Simultaneous determination of intraparticle diffusivities from ternary component uptake curves using the shallow bed technique

K. Satoh[a], Huan-Jung Fan[b,*], Hideo Hattori[c], Kiyohiko Tajima[c], Eiji Furuya[a]

[a] Department of Applied Chemistry, Meiji University Kawasaki, Japan
[b] Department of Environmental Engineering, Hungkuang University, Taichung, Taiwan
[c] Research and Development Section, Genesis Research Institute, Nagoya, Japan

Abstract

In order to design and operate a fixed-bed reactor, accurate modeling is important. For a single component system, the determination of intraparticle diffusivity is rather easy. However, the calculations of multi-component systems are normally complicated and very time-consuming. Therefore, an alternative simple determination procedure using the shallow bed technique is proposed in this research to determine the intraparticle diffusivities for multi-component systems. Ternary component systems of phenol (PH), benzoic acid (BA), and p-nitro-phenol (PNP) were investigated as model components. This study illustrated that adsorption uptake curves of different components in ternary systems can be converted into one typical characteristic curve (theoretical uptake curve, TUC) by using a set of dimensionless groups. By matching the dimensionless experimental uptake curve (DEUC) with TUC, diffusivities of PH, BA and PNP were determined as 8.00×10^{-8}, 5.92×10^{-8} and 5.05×10^{-8} cm^2 s^{-1}, respectively. These values are in good agreement with simulated experimental values. This study demonstrated that the shallow bed technique can be used to simultaneous determination of intraparticle diffusivities from multi-component systems.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Adsorption; Intraparticle diffusivity; Ternary component systems; Uptake curve

1. Introduction

For application of adsorption technology in advanced water and wastewater treatment, the fixed-bed reactor is considered the most efficient [1]. However, the adsorption of multi-component systems is much more complicated as compared to the adsorption in single component systems [1]. For single component fixed bed reactors, many design methods were presented such as the analytical solution using an approximation approach (MTZ method) [2], the graphical solutions based on linear driving force (LDF) approximation approaches [3–4], the analytical solution using LDF approximation approaches [5], and the numerical solution of partial differential equations approach [6] (the numerical breakthrough curve method). In general, the MTZ method is the simplest among these methods, while the numerical breakthrough curve method is the most difficult as well as the most accurate method.

For multi-component adsorption systems, only a few design methods are presented in the literature. All of these methods required equilibrium parameters for multi-component systems and adsorption kinetic parameters from a single adsorption test. The multi-component adsorption equilibria can be estimated using single component isotherms [7–14]. For multi-component adsorption kinetic parameters, the extended-MTZ method can possible to be used [15,16]. The extended-MTZ method is similar to the traditional MTZ method except using transient equilibrium relationship for adsorption zone. However, the estimation of the transient adsorption equilibria is very complex and hence the extended-MTZ method is not easy to use. Therefore, there is a need for developing a simple procedure for the determination of kinetic parameters for multi-component systems.

In order to design and operate a fixed-bed reactor, accurate modeling is important, which can be done by solving a series of nonlinear partial differential equations. The calculation is normally very time-consuming and complicated [17]. A good procedure for determination of kinetic parameters must be composed of simple experimental and analytical procedures.

* Corresponding author. Tel.: +886 4 26318652x4105; fax: +886 4 26525245.
E-mail address: fan@sunrise.hk.edu.tw (H.-J. Fan).

For single component kinetic adsorption, one of the simple experimental procedures is the completely mixed batch reactor (CMBR) method and the analytical procedure is very easy to use. However, for multi-component adsorption systems in the CMBR, the analytical procedure is very complex because the procedure involves sophisticated numerical estimation of concentration decay curves using multi-component adsorption equilibria. An alternative simple determination procedure for kinetic parameters is the shallow bed technique for single component adsorption systems. In general, in order to simulate the adsorption kinetics, equilibrium models such as the linear isotherm, Freundlich isotherm, Langmuir isotherm and surface complex formation models must be obtained first [17]. One major advantage of the shallow bed technique is that the kinetic parameters can be determined from experimental uptake curve (EUC) without knowledge of equilibrium data. However, the method is only applicable to single component systems; there is no simple analytical solution for multi-component systems. Therefore, the objective of this paper is to propose an alternative method using the shallow bed technique for simultaneous determination of intraparticle diffusivities in multi-component systems.

2. Fundamental equations and estimation procedure

In a shallow bed reactor, since the bed length is very short, the adsorbate concentration at the effluent is the same as the concentration at the influent. The mass-transfer resistance at the fluid-to-solid film surrounding adsorbent particles in a shallow bed reactor can be negligible under high fluid velocity. Hence, the adsorbate concentration at the interface between fluid and solid is the same as the concentration of the fluid running through spaces among particles. The rate equation for component i within a spherical adsorbent particles is listed in Eq. (1) with the assumption that the surface diffusion controlling and the solid concentration difference is the main driving force for intraparticle mass transfer. When a virgin adsorbent particle is employed, the amount adsorbed for each component at any points within the particle is initially zero in multi-component systems. At the surface of adsorbent (r_p), the amount adsorbed for each component is equilibrium with fluid concentrations at time (t) = zero. At the center of particles ($r = 0$), the differential coefficient ($\partial q_{m,i}/\partial r$) is zero, because of the symmetry. The initial and boundary conditions of Eq. (1) are listed in Eqs. (2)–(4).

$$\left(\frac{\partial q_{m,i}}{\partial t}\right) = \left(\frac{D_{s,i}}{r^2}\right)\frac{\partial}{\partial r}\left(r^2\frac{\partial q_{m,i}}{\partial r}\right) \tag{1}$$

I.C. $q_{m,i} = 0$,   at $t = 0$ (2)

B.C. $\dfrac{\partial q_{m,i}}{\partial r} = 0$,   at $r = 0$ (3)

$q_{m,i} = q_{s,i} = q_{0,i}$,   at $r = r_p$ (4)

where $q_{m,i}$ and $q_{s,i}$ denotes the amount of component i adsorbed at r and r_p, respectively. $q_{0,i}$ is the amount of component i adsorbed at the equilibrium conditions. $D_{s,i}$ is effective sur-

face diffusivity of component i. In multi-component systems, for component i, the equilibrium amount adsorbed ($q_{0,i}$) is dependent on not only the corresponding component concentration ($c_{0,i}$) but also the concentrations for other components in the solution [10–14,18]. Amount adsorbed within particles ($q_{m,i}$) cannot be evaluated analytically and hence the finite difference equations were derived from Eq. (1). In this case, central difference method was employed with I.C. and B.C listed in Eqs. (2)–(3) to determine theoretical values of $q_{m,i}$.

The amount adsorbed within particles ($q_{m,i}$) cannot be obtained experimentally and hence the value of $q_{m,i}$ is converted to a measurable particle mean amount adsorbed ($q_{t,i}$). The value of $q_{t,i}$ is obtained by the integration of the local value, as shown in Eq. (5). The numerator in right-hand-side of Eq. (5) denotes total amount adsorbed on one adsorbent particle and the denominator is the weight of the single particle. Particle density in both numerator and denominator are omitted.

$$q_{t,i} = \frac{\int_0^{r_p} 4\pi q_{m,i} r^2\, dr}{(4/3)\pi r_p^3} \tag{5}$$

For a virgin adsorbent particles, the value of $q_{t,i}$ for each component varies from zero to the corresponding $q_{0,i}$. The value of $q_{0,i}$ depends on the concentrations of all components dissolved in the solution. For single component system, an analytical solution is available for Eq. (1) [19–21]. However, in the case of a non-linear and multi-component systems, Eq. (1) with initial and boundary conditions cannot be solved yet due to the fact that the $q_{0,i}$ depends on the concentrations of all component dissolved in the solution as mentioned above. Therefore, these equations were solved numerically using the finite difference method to yield uptake curves for ternary component systems in this research. The increment for dimensionless radial length, ΔR, was used to be 1/30 based on a preliminary estimation. The simulated uptake curves were matched with the theoretical uptake curve (TUC) to determine the diffusivity of each component in the ternary component systems. The definition of TUC and the determination method are illustrated in Section 3.2. Computation software was written with the Borland C++ Builder and the calculation time was a few minutes on a 800 MHz Pentium III computer.

3. Results and discussion

3.1. Dependency of uptake curves

Ternary component systems including phenol (PH), benzoic acid (BA), and *p*-nitro-phenol (PNP) were investigated in this study. Characteristic of these components are listed in Table 1. The adsorbent particle radius (r_p) was 0.0298 cm. Under conditions listed in Table 2 with various influent concentrations, ternary component uptake curves were simulated by the technique mentioned above. The simulated uptake curves are illustrated in Fig. 1. The figure shows all uptake curves reached similar values of the corresponding $q_{0,i}$. It shows that the final values reached in the uptake curves of PH, BA, and PNP in various ternary component systems are shown in Fig. 2. As shown

Table 1
Characteristics of adsorbate

Component	Phenol	Benzoic acid	*p*-Nitro-phenol
Freundlich constant k (mmol g^{-1})	1.62	2.09	2.47
Freundlich constant n	4.32	4.03	5.83
Intraparticle diffusivity (cm^2 s^{-1})	8.0×10^{-8}	6.0×10^{-8}	5.0×10^{-8}
Molecular weight	94.11	122.13	139.11

Table 2
Simulated conditions

Run	Component	Phenol (PH)	Benzoic acid (BA)	*p*-Nitro-phenol (PNP)
1	Concentration (g L^{-1})	1.0	1.0	1.0
2	Concentration (g L^{-1})	2.0	1.0	1.0
3	Concentration (g L^{-1})	1.0	2.0	1.0
4	Concentration (g L^{-1})	1.0	1.0	2.0

in Fig. 2, the shapes of uptake curves $q_{0,i}$ were dependent on the concentrations of other components in solution. For example, phenol with the concentration ratios of 1:1:1 for PH:BA:PNP has the highest uptake curve as shown in Fig. 2a. The uptake curves of phenol were significantly reduced under conditions of higher concentration ratios of BA or PNP, such as 1:2:1 and 1:1:2 for PH:BA:PNP, respectively. Similar simulated results were observed for BA and PNP as shown in Fig. 2b and c, respectively.

The dimensionless mean amount adsorbed ($Q_{t,i}$) can be obtained by dividing $q_{t,i}$ by its corresponding $q_{0,i}$ as shown in Eq. (6).

$$Q_{t,i} = \frac{q_{t,i}}{q_{0,i}} \tag{6}$$

The resulting modified uptake curves for each component are shown in Fig. 3. Each component or adsorbate converged into one characteristic curve and unlike in Fig. 2, the curve is independent of the solution compositions. For example, the PH uptake curve (Fig. 2a) with three different influent compositions converges into one characteristic curve as shown in Fig. 3. Similar results were obtained for BA and PNP.

Furthermore, the dimensionless time (T_i) was introduced into these curves in Fig. 3 to further consolidate these curves into one typical characteristic uptake curve. T_i is defined in Eq. (7).

$$T_i = \left(\frac{D_{s,i}}{r_p^2} \right) t \tag{7}$$

The resulting dimensionless uptake curves are shown in Fig. 4. It is apparent that all uptake curves with different compositions as shown in Fig. 3 converted into one typical characteristic uptake curve regardless of different types of adsorbate. The curve shown in Fig. 4 is referred as TUC (theoretical uptake curve). TUC would be used to determine the intraparticle diffusivities in multi-component systems.
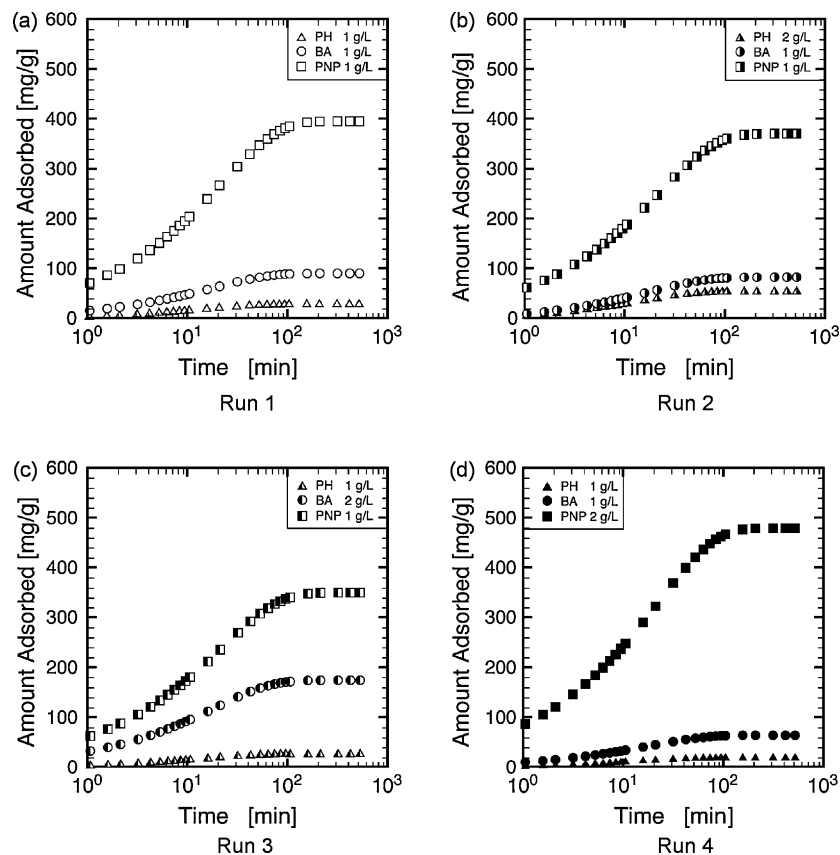

Fig. 1. Simulated uptake curves for ternary component systems under conditions listed in Table 2.
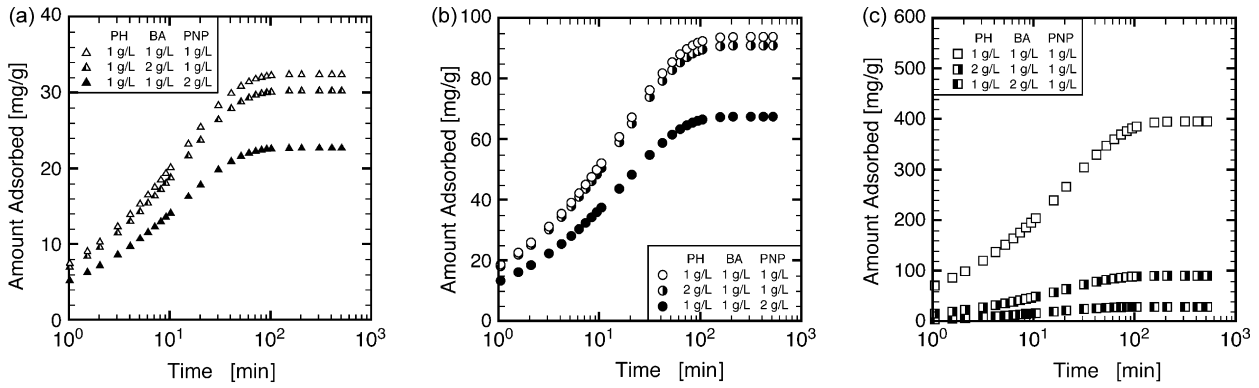
Fig. 2. Simulated of uptake curves of (a) PA, (b) BA and (c) PNP in various ternary component systems.

Two additional dimensionless variables are defined in Eqs. (8)–(9).

$$R = \frac{r}{r_p} \tag{8}$$

$$Q_{m,i} = \frac{q_{m,i}}{q_{0,i}} \tag{9}$$

where R and $Q_{m,i}$ denotes dimensionless particle radius and the dimensionless amount of component i adsorbed at $R = R$, respectively.

Based on the results presented in Fig. 4, the dimensionless variables listed in Eqs. (6)–(9) were applied into Eqs. (1)–(5). The resulting equations are as shown in Eqs. (10)–(14) which are the same as those for single compound systems except that dimensionless variable are employed.

$$\left(\frac{\partial Q_{m,i}}{\partial T_i}\right) = \left(\frac{1}{R^2}\right) \frac{\partial}{\partial R}\left(R^2 \frac{\partial Q_{m,i}}{\partial R}\right) \tag{10}$$

I.C. $Q_{m,i} = 0$, at $T_i = 0$ (11)

B.C. $\frac{\partial Q_{m,i}}{\partial R} = 0$, at $R = 0$ (12)

$$Q_{m,i} = Q_{s,i} = 1, \quad \text{at } R = 1 \tag{13}$$

$$Q_{t,i} = 3 \int_0^1 Q_{m,i} R^2 \, dR \tag{14}$$

In Eqs. (10)–(14), $Q_{t,i}$ is a function of T_i and the relationship between $Q_{t,i}$ and T_i can be solved analytically as for single component systems [19–21] as shown in the following equation.

$$Q_{t,i} = 1 - \frac{6}{\pi^2} \sum_{k=1}^{\infty} \frac{1}{k^2} \exp(-\pi^2 k^2 T_i) \tag{15}$$

Based on Eq. (15), different components uptake curves in multi-component systems can be converted into one typical characteristic curve with the help of dimensionless groups listed above. This finding agrees with the results illustrated in Fig. 4 which shows that all components can be converted into one typical characteristic curve. Therefore, the uptake curves of adsorbates in multi-component systems can be solved as that of single component systems.

3.2. Determination of intraparticle diffusivities

Based on the results presented above, the intraparticle diffusivity for multi-component system can be estimated by matching
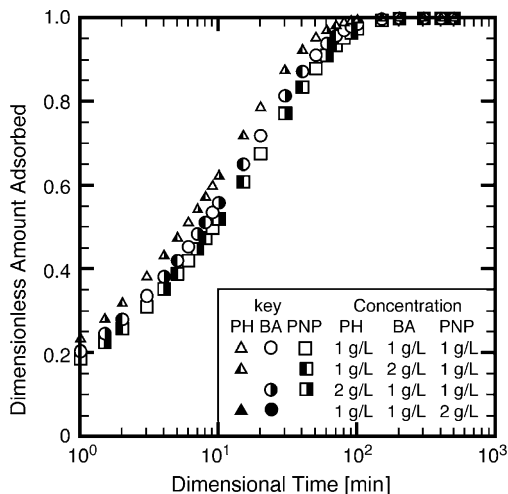

Fig. 3. Dimensionless uptake curves with dimensional time for ternary component systems.
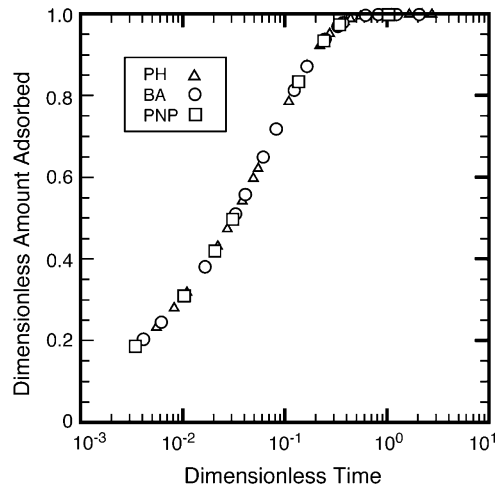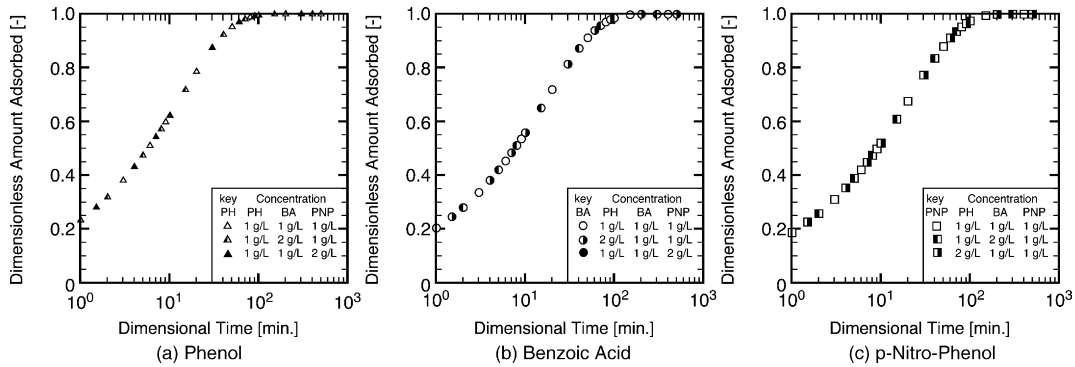

Fig. 4. Theoretical uptake curve (TUC).

Fig. 5. DEUC of (a) PA, (b) BA and (c) PNP in various ternary components.

both the dimensionless experimental uptake curve (DEUC) and TUC. (1) DEUC: DEUC can be obtained by conducting multi-component adsorption tests. Assuming the simulated results presented in Fig. 1 are EUCs. Plot $Q_{t,i}$, against $\log(t)$ and the resulting figure is referred as DEUC. $Q_{t,i}$ is obtained by divided $q_{t,i}$ by its corresponding $q_{0,i}$. (2) TUC: as shown in Fig. 4, plot $Q_{t,i}$ against $\log(T_i)$. The figure is referred as TUC and the curve is used as a model curve. The two uptake curves (DEUC and TUC) are overlaid and one of the curves is shifted horizontally until a match between the two curves is found. The match would yield a ratio value of t/T_i. The value is applied into Eq. (7) to calculate the corresponding effective diffusivity $D_{s,i}$ as shown in the following equation.

$$D_{s,i} = \left(\frac{T}{t}\right) r_p^2 \tag{16}$$

Assuming the results presented in Fig. 1 are typical EUCs for ternary systems of PH, BA and PNP. The EUCs are converted into DEUCs as shown in Fig. 5a–c for PH, BA and PNP, respectively. Overlay Fig. 5a–c with Fig. 4, respectively and results are presented in Fig. 6a–c, respectively. Lines in Fig. 6a–c are corresponding to the TUC in Fig. 4. The ratios of t/T_i (dimensional time (min)/dimensionless time) of PH, BA, and PNP can be found in Fig. 6a–c, respectively. The ratios are 185, 250, and

293 min for PH, BA, and PNP, respectively. The obtained diffusivities through Eq. (16) are 8.00×10^{-8}, 5.92×10^{-8} and 5.05×10^{-8} cm^2 s^{-1} for PH, BA and PNP, respectively. For example, diffusivity of PH is calculated as follows:

$$D_{s,PH} = \left(\frac{T_{PH}}{t}\right) r_p^2 = \left(\frac{1}{185 \text{ min}} \frac{1 \text{ min}}{60 \text{ s}}\right) (0.0298 \text{ cm})^2$$

$$= 8.00 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$$

These obtained diffusivities are in good agreement with values presented in Table 1.

4. Conclusion

This study demonstrated that the shallow bed technique can be used to determine the intraparticle diffusivities for the ternary component system. For example, by matching DEUC with TUC, diffusivities of PH, BA and PNP were determined as 8.00×10^{-8}, 5.92×10^{-8} and 5.05×10^{-8} cm^2 s^{-1}, respectively. These values are in good agreement with simulated experimental values. This method developed in this study might be useful for future design and operation of fixed-bed reactors.
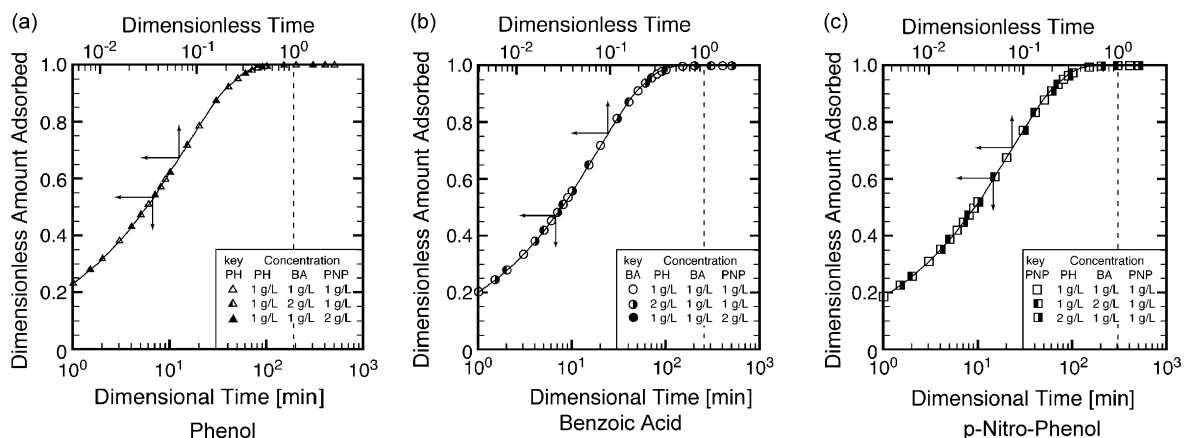

Fig. 6. Overlay uptake curves of DEUC with TUC (a) PA, (b) BA and (c) PNP.

Acknowledgement

References

[1] F. Li, A. Yuasa, K. Fbie, Y. Azuma, Microcolumn test and model analysis of activated carbon adsorption of dissolved organic matter after precoagulation: effects of pH and pore size distribution, J. Colloid Interface Sci. 262 (2003) 331–341.

[2] K. Hashimoto, K. Miura, A simplified method to design fixed-bed adsorbers for the Freundlich isotherm, J. Chem. Eng. Jpn. 9 (1976) 388.

[3] K. Kawazoe, PhD dissertation University of Tokyo, 1965.

[4] K. Miura, K. Hashimoto, Analytical solutions for the breakthrough curves of fixed-bed adsorbers under constant pattern and linear driving force approximations, J. Chem. Eng. Jpn. 10 (1977) 490.

[5] Y. Takeuchi, E. Furuya, A simple method to estimate effective surface diffusivity for Freundlich isotherm systems from breakthrough curves based on numerical results, J. Chem. Eng. Jpn. 13 (1980) 500.

[6] Y. Takeuchi, Y. Suzuki, E. Furuya, On the break time and concentration distribution in multicomponent fixed-bed adsorption when constant pattern is established, J. Chem. Eng. Jpn. 12 (1979) 486.

[7] C.J. Radke, J.M. Prausnitz, Thermodynamics of multi-solute adsorption from dilute liquid solutions, AIChE J. 18 (1972) 761–768.

[8] E. Furuya, Y. Suzuki, Y. Takeuchi, Adsorption equilibria of multicomponent substances dissolved in water on activated carbon, in: Proceedings of World Congress III, vol. 8f-202, Tokyo, 1986, pp. 817–820.

[9] D.D. Do, Adsorption Analysis: Equilibria and Kinetics, vol. 2, Imperial College Press, 1998, pp. 198–221.

[10] S. Al-Asheh, F. Banat, R. Al-Omari, Z. Duvnjak, Predictions of binary sorption isotherms for the sorption of heavy metals by pine bark using single isotherm data, Chemosphere 41 (2000) 659–665.

[11] D.E. Wurster, K.A. Alkhamis, L.E. Matheson, Prediction of adsorption from multicomponent solutions by activated carbon using single-solute parameters, AAPS PharmSciTech. 1 (2000) (article 25).

[12] K. Abburi, Adsorption of phenol and *p*-chlorophenol from their single and bisolute aqueous solutions on Amberlite XAD-16 resin, J. Hazard. Mater. B105 (2003) 143–156.

[13] R.L. Tseng, F.C. Wu, R.S. Juang, Liquid-phase adsorption of dyes and phenols using pinewood-based activated carbons, Carbon 41 (2003) 487–495.

[14] A. Leitão, R. Serrão, Adsorption of phenolic compounds from water on activated carbon: prediction of multicomponent equilibrium isotherms using single-component data, Adsorption 11 (2005) 167–179.

[15] Y. Takeuchi, T. Wasai, S. Suginaka, Fixed-bed breakthrough curves in binary and ternary trace component adsorption from aqueous solutions, J. Chem. Eng. Jpn. 11 (1978) 458.

[16] E. Furuya, Y. Takeuchi, Research Report of the Faculty of Engineering, Meiji Univ., No. 35, 1978, p. 95.

[17] J.P. Chen, L. Wang, Characterization of metal adsorption kinetic properties in batch and fixed-bed reactors, Chemosphere 54 (2004) 397–404.

[18] H.J Fan, H.S.Yang, Y.S. Tsai, E. Furuya, Prediction of individual Freundlich isotherms from binary and ternary phenolic compounds mixtures. Chemosphere. (2007), doi:10.1016/j.chemosphere.2007.11.016.

[19] J. Crank, The Mathematics of Diffusion, 2nd ed., Clarendon Press, Oxford, 1975.

[20] K.E. Noll, V. Gounaris, W.S. Hou, Adsorption Technology for Air and Water Pollution Control, Lewis publishers, Inc., Michigan, USA, 1991.

[21] A.A. Aguwa, J.W. Patterson, C.N. Haas, K.E. Noll, Estimation of effective intraparticle diffusion coefficients with differential reactor columns, J. WPCF 56 (1984) 442–448.