

Effect of Surface Properties of Activated Carbons on Surfactant Adsorption Kinetics

Jung-Hee Kim, Sophie H. Wu* and Phillip Pendleton*,†

Department of Chemical Engineering, Pukyong National University, Busan 608-739, Korea

*Center for Molecular and Materials Sciences, University of South Australia, Mawson Lakes, SA, 5095, Australia

(Received 23 December 2004 • accepted 8 June 2005)

Abstract—This research investigates the adsorption properties of three activated carbons (AC) derived from coconut, coal, and wood origin. A linear relationship exists between the number of water molecules adsorbed onto each AC and the oxygen content determined elemental analysis and XPS. An inverse linear relationship exists between the plateau amount of dodecanoic acid anionic surfactant and the oxygen content on the surface of ACs. The surface charge on each AC's surface had a linear relationship with the plateau amount of dodecanoic acid. A plug-flow heterogeneous surface diffusion model (PFHSDM) for a fixed-bed adsorption process was developed to describe the adsorption kinetics in a fixed-bed column. The model represents axially dispersed plug-flow, external mass transfer, adsorption equilibrium on the fluid-particle interface, and intraparticle diffusion. The larger molecular dimension of the dodecanoic acid as a more hydrophobic entity than octanoic acid led to a faster external mass transfer rate but a slower surface diffusion rate as estimated from the PFHSDM. The interaction between the organic moiety of surfactant and the AC surface chemistry such as surface oxygen content and surface charge contributes to the adsorption performance in both to the adsorption equilibrium and kinetics.

Key words: Surface Chemistry, Mathematical Model, Fixed-Bed Adsorption, Activated Carbons, Anionic Surfactants

INTRODUCTION

Activated carbons (ACs) are increasingly used as an economic and stable mass separation agent for the removal of surfactants to raise the final product quality in many industrial processes [Garcia-Delgado, 1992]. The usage of ACs for removing surfactants from industrial process streams is increasing [Wu and Pendleton, 2001]. Surfactant removal processes involved in large-scale continuous industrial processes have consumed a large quantity of ACs. For example, the expected usage of ACs in one aluminium plant in West Australia is up to 4-5 tons per day [Alcoa, 1998; Hind et al., 1999]. With such large amounts consumed, choosing an appropriate type of AC for the adsorption process becomes very important from the perspective of improving the adsorption process efficiency and reducing the overall cost of materials. Many industrial processes are developed empirically. A large number of ACs are available from commercial suppliers; hence, it is difficult for industrial researchers to identify and select an appropriate AC with the intention of achieving a highly efficient surfactant removal without knowing the proper characteristics of ACs.

It is well known that the physical properties of ACs are significant in an adsorption process, and also the AC surface chemistry has been revealed to play a considerable role in the dilute solution adsorption process [Considine et al., 2001; Pendleton et al., 1997]. Recently, the surface chemistry of ACs as adsorbents has been investigated and shown to affect the adsorption process and capacity in conjunction with physical properties such as pore size and pore distribution [Wu and Pendleton, 2001]. AC surfaces exhibit chemical heterogeneity due to the presence of several types of heteroat-

oms, oxygen, hydrogen, phosphorus, and/or sulfur, contained within the carbon matrix [Boehm, 1994; Bandosz, 1999]. Oxygen forms surface functional groups bonded on the edge of carbon as carboxylic acids, carbonyls, phenols and lactones, and offers a strong influence on solution adsorption [Hind et al., 1999; Rodríguez-Reinoso and Molina-Sabio, 1998]. The concentration of surface functional groups affects the relative hydrophobicity of the AC and the AC surface charge due to the presence of carbonate, carboxylic, and phenolic functional groups, which are solution pH dependent. Thus the surface chemistry plays an important role in influencing the adsorption capacity and the mechanism for adsorptive removal in industrial processes.

In addition to the characteristics study of ACs, AC-surfactant adsorption kinetics studies have made a contribution towards a better understanding of the AC and provide valuable information on controlling the adsorption rate, and assist industrial researchers to improve AC adsorption efficiency for surfactant removal. Several researchers have reported that the AC adsorption kinetics normally involves three steps, which include external and internal mass transfer and surface diffusion [Baup et al., 2000; Komiyama, and Smith, 1974; McKay, 1985; Morris and Weber, 1962; Noll et al., 1992; Weber and Smith, 1987]. The kinetics, such as internal diffusivities and external mass transfer coefficients, has been studied for the dynamic behaviour of adsorbates [Park et al., 2003; Shim et al., 2004]. More recently, a plug-flow homogeneous surface model was applied to determine the intraparticle surface diffusivities for the optimal design and operation of effective adsorption process [Li et al., 2003]. In these communications the surface diffusivities were determined by simulation via a mathematical model, but nevertheless the external mass transfer coefficients relied on several empirical equations which do not consider the surface chemistry on AC. Also, most gas phase packed-bed adsorbents are analyzed via a linear driving

†To whom correspondence should be addressed.

E-mail: p.pendleton@unisa.edu.au

force or an adsorption-dominated model [Sircar and Hufton, 2000] and assumed sufficiently low concentration in the carrier gas that they adhere to Henry's law equilibrium contact [Yang, 1997] though nonlinear equations have been required as equilibrium isotherm. Though extensive literature has existed for the mass transfer rates of adsorption processes, researchers have neglected the nonlinear isotherm equations by simplifying the equation and the effect of the AC surface chemistry by using the empirical equations. So few publications exist in which the effect of the surface chemistry on mass transfer rates was investigated.

This study focused both to measure surface chemistry of ACs and to evaluate adsorption kinetics of octanoic acid and dodecanoic acid onto the ACs for surfactant removal in a fixed-bed reactor. This study measured the oxygen content and surface charge on the AC's surface, and water adsorption onto the ACs as AC's surface properties. A plug-flow heterogeneous surface diffusion model (PFHSDM) for fixed-bed reactor was employed to determine the mass transfer rate and diffusion rate. For a better understanding of the adsorption processes, this study then examines the effect of the AC surface chemistry on the adsorption kinetics in an aqueous solution and a caustic solution. The information presented in this paper will lead to a deeper understanding of the anionic surfactant adsorption process and will clarify the roles of adsorbent surface chemistry and the continuous phase solution properties on the dynamic adsorption process.

ADSORPTION EXPERIMENTAL

1. Materials

Three AC samples were chosen in this study: a coconut-based steam-activated carbon (carbon-A), a wood-based phosphoric acid-activated carbon (carbon-B) and a coal-based steam-activated carbon (carbon-C). Carbon-A and B were supplied by PICA Activated Carbon Australia Pty Ltd. and carbon-C was supplied by Char Processors, Western Australia. The physical properties of the ACs are summarized in Table 1. Prior to use, the samples were washed with Milli-Q water to remove any residual, physically adsorbed activating chemicals to provide a reproducible surface for the solution adsorption measurements. Washing was continuous until the effluent conductivity matched the influent value. After washing, the samples were dried at 105 °C for 24 hr and stored in a desiccator until used.

The two anionic surfactants used in this study were octanoic acid (C_8 -acid) and dodecanoic acid (C_{12} -acid) as representatives of the surfactant mixture found in a typical Bayer process. The surfactants supplied by Sigma Aldrich (Australia) exhibit very low solubilities in pure water (≈ 1.0 mg/L for C_8 and 0.4 mg/L for C_{12}). Isopropyl alcohol (IPA) was added with 5-vol% into the solvents to improve their solubility allowing 2.0 mg/L surfactant solutions.

Table 1. The physical and chemical properties of activated carbons

	A	B	C
Surface area [m^2/g]	1369	1149	1738
Mean particle size [μm]	15.00	-	15.00
Density [g/cm^3]	0.66	-	0.38
Total pore volume [cm^3/g]	0.73	0.87	1.30
Micropore volume	0.69	0.44	0.48
Mesopore volume	0.04	0.43	0.82

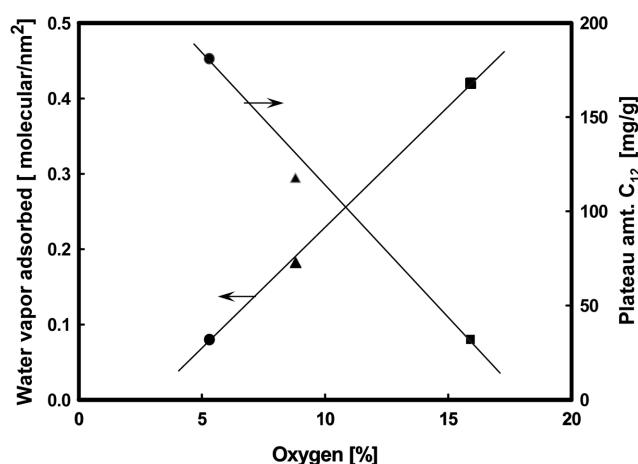


Fig. 1. Correlation water vapor and C_{12} adsorbed of oxygen on activated carbons (●: A, ▲: B, and ■: C).

2. Surfactant Concentration Analysis

Accurate and reproducible surfactant concentration determination required an extraction, derivatization and concentration process prior to GC measurements. The residual dissolved surfactants were extracted from the aqueous solutions into methyl-*t*-butyl ether phase at $1 < pH < 2$, and then reacted with diazomethane to generate the non-polar methylated surfactant from the polar surfactant [Kim, 2003; Wu, 2002]. The methylated surfactant gives a sharp response when separated on the non-polar GC column. For concentration analysis of the surfactant, we used an HP 5890 Series II GC-FID and a BPX5 column with 25 m of length and 0.22 mm of diameter supported by SGE (Australia).

3. Activated Carbon Surface Analysis

The AC's oxygen-containing surface functional groups were determined by using X-ray photoelectron spectroscopy (XPS). These analyses were operated with a PHI Model 5600 hemispheric electron spectrometer with the pass energy set at 18 eV for surface analysis and 26.8 eV during depth profiles. The X-ray source was non-monochromatized K_{α} operating at 300 W. The main chamber pres-

Table 2. Mass transfer coefficients and surface diffusivities of C_8 -acid and C_{12} -acid in H_2O and 1 M NaOH solution

Adsorbate	H_2O		1 M NaOH		2 M NaOH in batch*	
	$k_f \times 10^3$ (cm/s)	$D_s \times 10^{11}$ (cm^2/s)	$k_f \times 10^3$ (cm/s)	$D_s \times 10^{11}$ (cm^2/s)	$k_f \times 10^3$ (cm/s)	$D_{eff} \times 10^{12}$ (cm^2/s)
C_8	3.0	5.0	2.9	1.0	1.4	6.6
C_{12}	3.5	1.5	3.4	0.5	3.2	5.9

*an initial concentration of 0.4 mg/L in 2 M NaOH and carbon dosage of 0.16 mg [Wu and Pendleton, 2003].

sure was $\approx 10^{-9}$ mmHg. The spectrometer energy scale was calibrated by using the Fermi edge and the $3d_{5/2}$ line (367.9 eV) for silver. Complementing this calibration, the retardation voltage was calibrated from the positions of the Cu $2p_{3/2}$ (932.7 eV) and Cu $3p_{3/2}$ (75.1 eV) peaks relative to the excitation voltages. The resultant position of the C_{1s} photo-peak due to adventitious hydrocarbon was found at 284.8 eV. A 45° take-off angle was employed in all XPS measurements. The photo-peak area was used to calculate the atomic concentrations for each element.

4. Water Vapor Adsorption

The water adsorption isotherms were measured at 25°C for 0.05 g accurately weighed AC sample by using an automated gravimetric instrument employing a computer-controlled, modified Cahn microbalance arrangement. Prior to measurement, each AC sample was evacuated at 398 K to a background pressure of $<5 \times 10^{-6}$ Torr to eliminate the previously adsorbed vapors. Water vapor pressures were measured with a Texas gauge. The balance and the vapor source were contained in a thermostatically controlled unit. Since we were only interested in defining the specific adsorption capacity of the ACs, isotherms were determined up to the relative pressure of about 0.4.

5. Fixed Bed Adsorption Experiment Method

The fixed bed adsorption column had 3 mm internal diameter with 13 mm length made of stainless steel, and was filled up with 10 mg of AC sample giving a bed depth of 2.2 mm with ε_b (bed porosity)=0.2494. The feed tank made of Pyrex glass was capped to reduce IPA evaporation for maintaining solubility of the surfactants [Kim, 2004]. Typical operating conditions for continuous adsorption experiment were 1.0 mL/min of flow rate of solution, u , with initial concentration 2.0 mg/L, C_{in} , through the bed at 25°C and samples were taken every 1-2 hours with a 10 min collection period.

MATHEMATICAL MODEL

1. Adsorption Model in Fixed-bed

Adsorbates in bulk solution migrate toward an adsorbent particle or pass through the fixed-bed to lead to the breakthrough curve. The migration process of adsorbates into the particle can be represented by four consecutive steps: diffusion and convection from the bulk to the outer layer of the adsorbent, external mass transfer (k_f) from the outer layer of the adsorbent to the surface of the adsorbent, instantaneous adsorption, and intra particle mass transfer as diffusions.

The following assumptions were made in the development of the fixed-bed model:

- (1) The flow is plug-flow in fixed-bed;
- (2) Liquid-phase concentration gradients only exist in the flow direction;
- (3) External mass transfer is governed by a linear driving force;
- (4) Internal mass transfer is only governed by surface diffusion;
- (5) There is continuity between the adsorbate concentration in the bulk and adsorbate load at the surface;
- (6) The adsorbent is a smooth, spherical and isotropic particle; and
- (7) The adsorption process is reversible.

The model with these assumptions is consistent with PFHSDM

developed by Sontheimer and co-workers [Sontheimer et al., 1988], representing axial dispersed plug-flow, external mass transfer, adsorption equilibrium on the fluid-particle interface, and intraparticle diffusion for a fixed-bed adsorption column.

2. Governing Equations

2-1. Mass Balance for the Bulk Phase

The bulk phase mass balance includes axial fluid transport rates and a transport rate of adsorbate from the bulk phase onto the particle phase. The transport rate is dependent upon the external mass transfer rate (k_f) and the different concentration between bulk phase and particle phases.

$$\varepsilon_b \frac{\partial C_b}{\partial t} = -u \frac{\partial C_b}{\partial z} + D_b \frac{\partial^2 C_b}{\partial z^2} - \frac{3(1-\varepsilon_b)}{r_p} k_f (C_b - C_b^*) \quad (1)$$

where C_b^* is the bulk phase concentration in equilibrium with particle phase concentration on the external surface of the particle. The boundary and initial conditions for the bulk equation are given by:

$$-D_b \left. \frac{\partial C_b}{\partial z} \right|_{z=0} = u(C_{in}|_{z=0} - C_b|_{z=0}) \quad (2)$$

$$- \left. \frac{\partial C_b}{\partial z} \right|_{z=L} = 0 \quad (3)$$

$$C_b(z, 0) = 0 \quad (4)$$

where C_{in} is the feed concentration. To solve the bulk phase mass balance at a given position, a mean bulk concentration on the external surface of the particle at any position has to be determined. The mean bulk concentration on the AC external surface is dependent upon the adsorption isotherm, the external mass transfer rate, and the diffusion rate inside the AC particle pore network.

2-2. Mass Balance for the Solid Phase

The mass balance equation and the boundary and initial conditions of particle phase are represented as:

$$\frac{\partial C_s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_s \frac{\partial C_s}{\partial r} \right) \quad (5)$$

$$\left. \frac{\partial C_s}{\partial r} \right|_{r=0} = 0 \quad (6)$$

$$D_s \left. \frac{\partial C_s}{\partial r} \right|_{r=r_p} = k_f (C_b|_{r=r_p} - C_b^*|_{r=r_p}) \quad (7)$$

$$C_s(r, 0) = 0 \quad (8)$$

2-3. The Adsorption Isotherm

An adsorption isotherm represents the local equilibrium relationship between the adsorbate concentration of bulk phase and the adsorbate load of particle phase. In this study, the Langmuir isotherm equation was introduced to represent the relation of C_b^* and C_s on the surface of the particle.

$$C_s = \frac{Q_{max} K C_b^*}{1 + K C_b^*} \quad (9)$$

where Q_{max} and K are Langmuir isotherm parameters.

3. Numerical Method

Since an exact analytical solution is non-trivial for the above expression due to the nonlinear adsorption isotherm, the mass balances Eqs. (1)-(9) were solved numerically via a finite element meth-

od (FEM) linked with a Newton Raphson iteration procedure [Jeong, 1989; Kim, 2001]. The tolerance of the iteration was set at 10^{-10} . The mass transfer coefficients were also estimated against the constraint that the calculated C_b was equivalent to the experimental value with a tolerance of 10^{-10} .

RESULTS AND DISCUSSION

1. Effect of Surface Properties of Activated Carbon on Adsorption Capacity of Anionic Surfactant

Müller et al. [1985] suggest that AC aqueous solution adsorption processes are complex processes that may be classified via three adsorption mechanisms: physical adsorption, chemical adsorption, and electrostatic adsorption. Chemical adsorption relies on the formation of a chemically bound adsorbate layer over the surface through residual valance forces of the surface atoms or chemically bound functional groups, and electrostatic adsorption is the result of electrical attractive forces between the adsorbate and adsorbent due to localised ionisation of the surface and adsorptive dissociation [Jaroniec and Madey, 1988]. Also, the adsorption system with solid-liquid interface involves at least three components: the adsorbate (a single solute), the adsorbent (solid), and the solvent (liquid medium for adsorptive). The complexity of such a system is often reflected by the interactions between these components, such as adsorbate-adsorbent, adsorbate-solvent, and solvent-adsorbent interactions. Each of these interactions leads to an individual effect on the adsorption process. To present a systematic analysis of the surfactant-AC system, one also needs to consider the individual effect of the solvent, adsorbate, and adsorbent chemical properties on the adsorption process. In this study we investigated each of those interactions leading to an individual effect on the adsorption process. To interpret the surface chemistry of an adsorbent, a water adsorption isotherm measurement is employed, which is a proven method to probe the extent of hydrophilic character of an AC's surface [Rouquerol et al., 1995; Zettlemoyer et al., 1980, 1983]. The amount of water vapour adsorbed by the carbon surface indicates the extent of interaction between the water molecules and the carbon surface. During adsorption, the oxygen groups on the carbon surface act as the primary adsorption centers. Water molecules adsorb on the surface oxygen functional groups via hydrogen bonding [Barton et al., 1984; Carrott and Sing, 1988; Pendleton et al., 1983]. So water vapor adsorption isotherms were used to define each AC's relative hydrophilicity (or relative hydrophobicity), and oxygen content on AC's surface was evaluated using XPS. Adsorption isotherms for C_{12} -acid from 2 M NaOH solution reached a plateau amount adsorbed at 181, 117, and 32 mg/g for carbon A, B, and C supported by an equilibrium solution concentration of 0.4 mg/L. The relationships between the water adsorption, the plateau amount adsorbed of C_{12} -acid, and the oxygen content of the ACs are shown in Fig. 1. The amount of water vapor adsorbed is directly proportional to a carbon's surface oxygen content. It indicates that ACs containing lower oxygen content offer relatively greater hydrophobicity so that Carbon A is relatively more hydrophobic than carbon B and C. And the amount of adsorbed C_{12} -acid for each AC may be expressed as inversely proportional to the oxygen content of adsorbents. Overall, the relatively more hydrophobic AC surface showed a greater affinity for C_{12} -acid adsorption.

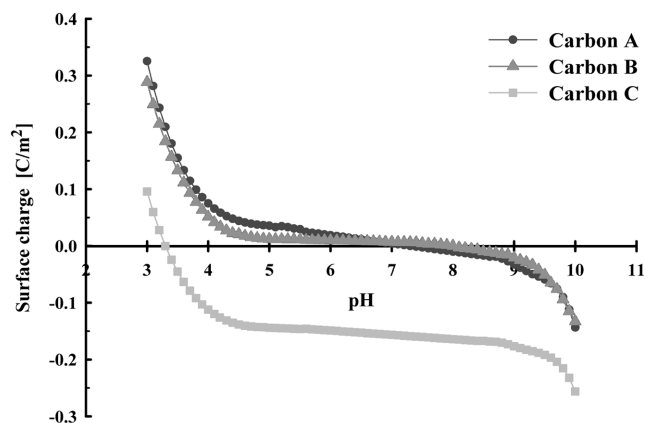


Fig. 2. The surface charge plots of activated carbons obtained in the pH range between 3 to 10.

The surface charge of the ACs reflects the dissociation of these AC functional groups. The surface charge of the ACs changes with change in solution pH and the pH influence on AC surface charge was investigated. Fig. 2 shows surface charge plots of carbon A, B and C in the pH range 3-10. The pH for a net zero charge on carbon A is ≈ 7 ; however, the rate of change of charge with pH is low. A net zero surface charge on carbon B over the pH range 5.5-7.5 approaches zero and remains negative, over the pH range 7-13. Over the pH range >3.5 the carbon C surface remains negatively charged. Fig. 2 shows that carbon A contains probably more slightly positive charges per unit area than the others. The anionic surfactants exhibit a net negative charge in the solution. Therefore, electrostatic interactions act as the adsorption driving force when the positively charged AC surfaces attract the negatively charged surfactants, leading to a higher adsorption capacity for anionic surfactants than the negatively charged AC surfaces. A repulsive force is expected between the negatively charged AC surfaces and the surfactants, indicating why carbon C exhibits the least amount of surfactant adsorbed from the water phase [Hoeft, 1996].

The adsorption isotherms of each AC for C_{12} -acid in the aqueous solution were determined to interpret the relation of surface charge

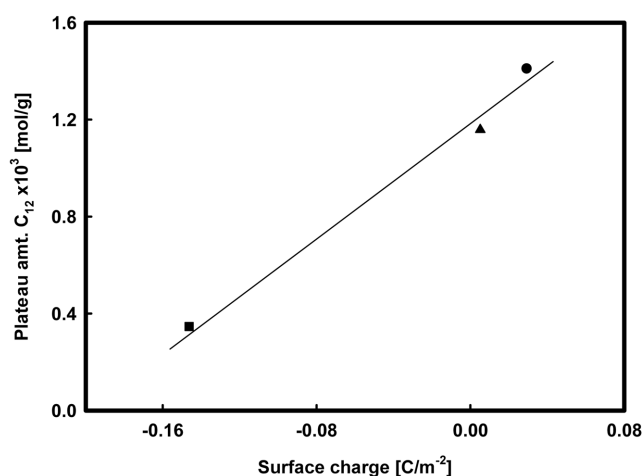


Fig. 3. Correlation between the amount of C_{12} -acid adsorbed with surface charge at pH 5.5.

and adsorption capacity. The aqueous solution used in this study was at approximately pH=5.5 and the surface charges of each ACs at pH=5.5 were extracted from Fig. 2. Fig. 3 shows the the amount of C_{12} -acid adsorbed is directly proportional to the each ACs surface charge.

To interpret the effect of surfactants on adsorption capacities in the fixed-bed adsorption from a water solution with 5% IPA (aqueous solution) the breakthrough curve of C_8 -acid was completed in about 12 hours, and that of C_{12} -acid was completed in 48 hours as shown in (a) and (b) of Fig. 4, respectively. By integrating the curves the adsorbed amount of surfactants could be calculated, and the adsorption capacity of carbon-A for C_8 was 0.71×10^{-3} mol/g and 1.69×10^{-3} mol/g for C_{12} -acid, respectively. The capacity of carbon-A for C_{12} -acid adsorption was 2.38 times greater on a molar and hence molecular basis than for C_8 -acid. Carbon A shows a greater affinity for the more relatively hydrophobic C_{12} -acid than C_8 -acid for the fixed-bed contact, which it is consistent with the batch reactor adsorption systems [Wu, 2002].

To interpret the effect of solution properties on the surfactant adsorption, the 1M NaOH solution with 5% IPA (caustic solution) was used in the fixed-bed adsorption. The adsorption capacity of carbon A was 0.62×10^{-3} mol/g for C_8 and 1.31×10^{-3} mol/g for C_{12} -acid, respectively. Carbon A offers a lower capacity for the anionic surfactants from caustic solution than from the aqueous solution. This difference is due to the greater repulsive force between the surfactant and the AC surface charge as shown Fig. 2. The anionic sur-

factants dissociate to form negative ions ($CH_3(CH_2)_nCOO^-$) in both solutions, but the caustic solution creates a greater dissociation and, at pH 13, the solution promotes a strong negative surface charge. Comparing the differences in negative surface charges at pH 13 (caustic solution) and pH 5.5 (aqueous solution), the latter offer negligible net surface charge, promoting adsorption.

2. Effect of AC Surface Properties on Adsorption Kinetics

A number of researchers [Baup et al., 2000; Mathews and Weber, 1984; McKay, 1985; McKay et al., 1981, 1986; McKay and Bino, 1988; Sontheimer et al., 1988] have suggested that the adsorption kinetics is controlled by the external mass transfer (k_f) and/or internal diffusion (D_s) for various dilute aqueous solutions of organic materials in contact with ACs of different physical and chemical properties. This work would apply the PFHSDM model to describe the AC adsorption rate and the concentration distribution in adsorption reactor and within the carbon particle up to the surface of the particle.

To estimate the k_f and the D_s by using Eqs. (1)-(9), the D_s values were calculated by the empirical Wilke-Chang equation [Seader and Henley, 1998]. The external mass transfer coefficient (k_f) and the surface diffusion coefficient (D_s) of the surfactant onto the AC can be estimated by fitting the data from the experiment with the result from the calculation of PFHSDM for the fixed-bed reactor as shown in Fig. 4. The k_f and the D_s values are 3.0×10^{-3} cm/s and 5.0×10^{-11} cm²/s for C_8 -acid, and 3.5×10^{-3} cm/s and 1.5×10^{-11} cm²/s for C_{12} -acid in the aqueous solutions. The k_f and D_s values compare favourably with Li's data, $k_f = 7.7\text{--}12.91 \times 10^{-3}$ cm/sec and $D_s = 0.65\text{--}6.51 \times 10^{-12}$ cm²/sec ionic surfactants for an activated carbon [Li et al., 2003], and Baup's data also $k_f = 2.6\text{--}2.75 \times 10^{-2}$ cm/sec and $D_s = 6.5\text{--}4.0 \times 10^{-10}$ cm²/sec for Atrazine, Bromoxynil, and Diuron via a homogeneous surface diffusion model [Baup et al., 2000]. Therefore, we suggest that the k_f and D_s values in this study are appropriate in magnitude.

The k_f value of C_{12} -acid was 1.17 times greater than that of C_8 -acid. We suggest that this is due to the hydrophobic attraction promoted by the stronger hydrophobic nature of C_{12} -acid over C_8 -acid. We also compared the k_f values from our model with those of an empirical equation, due to Wakao and Funazakri, 1978. Here, the k_f values were calculated to be 1.64×10^{-2} cm/s for C_8 -acid and 1.36×10^{-2} cm/s for C_{12} -acid. This trend is the reverse of our model. We attribute the difference to the empirical equation which omits a consideration of chemical properties between adsorbates and adsorbent. Secondly, our model recognizes the important contribution nature AC surface influence on the external mass transfer rate.

To interpret the effect of solution properties on the kinetics, the 1 M NaOH caustic solution was used in the fixed-bed adsorption. The estimated k_f values were 2.9×10^{-3} cm/s and 3.4×10^{-3} cm/s for C_8 -acid and C_{12} -acid and the D_s values were 1.0×10^{-11} cm²/s and 0.5×10^{-11} cm²/s, respectively. These trends, $k_f(C_8) < k_f(C_{12})$ and $D_s(C_8) > D_s(C_{12})$, are consistent with the result in 2 M NaOH caustic solution in a batch reactor as summarized in Table 2 [Pendleton and Wu, 2003]. The notable solution effect did not appear on k_f , but the D_s in caustic solution become up to 20% slower for C_8 -acid and 30% for C_{12} -acid than in aqueous solution. A lower D_s of surfactants occurred in strong caustic solution (pH>13) than aqueous solution (pH=5.5) owing to a strong repulsive force between the negatively charged AC surfaces and the negative anionic surfactants.

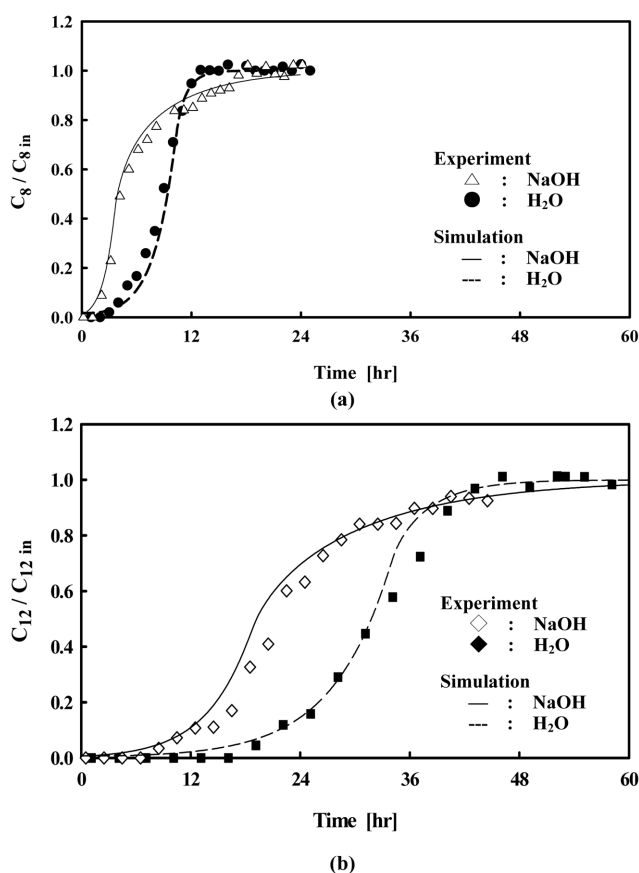


Fig. 4. Breakthrough curves of C_8 and C_{12} measured and simulated for adsorption in aqueous solution and caustic solution.

CONCLUSIONS

This study investigated the influence of AC surface properties such as the surface charge and oxygen content on the adsorption equilibrium of anionic surfactants. A linear relationship exists between the number of water molecules adsorbed onto each AC and the oxygen content on the AC's surface. An inverse linear relationship exists between the plateau amount of dodecanoic acid anionic surfactant and the oxygen content on the surface of ACs. The surface charge on each AC's surface had a linear relationship with the plateau amount of dodecanoic acid. A plug-flow heterogeneous surface diffusion model was employed to determine the adsorption kinetics of octanoic acid and dodecanoic acid on to activated carbon in a fixed-bed reactor. The larger molecular dimension of the C₁₂ anionic surfactant as a relatively more hydrophobic entity led to a faster external mass transfer rate but a slower surface diffusion rates. The surface charge of AC affected surface diffusion. Overall the interaction between the AC surface chemistry and adsorbate hydrophobicity contributed to the adsorption performance due to the adsorption equilibrium and kinetics of the anionic surfactant onto AC.

ACKNOWLEDGMENTS

The authors acknowledge the Australian Research Council for the provision of a SPIRT grant, APA(I) scholarship to S.-H. Wu, and Alcoa World Alumina and PICA (Australia) for financial support, and the Department of Foreign Affairs and Trade for the provision of an Australia-Asia (Korea) Scholarship to J.-H. Kim. The authors also thank Dr. Alexander Badalyan for constructing the computer-controlled sampling unit.

NOMENCLATURE

C_b	: liquid concentration in the bulk [mol cm ⁻³]
C_b^*	: liquid concentration at liquid/solid interface [mol cm ⁻³]
C_{in}	: liquid concentration at inlet of the fixed bed [mol cm ⁻³]
C_s	: adsorbate load [mol cm ⁻³]
D_b	: mass diffusivity for bulk [cm ² s ⁻¹]
D_s	: surface diffusivity [cm ² s ⁻¹]
k_f	: external mass transfer coefficient across liquid/solid interface [cm ² s ⁻¹]
L	: axial length of the fixed bed [cm]
r	: radial distance inside the particle of adsorbent [cm]
r_p	: mean radius of adsorbent particle [cm]
u	: superficial velocity [cm s ⁻¹]
t	: time [s]
z	: axial distance [cm]
ε_b	: bed porosity [-]

REFERENCES

- Alcoa, "Alcoa Annual Report," www.alcoa.com.au (1998).
- Barton, S. S., Evans, M. J. B., Holland, J. and Koresch, J. E., "Water and Cyclohexane Vapour Adsorption on Oxidised Porous Carbon," *Carbon*, **22**, 265 (1984).
- Baup, S., Jaffre, C., Wolbert, D. and LaPlanche, A., "Adsorption of Pesticides onto Granular Activated Carbon: Determination of Surface Diffusivities using Simple Batch Experiments," *Adsorption*, **6**, 219 (2000).
- Boehm, H. P., "Some Aspects of the Surface Chemistry of Carbon Blacks and Other Carbons," *Carbon*, **32**, 759 (1994).
- Bandosz, T., "Effect of Pore Structure and Surface Chemistry of Virgin Activated Carbons on Removal of Hydrogen Sulfide," *Carbon*, **37**, 483 (1999).
- Carrott, P. J. M. and Sing, K. S. W., *Assessment of Microporosity*, Elsevier, Amsterdam (1988).
- Considine, R., Denoyel, R., Pendleton, P., Schumann, R. and Wong, S.-H., "The Influence of Surface Chemistry on Activated Carbon Adsorption of 2-Methylisoborneol from Aqueous Solution," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **179**, 271 (2001).
- Garcia-Delgado, R. A., Cotoruelo, L. M. and Rodriguez, J. J., *Sep. Sci. Technol.*, **27**, 1065 (1992).
- Hind, A. R., Bhargava, S. K. and Grocott, S. C., "The Surface Chemistry of Bayer Process Solids: A Review," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **146**, 359 (1999).
- Hoelt, C. E. and Zollars, R. L., "Adsorption of Single Anionic Surfactants on Hydrophobic Surfaces," *J. of Colloid and Interface Science*, **177**, 171 (1996).
- Jaroniec, M. and Madey, R., *Physical Adsorption on Heterogeneous Solids*, Elsevier, Amsterdam (1988).
- Jeong, Y. O., *Thermal Effects on Single-Well Chemical Tracer Tests for Measuring Residual Oil Saturation*, Ph. D. Thesis, Houston University, Houston, U.S.A. (1989).
- Kim, J. H., Park, P. W., Chung, J. K., Huh, W. W. and Jeong, Y. O., "Effects of Pulverized Coal Injection on Blast Furnace at Steady State," *HWAHAK KONGHAK*, **40**, 169 (2002).
- Kim, J. H., *Numerical Simulation of Blast Furnace Injected with Pulverized Coal and Fixed-bed Adsorption of Organic Acids by Activated Carbon in Heterogeneous Chemical Reaction Systems*, Ph. D. Thesis, Pukyong National University, Korea (2003).
- Kim, J. H., Jeong, Y. O. and Pendleton, P., "Adsorption Kinetics of Anionic Surfactants onto Activated Carbon in Fixed Bed," *J. Ind. Eng. Chem.*, **10**, 1025 (2004).
- Kim, T. Y., Kim, S. J. and Choi, S. Y., "Effect of Relative Humidity on the Adsorption Characteristics of Carbon Tetrachloride in a Fixed Bed," *J. Ind. Eng. Chem.*, **10**, 188 (2004).
- Komiyama, H. and Smith, J. M., "Surface Diffusion in Liquid - Filled Pores," *AIChE J.*, **20**, 1110 (1974).
- Li, F., Yuasa, A., Ebie, K. and Azuma, Y., "Microcolumn Test and Model Analysis of Activated Carbon Adsorption of Dissolved Organic Matter after Precoagulation. Effects of pH and Pore Size Distribution," *J. Colloid and Interface Science*, **262**, 331 (2003).
- Mathews, A. P. and Weber, W. J., "Modelling and Parameter Evaluation for Adsorption in Slurry Reactors," *Chemical Engineering Comment*, **25**, 157 (1984).
- McKay, G., Allen, S. J., Mcconvey, I. F. and Otterburn, M. S., "Transport Processes in the Sorption of Coloured Ions by Peat Particles," *Journal of Colloid Interface Science*, **80**, 323 (1981).
- McKay, G., "The Adsorption of Dyestuffs from Aqueous Solutions using Activated Carbon: An External Mass Transfer and Homogeneous Surface Diffusion Model," *AIChE J.*, **31**, 335 (1985).
- McKay, G., Bino, M. J. and Altememi, A., "External Mass Transfer During the Adsorption of Various Pollutants onto Activated Carbon,"

- Water Research*, **20**, 435 (1986).
- McKay, G and Bino, M. J., "Adsorption of Pollutants from Wastewater onto Activated Carbon Based on External Mass Transfer and Pore Diffusion," *Water Research*, **22**, 279 (1988).
- Morris, J. C. and Weber, W. J., *Removal of Biologically Resistant Pollutants from Wastewater by Adsorption*, in First international conference on water pollution (1962).
- Müller, G, Radke, C. J. and Prausnitz, J. M., "Adsorption of Weak Organic Electrolytes from Dilute Aqueous Solution onto Activated Carbon. Part I. Single-solute Systems," *Journal of Colloid Interface Science*, **103**, 466 (1985).
- Noll, K. E., Gouranis, V. and Hou, W. S., *Adsorption Technology for Air and Water Pollution Control*, Lewis Publishers, New York (1992).
- Park, J. W., Lee, Y. W., Choi, D. K. and Lee, S. S., "Adsorption Characteristics of Toluene and Trichloroethylene onto Activated Carbon Fiber," *J. Ind. Eng. Chem.*, **9**, 381 (2003).
- Pendleton, P., Zettlemoyer, A. C. and Micale, F. J., *Adsorption from Solution*, Academic Press, London (1983).
- Pendleton, P., Wong, S.-H., Schumann, R., Levay, G., Denoyel, R. and Rouquerol, J., "Properties of Activated Carbon Controlling 2-Methylisoborneol Adsorption," *Carbon*, **35**, 1141 (1997).
- Pendleton, P. and Wu, S. H., "Kinetics of Dodecanoic Acid Adsorption from Caustic Solution by Activated Carbon," *J. of Colloid and Interface Science*, **266**, 245 (2003).
- Rodríguez-Reinoso, F. and Molina-Sabio, M., "Textural and Chemical Characterization of Microporous Carbons," *Advances in Colloid and Interface Science*, **76-77**, 271 (1998).
- Rouquerol, J., Avnir, D., Fairbridge, C. W., Everett, D. H., Haynes, J. M., Pernicone, N., Ramsay, J. D. F., Sing, K. S. W. and Unger, K. K., "Recommendation for the Characterisation of Porous Solids," *Pure and Applied Chemistry*, **67**, 1741 (1995).
- Seader, J. and Henley, M., *Separation Process Principles*, Wiley, New York, U.S.A (1998).
- Sircar, S. and Hufton, J. R., "Why Does the Linear Driving Force Model for Adsorption Kinetics Work?" *Adsorption*, **6**, 137 (2000).
- Shim, W. G., Chaudhary, D. S., Vigneswaran, S., Ngo, H. H., Lee, J. W. and Moon, H., "Mathematical Modeling of Granular Activated Carbon (GAC) Biofiltration System," *Korean J. Chem. Eng.*, **21**, 212 (2004).
- Sontheimer, H., Crittenden, J. C. and Summers, S., *Activated Carbon for Water Treatment*, AWWA Research Foundation, Karlsruhe (1988).
- Wakao, H. and Funazkri, T., "Effect of Fluid Dispersion Coefficients on Particle-to-fluid Mass Transfer Coefficients in Packed Beds. Correlation of Sherwood Numbers," *Chem. Eng. Sci.*, **33**, 1375 (1978).
- Wang, Z. M., Yamashita, N., Wang, Z. X., Hoshinoo, K. and Kanoh, H., "Air Oxidation Effects on Microporosity, Surface Property, and CH₄ Adsorptivity of Pitch-based Activated Carbon Fibers," *Journal of Colloid and Interface Science*, **276**, 143 (2004).
- Weber, W. J. and Smith, J. M., "Simulation and Design Models for Adsorption Processes," *Environmental Science and Technology*, **21**, 1040 (1987).
- Wu, H., *The Influence of Activated Carbon Surface Chemistry and Physical Properties and Solution Properties on Ionic Surfactant Adsorption from Dilute Solution*, Ph.D. Thesis, University of South Australia, Adelaide, pp. 190 (2002).
- Wu, S. H. and Pendleton, P., "Adsorption of Anionic Surfactant by Activated Carbon: Effect of Surface Chemistry, Ionic Strength, and Hydrophobicity," *J. of Colloid and Interface Science*, **243**, 306 (2001).
- Yang, R. T., *Gas Separation by Adsorption Processes*, Imperial College, London, pp. 352 (1997).
- Zettlemoyer, A. C., Siddiq, M., Kovacs, P. and Micale, F. J., "Sorption of Water and Non-polar Organic Vapors on Microporous Chromia," *Croatia Chemica Acta*, **53**, 319 (1980).
- Zettlemoyer, A. C., Pendleton, P. and Micale, F. J., "A Study of the Adsorption Mechanism of Micropores," *Croatia Chemica Acta*, **56**, 633 (1983).