

Fixed Bed Adsorption of Acetone and Ammonia onto Oxidized Activated Carbon Fibers

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The tailoring of the pore surface chemistry of activated carbon fibers is shown to be an effective method for increasing the removal efficiencies of various contaminants under a fixed bed configuration. An oxidation treatment with nitric and sulfuric acids resulted in a significant increase in the adsorption capacities and breakthrough times. The adsorption kinetics were described by a homogeneous surface diffusion model. Although the effective diffusion coefficients were actually reduced by the oxidation process, the improvement in equilibrium adsorption capacities more than compensated, to result in the overall improved breakthrough times.

1. Introduction

One of the undesirable features of the modern day world is widespread contamination associated with the release of chemicals into the environment. In recent years there has been a significant amount of work done to quantify the harmful effect of these trace contaminants. Society's growing concern has led many governments to establish stricter standards for clean air and water, many of them in the parts-per-billion (ppb) range. This necessitates the development of improved methods for controlling the release of toxic contaminants and the design of new materials tailored to selectively remove a wide range of contaminants and permit for recovery and reuse. Industry has also recognized the potential economic benefit that can be achieved through the recycling of chemicals instead of disposal. One technology which is attractive for this purpose is the use of dry adsorbents such as activated carbons.

Commercially available activated carbon granules (ACG's) have been an industry standard for many years.^{1–4} They are used as adsorbents to purify polluted waste streams because of their low cost and because they have been determined to be the best available technology for the removal of many contaminants. However, ACG's suffer from a number of drawbacks including poor selectivity, slow kinetics, the need for expensive containment systems, less than 100% working capacity, and costly reactivation. Perhaps the most serious problem is the absence of a comprehensive understanding as to the effect of pore size and chemistry on the adsorption properties. Such knowledge would allow the tailoring of activated carbons for the control of specific contaminants. Another problem is the lack of design flexibility when using granulated carbons. There is a definite need for the development of improved materials designed specifically for a wide range of environmental problems.

To address some of these disadvantages, Economy and Lin^{5,6} reported on the development of phenolic-based

activated carbon fibers (ACF's), which displayed significantly improved adsorption capabilities over those of ACG's. Today, these ACF's are commercially available from Nippon Kynol and are prepared by the direct activation of a cross-linked phenolic fiber at 800–1000 °C using a mixture of steam and carbon dioxide. The ACF's have the added advantage of simplified containment, capability for in situ electrical reactivation, and greater rates of adsorption over those of conventional granulated activated carbons due to much better contact efficiency.^{5,7}

Historically, the ACF's have only been used in niche markets due to their high cost, poor abrasion resistance, and limited adsorption versatility. This is because the adsorption characteristics are controlled to a considerable extent by the acidic nature of the surface. Recently some new approaches have been reported to eliminate or reduce the drawbacks associated with the ACF's.^{7–11} In order to tailor the ACF's for adsorption of specific contaminants, they were chemically converted to a nitrated, hydrogenated, chlorinated, or more highly oxidized surface.^{8,9} The problem of poor abrasion resistance has been partially addressed by activating the precursor phenolic fibers at temperatures of 400–450 °C in air.⁷ This greatly improves both the activation yields (lower cost) and the abrasion resistance. These and related studies¹² have indicated the usefulness of tailored ACF's for gas separation and for the removal of very low levels of contaminants in the ppb range.

The goal of kinetic data analysis is to develop a predictive model that can be used for designing commercial-scale adsorbents. Although initial experimental studies with ACF's have been promising, there are very few studies that construct a phenomenological model of their adsorption kinetics.¹² This is in contrast to the case for ACG's, where methods for analyzing adsorption kinetics have been extensively developed over the past two decades.^{13–18} The adsorption kinetics for ACG's are usually characterized by the homogeneous surface diffusion model, which assumes that the adsorbate molecules creep along the internal pore surfaces while in an adsorbed state.^{18,19} An alternative is the pore diffusion model, in which the adsorbate is assumed to diffuse through a fluid phase within the pores.¹⁹ The flux of adsorbate through the adsorbent is affected by pore

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tortuosity, constriction, and branching. In a real adsorbent, however, these pore structure characteristics cannot be estimated or measured in a reasonably accurate manner. Instead, the flux is assumed to occur in the radial dimension, and an "effective" surface diffusion coefficient is estimated from experimental data.^{14,15} Another mode of mass-transfer resistance that can be significant for some adsorbent systems is that of an external film surrounding the adsorbent. It has been found that the external mass-transfer resistance can be neglected for many adsorbent systems, including those with activated carbon as the adsorbent.^{20–22} One of the goals of this study is determine how well such models represent the performance of ACF's.

The potential of tailored ACF's motivated this fixed bed study to determine their utility in an applied system. It was of interest to investigate how the adsorption kinetics would be affected by chemical treatment of the ACF's. Another goal of this study was to determine if the homogeneous surface diffusion model would be adequate for modeling diffusion in ACF's. Although four major types of chemical treatment for ACF's have been developed,^{8,9} for specificity the study focuses on the adsorption of acetone and ammonia onto untreated and oxidized ACF's. Acetone represents a polar organic molecule, and ammonia a basic molecule. The breakthrough curves are measured, and the effective diffusion coefficients are computed. This is followed by discussion and conclusions.

2. Materials and Methods

2.1. Activated Carbon Fibers. Activated carbon fibers can be made from a variety of precursors including pitch, polyacrylonitrile, and phenolics.^{12,23} For this study, the ACF's were obtained from Nippon Kynol in Japan. These fibers are made from a phenol-formaldehyde resin which has been melt-spun and then acid-cured to form a fully cross-linked amorphous polymer structure. This precursor fiber, known as Kynol, is then carbonized and activated using the combustion byproducts of liquefied petroleum (mostly water and carbon dioxide). The fibers can be produced in a range of surface areas between 600 and 2500 m²/g, depending on the time and temperature of activation. The micropore structure has been shown to be very uniform across approximately 95% of the fiber diameter core by scanning tunneling microscopy.^{24,25} In addition, activation also results in the initial fiber diameter being reduced from approximately 16 μ m to 9–15 μ m, depending on the degree of activation. The fibers used in this study consisted of a series of ACF's with increasing surface area (increasing degree of burnoff): ACC-5092-10 (ACF-10), ACC-5092-15 (ACF-15), and ACC-5092-25 (ACF-25).

All ACF's used in this study came from the same production batch, as identified by Nippon Kynol. All treated ACF-10's were oxidized in the same apparatus at the same time; half were used for acetone experiments, and half for the ammonia experiments. A similar method was used for ACF-15 and ACF-25. Regenerated ACF's were not used in any of the experiments.

2.2. Characterization of Physical Structure: SEM Techniques. A commercial scanning electron microscope (Hitachi model S800) was used to measure the fiber diameters of the ACF's. The fibers were cut perpendicularly, and several photographs were taken of the cross-sectional surface. The individual fiber

diameters were then measured by hand and reported as an average value. The accelerating voltage used for all runs was 20 keV, and the field electron source provided a resolution of 2 nm. The fiber diameters were measured to be 15.4 μ m for ACF-10, 13.75 for ACF-15, and 11.25 for ACF-25.

2.3. Effect of Chemical Modification: Elemental Analysis. The carbon edge atoms can be combined with a number of different atoms, depending on the activation conditions and post-treatment. Conversely, heteroatoms can be removed upon heat treatment. Since the ACF's are produced by a high-temperature oxidative etching process, the pore surface tends to be acidic due to the presence of carboxylic acid and phenolic hydroxyl groups. This acidic surface chemistry can be modified using a variety of reactions, often at high temperatures (700–900 °C).^{8,9} In particular, the acidity of the pore surface can be increased by treatment with a strong oxidizer such as a mixture of nitric and sulphuric acids;^{8,9} an ACF that undergoes this treatment is said to be "oxidized". Conversely, a high-temperature treatment with ammonia yields a surface rich in basic nitrogen groups⁹ which has shown enhanced adsorption of acidic gases such as HCl.²⁶

A model CE440 elemental analyzer utilizes a combustion technique in which the carbon, hydrogen, and nitrogen weight percentages are determined. The sample is burned in an oxygen atmosphere at approximately 960 °C while the amounts of evolved carbon (CO₂), hydrogen (H₂O), and nitrogen (N₂) are measured by thermal conductivity detectors. Oxygen was determined by mass difference, assuming only these elements are present.

2.4. Structural Properties: Nitrogen Adsorption Isotherms. Nitrogen adsorption isotherms were used to characterize the surface area and micropore volume. A Coulter Omnisorb (Hialeah, Florida) was used for the volumetric measurement of the nitrogen adsorption isotherm at 77 K (for details, see ref 26). Type I isotherms, which are indicative of microporous carbons, were observed. This data was used to calculate the BET surface area using the standard method,^{3,27} applied over the relative pressure range 0.01–20. The micropore volume was calculated by applying the Dubinin–Radushkevich equation to the experimental nitrogen isotherm.^{28,29}

2.5. Fixed Bed Analysis. A flame ionization detector (FID) of a Hewlett-Packard gas chromatograph model 5890 (HPCG) was used to monitor the concentration of the outlet gas stream for acetone and ammonia. The flow rate was set at 50 mL/min using a Tylan General flow controller for all experiments. Sample preparation consisted of cutting the ACF samples into eight 1 in. diameter circles. These were mounted into a stainless steel cylinder using rings as spacers between each fiber layer, with the distance between each fiber layer being 6.33 mm. The rings were then compressed by an internal spring. The inlet stream hit a perpendicular plate immediately upon entering the cylinder to promote a constant velocity profile upon entering the fixed bed.

After loading, a flow rate of 50 mL/min of nitrogen at a temperature of 100 °C was used to remove adsorbed water and other impurities. After 12 h, the bed was cooled to 25 °C and held isothermally during the entire breakthrough experiment. To ensure that the detector was operating within a linear detection regime, calibra-

tions were performed that showed that the concentration and signal output were linearly related with $R^2 \geq 0.999$.

The concentration of acetone in the inlet stream was 1000 ppmv for all experiments. The concentration of ammonia used was 980 ppmv for all experiments. Once the data were collected, the signal was normalized with the highest plateau signal to obtain a normalized concentration curve (C/C_0) and the time values were normalized by the bed weight.

3. Theory

In the homogeneous surface diffusion model,^{18,19} the intraparticle material balance for a cylindrical activated carbon fiber is

$$\frac{\partial q}{\partial t} = \frac{D_s}{r} \frac{\partial}{\partial r} \left(r \frac{\partial q}{\partial r} \right) \quad (1)$$

where D_s is the effective surface diffusion coefficient, $q(z, t, R)$ is the adsorbate concentration in the adsorbent, z is the distance downstream from the inlet of the fixed bed, r is the radial position in the fiber, and t is time. This assumes diffusion only in the radial direction, which is a good assumption, since the aspect ratio $> 10\,000$ and STM images indicate that the material is uniform.

An adsorbate material balance in the gas phase is

$$\frac{\partial C}{\partial t} + v \frac{\partial C}{\partial z} + \frac{2\rho_A D_s (1 - \epsilon)}{\epsilon R} \left[\frac{\partial q}{\partial r} \right]_{r=R} = 0 \quad (2)$$

where $C(z, t)$ is the concentration of adsorbate in the bulk fluid, ϵ is the external void fraction, v is the interstitial fluid velocity, ρ_A is the adsorbent density, and R is the radius of an activated carbon fiber. This balance assumes negligible axial dispersion, constant velocity through the fixed bed, and negligible film mass-transfer resistance. The validity of the last assumption was confirmed by comparing numerical predictions with experimental data and has been found in many other adsorption studies on activated carbon.^{20,21} The constant velocity assumption is valid because of the low adsorbate concentration in the bulk fluid and the short length of the fixed bed.

The fixed bed is initially adsorbate free, which gives the initial conditions

$$q(z, 0, r) = C(z, 0) = 0, \quad \forall r \in [0, R], \quad \forall z \in [0, L] \quad (3)$$

where L is the length of the fixed bed. The boundary conditions are

$$C(0, t) = C_0, \quad \forall t \geq 0 \quad (4)$$

and

$$\log_{10} q(z, t, R) = \log_{10} q_0 - M \log_{10}^2 (P_0/P(z, t)) \quad (5)$$

where the two parameters q_0 and M are fit to equilibrium data, $P(z, t)$ is the partial pressure of the adsorbate in the gas phase, and P_0 is the saturation pressure. This last boundary condition is the Dubinin equation, which relates equilibrium adsorbate concentrations between the adsorbent and the gas phase.^{28,29}

The partial pressure $P(z, t)$ is related to the concentration in the gas phase $C(z, t)$ using the ideal gas law. The

Table 1. Elemental Analysis for Activated Carbon Fibers

sample	%C	%H	%N	%O
ACF-10 untreated	92.41	0.76	0.21	6.62
ACF-10 oxidized	70.61	0.83	0.89	21.47
ACF-15 untreated	95.23	0.24	0.20	4.33
ACF-15 oxidized	69.20	1.89	0.95	25.39
ACF-25 untreated	95.61	0.15	0.22	4.02
ACF-25 oxidized	68.30	1.57	0.90	27.92

Table 2. Physical Parameters for the Activated Carbon Fibers

sample	B.E.T.S.A (m ² /g)	micropore volume (mL/g)	bulk density (g/cm ³)
ACF-10 untreated	760	0.328	0.4226
ACF-10 oxidized	557	0.235	0.4771
ACF-15 untreated	1670	0.721	0.3161
ACF-15 oxidized	1236	0.571	0.3533
ACF-25 untreated	2158	0.864	0.2786
ACF-25 oxidized	1496	0.562	0.3079

coupled partial differential equations were solved using the numerical method of lines.^{30,31} A sparse Gear's method was used to solve the resulting system of ordinary differential equations (LSODES).^{32,33} For each breakthrough curve, the one parameter, the effective diffusion coefficient, was fit using nonlinear least squares parameter estimation,³⁴ with the optimization performed using the complex algorithm (DBCPOL³⁵).^{36,37} In all results reported here, the simulated breakthrough curve using the above model with the least squares optimal effective diffusion coefficient gave a good fit to experimental data.

4. Results

4.1. Characterization of ACF's. Table 1 gives the elemental analysis results for the ACF's used in the fixed beds. ACF's receiving the treatment with nitric/sulfuric acid for 1 h are referred to as being "oxidized". This treatment raised the oxygen content from ~5 wt % up to values as high as 28 wt %. The higher surface areas allowed more room for functional groups, resulting in an increasing amount of oxygen. Table 2 shows a significant decrease in both the surface area and the micropore volume of the ACF samples after oxidation. This decrease in surface area might seem to imply that the micropores are being blocked by oxygen groups on the surface. However, the surface area decrease can be explained by the additional weight of the oxygen groups. Since the added functional groups are not part of the carbonaceous microstructure, they do not contribute to the surface area, resulting in an artificial lowering of the surface area value. When the surface areas are normalized for the added mass of the functional groups, the surface areas do not change significantly. The bulk density of each fiber is also reported in Table 2, which is required for solving the modeling equations.

The adsorption equilibrium parameters in eq 5 for the two adsorbates and the ACF's are reported in Tables 3 and 4.

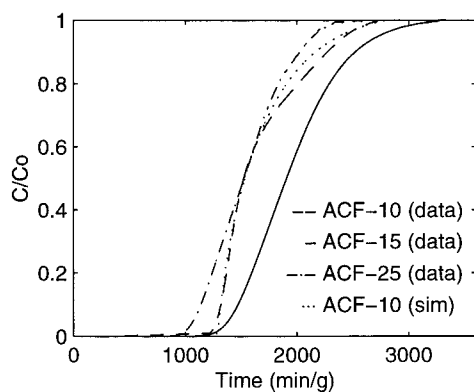
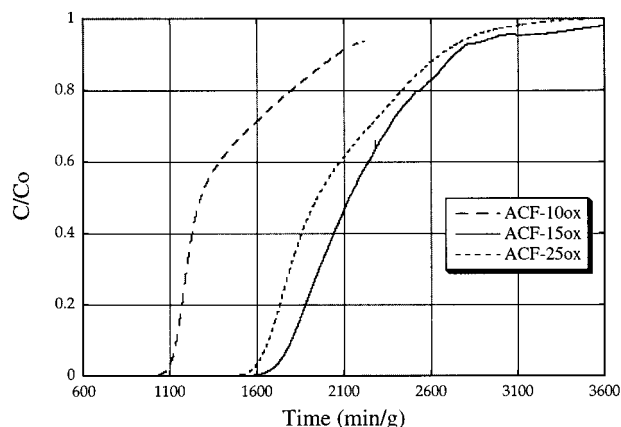
4.2. Breakthrough Curves. **4.2.1. Acetone.** The breakthrough curves are shown in Figures 1 and 2 for the untreated and oxidized ACF's. Consistent with an earlier study which did not consider chemical tailoring,³⁸ the ACF with the largest surface area does not necessarily adsorb the most acetone. Both ACF-15 and ACF-25 benefited by the oxidation treatment through increased breakthrough times and adsorption capacities. The polar molecule acetone is more attracted to the

Table 3. Adsorption Equilibrium Parameters for Acetone

sample	q_0 (mg of adsorbate/ g of adsorbate)	M
ACF-10 untreated	2.6428	0.03774
ACF-10 oxidized	2.5057	0.02891
ACF-15 untreated	2.9861	0.06732
ACF-15 oxidized	2.8393	0.04515
ACF-25 untreated	2.9563	0.07529
ACF-25 oxidized	2.8550	0.05040

Table 4. Adsorption Equilibrium Parameters for Ammonia

sample	q_0 (mg of adsorbate/ g of adsorbate)	M
ACF-10 untreated	0.9711	0.08533
ACF-10 oxidized	1.6080	0.02577
ACF-15 untreated	0.8480	0.08533
ACF-15 oxidized	1.8207	0.02988
ACF-25 untreated	0.7853	0.08533
ACF-25 oxidized	1.8903	0.03456

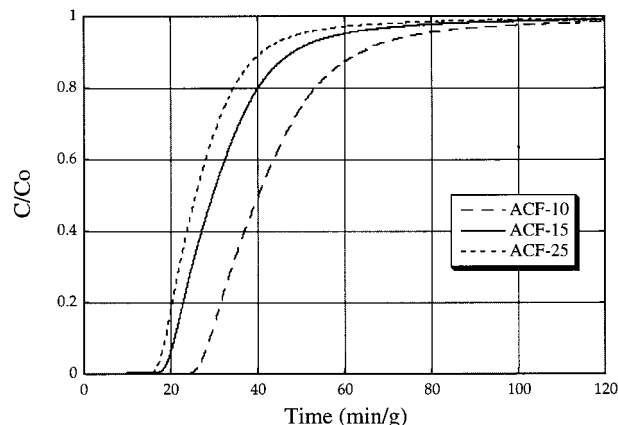
**Figure 1.** Normalized breakthrough curves for acetone on untreated ACF's.**Figure 2.** Normalized breakthrough curves for acetone on oxidized ACF's.

oxidized ACFs through hydrogen bonding and dipole interactions with the surface.⁹ However, the oxidation process was actually detrimental for the breakthrough times of ACF-10. The small pores (high overlap in potential) of the untreated ACF-10 already cause most of the micropore volume to be utilized. The added weight of the oxygen groups only serves to decrease the adsorption capacity due to loss of micropore volume. At this concentration, the oxidized ACF-15 was the best for removing acetone.

In all results reported here, the simulated breakthrough curve using the above model with the least squares optimal effective diffusion coefficient gave a

Table 5. Effective Diffusion Coefficients for Adsorption of Acetone

fiber type	$10^{14}D_s$ (m ² /s)
ACF-10 untreated	2.8
ACF-10 oxidized	2.3
ACF-15 untreated	3.9
ACF-15 oxidized	2.9
ACF-25 untreated	4.0
ACF-25 oxidized	2.4

**Figure 3.** Normalized breakthrough curves for ammonia on untreated ACF's.

fairly good fit to experimental data (see Figure 1 for a representative fit). The effective diffusion coefficients for the untreated and oxidized ACF's are reported in Table 5. The oxidized ACF's have smaller effective diffusion coefficients than the untreated ACF's. This could be because adsorption utilizing chemical functional groups requires a more site specific mechanism than if it was pure physical adsorption (van der Waals); that is, the contaminants may not be effectively adsorbed until they locate a group to "bind" with. Another possibility is that the addition of so many groups onto the pore walls could result in constriction; that is, the pores are effectively smaller. Also, in the case of surface diffusion, the presence of numerous chemical groups could interfere with the movement of molecules along the pore walls. The oxidized ACF's have increased breakthrough times in spite of the reduced effective diffusion coefficients. The improvement in equilibrium adsorption capacities caused by the oxidation process more than compensates for the reduction in effective diffusion coefficients.

This data complements the study³⁹ which considered the adsorption of acetone on an ACF in a similar fixed bed configuration. Lordgooei et al.³⁹ concluded that the main reason an ACF gave longer breakthrough times than a packed bed of ACG's was the ACF's greater adsorption capacity. Although the results suggested somewhat faster mass-transfer kinetics for the ACF than the ACG, this was not the dominant factor in causing the greatly different breakthrough times. Additional results of this study over ref 39 were the use of a homogeneous surface diffusion model to characterize the adsorption kinetics, and the experiments and analysis of how chemical tailoring affects the breakthrough times, adsorption equilibria, and adsorption kinetics.

4.2.2. Ammonia. The breakthrough curves are shown in Figures 3 and 4. The untreated ACF's do not adsorb an appreciable amount of ammonia, thus giving very short breakthrough curves. ACF-10 has the highest adsorption capacity due to its smaller pore size, which

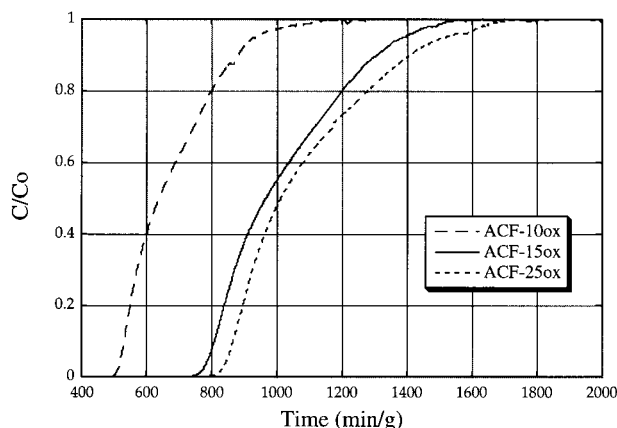


Figure 4. Normalized breakthrough curves for ammonia on oxidized ACF's.

Table 6. Effective Diffusion Coefficients for Adsorption of Ammonia

fiber type	D (m^2/s)
ACF-10 untreated	7.5×10^{-13}
ACF-10 oxidized	6.0×10^{-14}
ACF-15 untreated	7.7×10^{-13}
ACF-15 oxidized	5.4×10^{-14}
ACF-25 untreated	5.5×10^{-13}
ACF-25 oxidized	4.1×10^{-14}

is more effective for removal of gases. Following oxidation treatment, the breakthrough times increase tremendously, from 20 to 800 min/g in the case of ACF-15. This improvement is due to the interaction of the basic ammonia molecule with the acidic functional groups. After oxidation, the most effective fiber is ACF-25. From Table 1, oxidized ACF-25 has the highest amount of oxygen, followed closely by oxidized ACF-15 and then by oxidized ACF-10. As this same trend is seen in the breakthrough curves (Figure 4), it appears that the adsorption capacity scales with the amount of oxygen present.

The effective diffusion coefficients for the untreated and oxidized ACF's are reported in Table 6. Again, the oxidized ACF's have smaller effective diffusion coefficients than the untreated ACF's. As was found for acetone, the improvement in equilibrium adsorption capacities caused by the oxidation process more than compensates for the reduction in the effective diffusion coefficients, resulting in increased breakthrough times.

The results qualitatively agree with an earlier paper which studied the adsorption of ammonia and amines on ACF's impregnated by transition metal halides.⁴⁰ From a careful consideration of the batch adsorption data in Figure 3-17 of ref 40, it can be determined that the impregnation of an ACF with CuCl_2 slowed the adsorption of ammonia while greatly increasing the ACF's adsorption capacity. Quantitatively, the impregnation process increased the adsorption capacity of the ACF by approximately a factor of 10 compared to the $\text{HNO}_3/\text{H}_2\text{SO}_4$ process which increased the adsorption capacity by a factor of 15–30, depending on the surface area of the ACF.

5. Conclusions

The tailoring of pore surface chemistry was shown to be an effective method for increasing the removal efficiencies of acetone and ammonia under a fixed bed configuration. For acetone, the oxidized ACF-15 had the

right combination of pore size and pore volume to make it the most effective adsorbent. Adsorption of ammonia was poor on untreated ACF's. The oxidation treatment resulted in a tremendous increase in the adsorption capacities and breakthrough times, which scaled with the amount of oxygen groups present. In both cases, the effective diffusion coefficients were reduced by the oxidation process, but the improvement in equilibrium adsorption capacities more than compensated, to result in the overall improved breakthrough times. The fixed bed system gave steep concentration profiles consistent with a lack of channeling.

This appears to be the first study which constructs a phenomenological model for a fixed bed of activated carbon fibers. The phenomenological model was used to characterize how the oxidation process affected the adsorption kinetics. For all ACF's reported here, the simulated breakthrough curve using the homogeneous surface diffusion model with the least squares optimal effective diffusion coefficient gave a good fit to experimental data. As mentioned in section 3, including an external mass-transfer coefficient in the model did not significantly improve the fit to experimental data, which is consistent with many adsorption studies for activated carbon granules. However, this assumption would have to be re-evaluated during the design of a production-scale fixed bed adsorber using ACF's.

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