrounds the activated carbon into the porous matrix and then through the bulk of the macropores and mesopores into the micropore crystals.

The total resistance to the migration of the species inside the activated carbon matrix comprises resistances in the macro-, meso-, and micropores. Resistance to migration into the micropore crystals (as compared to the resistance due to migration in the macropores and mesopores) depends on the size of the micropore crystals, the size of the individual micropores, and the tortuosity of the network inside the micropore crystals. The adsorption resistance is also dependent on the sizes of the adsorbent. For example, if the adsorbent size were to be reduced tenfold, the outer surface area of a unit weight of the adsorbent would be increased tenfold. Assuming that the diffusion coefficient of the species migrating through the particle does not depend on the particle size, and that the adsorption rate during some initial time period is directly proportional to the outside surface area of the adsorbent particles, a tenfold increase in the outer surface area of the adsorbent particles should result in a tenfold increase in the speed of adsorption. For example, 50 μm particle size powdered activated carbon should adsorb 10 times faster than the 500 μm size granular activated carbon. In practice, however, the powdered carbon is typically only 2 or 3 times faster. The reason is that the bulk of the diffusion resistance is in the micropore crystals. Although the diffusion paths through the macro- and mesopores is much shorter for the powdered activated carbon than for the granular carbon, the micropore crystals in the powdered activated carbon and in the granular activated carbon have practically the same diffusion resistance.

Activated carbon adsorption is a two-stage process. The first stage is the adsorption and diffusion through a network of mesopores and macropores, and the second stage is the adsorption and diffusion into the micropore crystals. For adsorption of small to medium size molecules, the bulk of the diffusion resistance and the bulk of the adsorption capacity is in the micropore crystals. As a first approximation, the rate of adsorption into the adsorbent particle can be assumed to be proportional to the adsorbate concentration and to the number of adsorption sites available on the adsorbent particle. An adsorbent with a large density of macropores on its surface and the size and the pore structure of the micropore crystals are the key elements for a high adsorption rate and capacity. Larger surface pores, which lead directly into the network of internal micropores, allow a high adsorption rate because of their increased effective surface area, and even more importantly, sharply reduced migration distances. The open pore structure of the ACF is seen in Fig. 1.

Adsorption of Organic Solutes

The adsorption of organic solutes onto the activated carbon materials is described by

$$dc/dt = -k_1(G_1 m - c_0 + c)c - k_2 c^s \tag{1}$$

where c, c_0, and c^s are the solute concentration, the initial solute concentration and the solute concentration in the adsorbent, t is time, k_1 is the adsorption coefficient, k_2 is the desorption coefficient from the activated carbon surface, m is the weight of adsorbent per unit volume of solution, and G_1 is the adsorption capacity of activated carbon.

For the ACF, since the adsorption coefficient is much larger than the desorption coefficient, the second term on the RHS of Eq. (1) can be discarded, leading to

$$c = \frac{(G_1 m - c_0)e^{-k_1(G_1 m - c_0)t}}{G_1 m - c_0 e^{-k_1(G_1 m - c_0)t}}\, c_0 \tag{2}$$

Since the GAC is able to adsorb only a very small amount of the impurity during the initial time period, which is the period of interest in the current investigation, Eq. (2) simplifies to

$$c = c_0 e^{-kGmt} \tag{3}$$

where k is the adsorption coefficient and G is the total adsorption capacity for granular adsorbents.

The adsorption of organic species by activated carbon is due to the van der Waals force between the surface and the adsorbed molecule. This is a long-range but weak interaction, and the amount of energy released during adsorption is of the order of the enthalpy of condensation (9). The low binding energy is responsible for the adsorbed molecule leaving the surface. In other words, a molecule remains on the surface for only a short time before continuing the migration.

Since the van der Waals attractive force predominates within 10 Å distances, it is reasonable to assume that this is the force which predominates in the microporous matrix network. The Boltzmann distribution gives us the amount of species which is not adsorbed at any given moment and is thus diffusing.

Therefore, the average diffusion coefficient for the adsorbent at different temperatures follows the Arrhenius expression,

$$D = D_0 e^{-E_a/RT} \tag{4}$$

where D is the average micropore diffusion coefficient for the adsorbed species, D_0 is a diffusion coefficient, E_a is the desorption energy in micropores, R is the gas constant, and T is the temperature.

Equation (4) predicts that species with a larger adsorption force toward the carbon surface will diffuse and adsorb slowly inside the micropore crystals. This result is puzzling until one considers that the driving force for diffusion is the gradient of chemical potential and that the mechanism for the filling of micropores involves not a successive formation of adsorption layers but a filling of the adsorption space (9).

Methylene blue has a polycyclical structure. Its desorption energy is comparable to the desorption energies of molecules with structures involving benzene rings (10). E_a is approximately 25 kJ/mol and D_0 is 5×10^{-6} cm^2/s at 25°C. D is calculated to be 2.1×10^{-10} cm^2/s, which is twenty-five thousand times smaller than that for free diffusion.

As a first approximation, the migration of species into a long, cylindrical ACF can be described by the following equation of continuity

$$\frac{\partial c^s}{\partial t} = D \frac{1}{r} \frac{\partial}{\partial r}\left(r \frac{\partial c^s}{\partial r}\right) \tag{5}$$

where r is the distance from the center axis of the fiber.

Since species adsorb onto the fiber much more readily than they desorb or migrate into the carbon microcrystals even at low bulk concentration, 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 conditions are

$$c^s = G_1, \qquad @\ r = r_0 \tag{6}$$

$$c^s = 0, \qquad @\ t = 0 \quad \text{and} \quad 0 < r < r_0 \tag{7}$$

where r_0 is the fiber radius. The solution of Eq. (5) subject to these boundary conditions is available in Carlslaw and Jaeger (11). A graphical solution for migration of species inside the ACF at different times intervals is shown in Fig. 2.

Similarly, the migration of species inside granular activated carbon can be determined. The results are shown in Fig. 3.

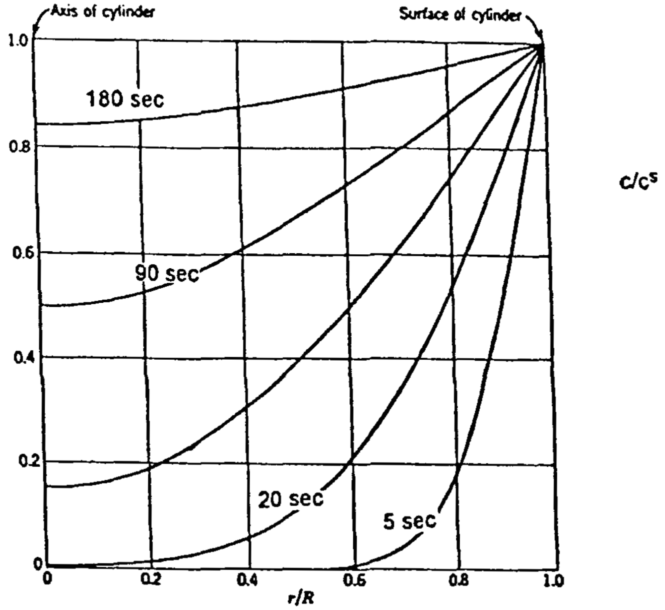

FIG. 2 Concentration profile of species inside a cylindrical activated carbon fiber with a 3-μm radius at different time intervals.

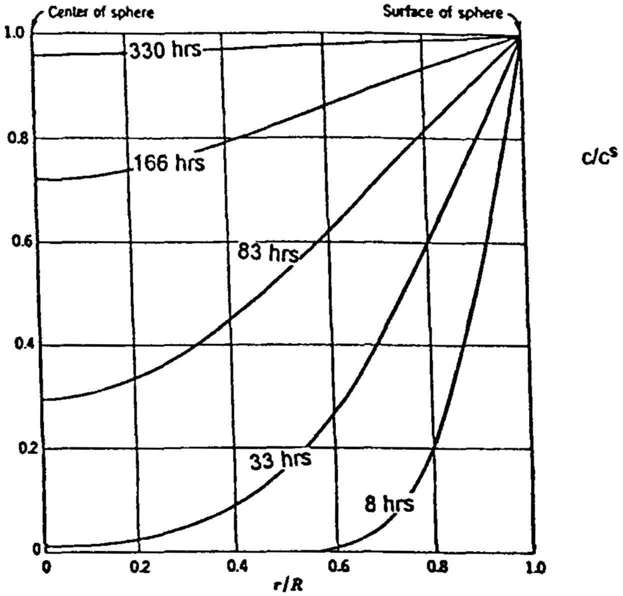

FIG. 3 Concentration profile of species inside a spherical granular activated carbon with a 250-μm radius at different time intervals.

Ion Exchange

Ion-exchange kinetics for cadmium adsorption onto the Aqualen fiber is described by Eq. (2). Ion-exchange kinetics by granular IER materials is described by Eq. (3).

EXPERIMENTAL STUDY

Aqualen fiber, the Calgon F400 (GAC), and Dowex-50W(H+) cation-exchange resin were used for comparison studies. The adsorption capacity of methylene blue was determined by taking a 500 mL flask containing 200 mL of a 1500 mg/L solution of methylene blue (Sigma Corporation) and 100 mg of Aqualen 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 absorbance at 622 nm. The experiment was repeated with 1 g GAC.

The cation-exchange capacity of adsorbents was determined by taking a 250 mL flask containing 100 mL of 0.1 M NaOH in 1 M NaCl solution

TABLE 1
Adsorption and Ion-Exchange Capacity[a]

	Methylene blue (mg/g)	Cation-exchange (meq/g)	Anion-exchange (meq/g)	Cadmium (meq/g)
Aqualen	500[b] (380)	0.75	0.4	0.13
GAC F400 Calgon	150[b] (5)	0	0.3	0
Dowex-50	—	4.0	—	4.0

[a] The numbers in parentheses are accelerated adsorption capacities within a 1-minute time period.

[b] Total adsorption capacity.

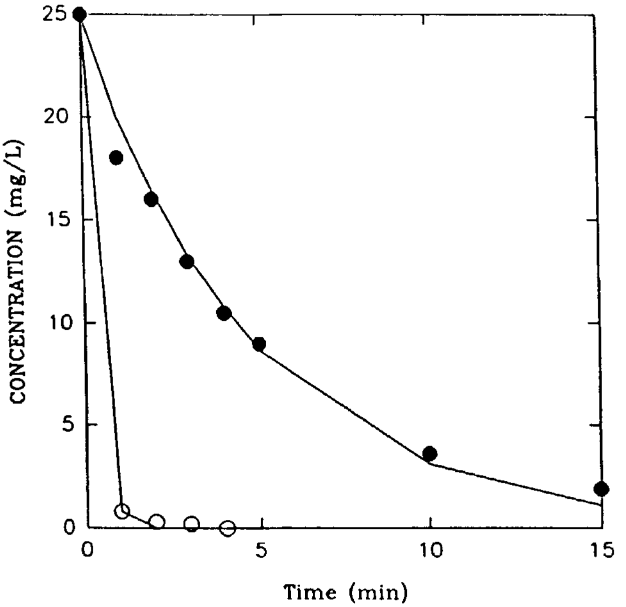

FIG. 4 Concentration of the methylene blue solution versus the time. (Experimental results are shown by filled circles for the granular activated carbon and by hollow circles for the activated carbon fiber. Theoretical predictions are shown with solid lines.)

and 1 g adsorbent and shaking it for 24 hours. The solution was then filtered and titrated with 0.1 M HCl to determine the amount of base neutralized by acidic groups of the adsorbent.

The anion-exchange capacity of adsorbents was determined in the same manner, except that 0.1 M HCl was used instead of the NaOH solution.

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.

Cadmium ion-exchange capacity was determined by taking a 250 mL flask containing 200 mL of a dilute cadmium nitrate solution (0.7 meq/g) and 1 g of adsorbent and stirring it magnetically. Cadmium concentration was measured with a cadmium ion selective electrode.

Results of experiments are shown in Table 1 and in Figs. 4–7.

Figures 4 and 5 shows the comparative adsorption by Aqualen and by GAC at two initial concentrations of methylene blue, 25 and 150 mg/L.

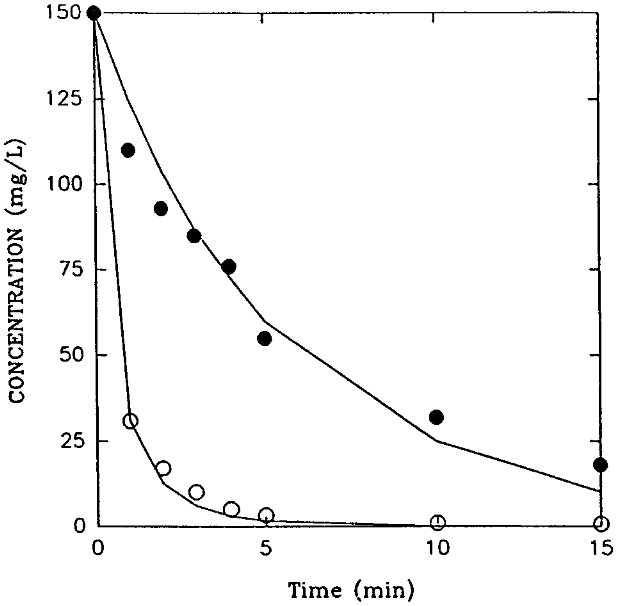

FIG. 5 Concentration of the methylene blue solution versus the time. (Experimental results are shown by filled circles for the granular activated carbon and by hollow circles for the activated carbon fiber. Theoretical predictions are shown with solid lines.)

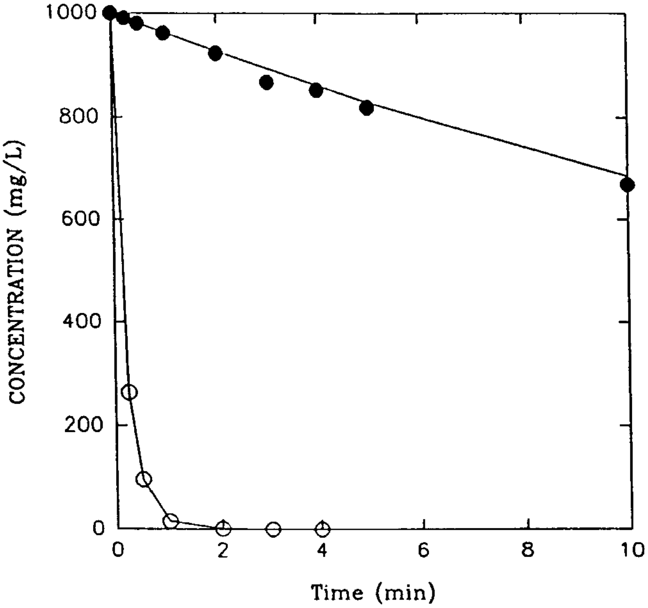

FIG. 6 Concentration of the methylene blue solution versus the time. (Experimental results are shown by filled circles for the granular activated carbon and by hollow circles for the activated carbon fiber. Theoretical predictions are shown with solid lines.)

Even though the amount of Aqualen was 10 times less than GAC (0.1 Aqualen and 1 g GAC), the rate of adsorption of Aqualen was at least an order of magnitude faster. Solid lines show theoretical predictions according to Eqs. (2) and (3), where k_1 for the Aqualen fiber is 0.02 L/(mg·min) at an initial methylene blue concentration of 25 mg/L and 0.015 L/(mg·min) at 150 mg/L concentration. The adsorption coefficient (k) for GAC was calculated to be 0.00028 L/(mg·min) for a 25 mg/L methylene blue concentration, and 0.00024 L/(mg·min) for a 150 mg/L concentration. The adsorption capacity of GAC at 1 minute was estimated to be less than 5 mg/g.

Figure 6 shows the comparative adsorption by Aqualen and by Calgon GAC at a 1000 mg/L initial concentration of methylene blue. One gram of Aqualen and 1 g Calgon GAC were used. Solid lines show theoretical predictions, where k_1 = 0.004 L/(mg·min) for the ACF, and k = 0.00005 L/(mg·min) for the Calgon GAC. Aqualen is shown to be two orders of magnitude more efficient than the Calgon GAC during the first 10 minutes.

Figure 2 shows the theoretical prediction of the methylene blue concentration across the ACF at different time intervals. A significant amount of methylene blue was expected to migrate inside the fiber within the first 5 seconds. Approximately 80% of the total adsorption capacity was saturated in as little as 3 minutes. Theoretical predictions in Fig. 2 correspond well with the experimental results shown in Fig. 6, where 30% of total adsorption capacity was reached in 15 seconds from the beginning of the separation.

The migration of methylene blue by a diffusion mechanism through a spherical granular adsorbent (500 μm in diameter) is shown in Fig. 3. Very little penetration was expected in as long as 28 hours. Actual migration distances in granular activated carbon were much less due to the macropores and mesopores which penetrated the adsorbent particle.

Figure 7 shows the adsorption of cadmium by Aqualen and by Dowex-50W(H+) ion-exchange resin. Aqualen was shown to adsorb cadmium an order of magnitude faster than Dowex-50W resin, although the total cation-exchange capacity of Aqualen was much smaller than that of Dowex-50W. Another advantage of Aqualen as compared to traditional cation-exchange resins, which contain strong acid groups on the surface,

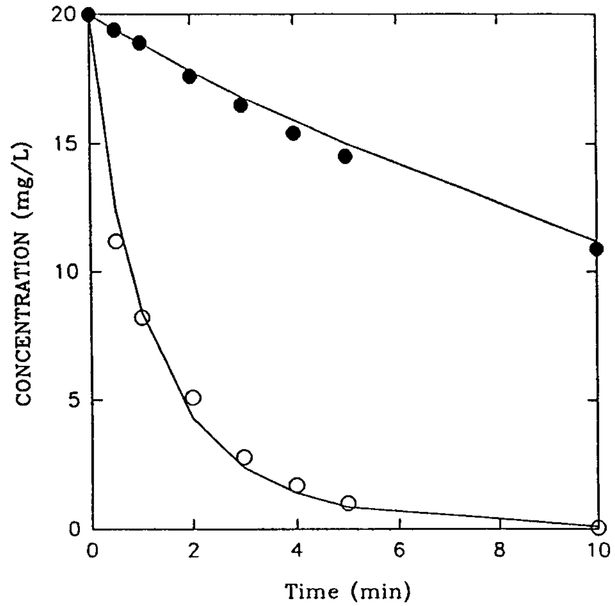

FIG. 7 Concentration of Cd ions in the solution versus the time. [Experimental results are shown by filled circles for the granular ion-exchange resin (Dowex-50W) and by hollow circles for the activated carbon fiber. Theoretical predictions are shown with solid lines.]

was that the bulk of the Aqualen cation-exchange capacity was the complex forming and weak acid groups which allowed preferential heavy metal adsorption in the presence of larger concentrations of alkaline and hardness metal ions.

CONCLUSIONS

The total adsorption capacity of Aqualen exceeds the total adsorption capacity of GAC threefold. More importantly, Aqualen adsorbes two orders of magnitude faster than granular or powdered adsorbents. The exceptionally fast adsorption properties of Aqualen are due in part to the small fiber diameter and the highly porous, open pore structure of its surface. The other reason is that the size of the micropore crystals in the ACF is smaller. The micropores are larger in width, and easier for the adsorbate to diffuse into.

Aqualen's significant ion-exchange capacity toward heavy metal ions is due mainly to the presence of complex forming groups on its surface. Aqualen is especially suitable for separation processes where both organic matter and heavy metal ions need to be removed.

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