Korean J. of Chem. Eng., **7**(1) (1990) 53-60

A NEW CHARACTERIZATION PROCEDURE FOR AQUFOUS SOLUTIONS WITH UNKNOWN COMPOSITION

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(Received 15 June 1989 • accepted 16 October 1989)

Abstract—A new characterization procedure for aqueous solutions with unknown composition was proposed based on the binomial distribution of TOC (total organic carbon) fraction in terms of a characterizing variable, the Freundlich coefficient, k, so that the solution in question can be described by a finite number of pseudospecies identified with a certain k value. The validity and computational accuracy of this procedure has been demonstrated by characterizing three sets of experimental data chosen from different sources. Predictions based on this procedure yielded acceptable results that agreed closely with experimental data.

INTRODUCTION

A potential application of activated carbon adsorption is in the purification and detoxication of wastewater. However, most of municipal and industrial wastewater contains a large number of dissolved organic substances which can not be completely identified and in most cases, the rational design of adsorpion equipment is handicapped because of the lack of information on the adsorbate identity and composition. Therefore, it is a worthwhile task to develop a new procedure for the characterization of unknown solutions to get information for the design of adsorption equipment. In developing this kind of procedure, one may confront two logical questions:

(1) How to assign the number of pseudospecies,

(2) How to identify all the pseudospecies.

Calligaris and Tien [1] examined 41 organic chemicals from a list of toxic substances [2] to verify the acceptability of the concept of species-grouping. They found that if the adsorption affinity of the individual species is of the same order of magnitude, the use of species-grouping assumption yields acceptable results. However, for an unknown solution with a larger number of species which can not be identified by any chemical analysis, one has to assign few pseudospecies to handle such a mixture according to the multicomponent adsorption calculation method. In recent years, some investigators [3-8] have suggested procedures to characterize the adsorption affinity of such solution. Kage [3] and Okazaki et al. [4] suggested a useful concept, the characteristic distribution of Langmuir coefficient, to describe adsorption equilibria of wastewater in which many unknown species are contained. A solution can then be characterized by its concentration frequency function assuming that the number of pseudospecies is infinite. While conceptually simple, it is difficult to implement this concentration frequency function in the case of fixed bed calculations. Jayaraj and Tien [5] proposed a characterization procedure with a finite number of pseudospecies based on the concept of species-grouping suggested by Calligaris and Tien [1]. They assumed that all the pseudospecies obey the Freundlich expression and the ideal adsorbed solution theory (IAST) is valid in describing multicomponent adsorption equilibria. In the Jayaraj-Tien procedure, the characterization is to assign individual concentration values to all the pseudospecies identified with specified adsorption constants of the Freundlich expression. The characterization by the Jayaraj-Tien procedure is very rigorous and flexible but it does not have a unique way in assigning individual concentrations because a lot of plausible combinations are possible in the optimization-search step. Furthermore, it is a bit ambiguous that adsorption constants could be specified by a stagewise manner from the characterization result with a fewer number of pseudospecies [5].

The present study establishes a more simple and systematic procedure for the characterization by using a binomial distribution of composition in terms of a characterizing variable, namely one of adsorption constants. In principle, this procedure gives a unique characterization result once the number of pseudospe-

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cies is specified, and the result can be easily incorporated into the conventional multicomponent adsorption calculation. To verify the accuracy and applicability of this procedure, comparisons between calculated and experimental results at different concentration levels are presented for three different aqueous solutions [4,7,8].

MULTICOMPONENT ADSORPTION CALCULATION

The theoretical framework for multicomponent adsorption calculations is the IAST developed by Radke and Prausnitz [9]. This theory appears to be adequate for the characterization procedure because of its ability to estimate multicomponent adsorption by using data of single-species equilibria. Detailed incorporation of the IAST into adsorption calculations is given elsewhere [1,10,11] and only a brief description will be given here as background for representing the results of the present study.

When a quantity of adsorbent of mass m, initially free of any adsorbates, is added to a volume of solution V containing N species, the solution and adsorbed phase concentrations c_i^* and q_i^* of the i-th species at equilibrium are related by the following mass balance equation;

$$V(c_{io}-c_i^*)=mq_i^* \quad \text{or}$$

$$c_i^*+(m/V)q_i^*=c_{io}. \tag{1}$$

The initial concentrations are given

$$c_{io}=x_{io}c_{TO} \quad i=0,1,2,\cdots,N \tag{2}$$

where c_{TO} is the total TOC concentration of the solution and x_{iO} is the initial TOC fraction of the i-th species. The species, i = 0, means a nonadsorbable species in the solution. If the multicomponent equilibria can be described by the IAST, the relationships among concentrations are given by the following set of equations:

$$c_i^*=c_i^o z_i \tag{3}$$

$$q_i^*=q_T z_i \tag{4}$$

$$q_T=[\sum_{i=1}^{N} z_i/q_i^o]^{-1} \tag{5}$$

$$\pi_i=(RT/A)\int_0^{c_i^o} q_i^o/c_i^o dc_i^o \tag{6}$$

where z_i is the mole fraction of the i-th species in the adsorbed phase and c_i^o is the concentration of the i-th species in its single-species state, corresponding to the spreading pressure, π_i, at equilibrium. q_i^o is the equilibrium concentration corresponding to c_i^o. The restriction of the mole fraction is also provided in the system of equations:

$$\sum_{i=1}^{N} z_i=1,0. \tag{7}$$

At equilibrium, the spreading pressure π_i of each species should be equal.

$$\pi=\pi_1=\pi_2=\cdots=\pi_N. \tag{8}$$

To simplify the subsequent computation work required in both the characterization and the adsorption calculations, one may assume that all the pseudospecies obey the Freundlich expression with a constant exponent, 1/n, as follows;

$$q_i^o=k_i c_i^{o1/n}. \tag{9}$$

In this case, the integration of Eq. (6) and Eq. (8) yield

$$\Pi=\pi_i A/RT=nk_i c_i^{o1/n} \quad \text{or} \quad n\, q_i^o. \tag{10}$$

From Eqs. (9) and (10), one can get the following relationships;

$$c_i^o=(\Pi/nk_i)^n \tag{11a}$$

$$q_i^o=\Pi/n. \tag{11b}$$

Substituting Eq. (11a) into Eq. (5), one has

$$q_T=q_1=q_2=\cdots=q_N=\Pi/n. \tag{12}$$

Eq. (12) represents that the total adsorption amount is equal to the adsorption amount of individual species at the single-species state. Substituting Eqs. (3), (4), (11a) and (12) into the material balance equation yields the mole fraction in the adsorbed phase as

$$z_i=\frac{c_{io}}{(\Pi/nk_i)^n+(m/V)(\Pi/n)}. \tag{13}$$

From Eq. (7), one gets

$$\sum_{i=1}^{N}\frac{c_{io}}{(\Pi/nk_i)^n+(m/V)(\Pi/n)}-1=0 \tag{14}$$

Π can be found by a Netwon's method from Eq. (14). Once Π is known, the equilibrium concentrations c_i^* and q_i^* can be calculated from the set of equations above. When all the species have the same value of n, one has to solve only one equation, Eq. (14), to evaluate the equilibrium concentrations so that subsequent adsorption calculations become quite straightforward.

NEW CHARACTERIZATION PROCEDURE

1. Distribution of TOC fractions

The concentration of pollutants in wastewater may be represented by a comprehensive index of concentration such as TOC since it represents the overall concentration regardless of the type of adsorbate. For a solution with a large number of adsorbates ranging from slightly adsorbable to highly adsorbable, one can assume that the adsorption affinity of species may be described by a distributed system of species in terms of characterizing variables. Jayaraj and Tien [5] combined some similar adsorbates into a pseudospecies represented by a point in the domain of two Freundlich constants, k and n, and in the subsequent studies by Kage and Tien [8] and Moon and Tien [12], using the same value of Freundlich exponent for all the pseudospecies has been justified in the light of certain calculation results. As the adsorption affinity is dependent upon both the Freundlich constants, one has some freedom to assign an arbitrary value to the reciprocal of the Freundlich exponent, n. In this study, the same value of n was assumed regardless of species and its value was determined by the optimization-search procedure.

Furthermore the composition of true solutions was assumed to be described through a discrete distribution function of the Freundlich coefficient, k. When a binomial distribution is used, the TOC fraction of the j-th species identified by a Freundlich coefficient, k_j, may be represented as follows:

$$x_j=\binom{N}{j}s^j(1-s)^{N-j} \qquad j=0,1,2,\cdots,N \tag{15}$$

where

$$\binom{N}{j}=N!/j!\,(N-j)! \tag{16}$$

s represents the skewness of the distribution which is called "the probability of success in a single trial" in mathematics [13] and N is the number of adsorbable pseudospecies in the solution. The Freundlich coefficient, k_j, of the j-th species is assigned by the following equation.

$$k_j=k_s j^2 \tag{17}$$

where k_s is the scale factor which represents the order of magnitude of the lowest k value for the solution in question. In most adsorption systems, a solution contains many species with diverse adsorption affinities, and slightly adsorbable species have a more decisive effect on the concentration history or the breakthrough curve [8,12]. Therefore, the range of the k value should be wide enough to cover all species, having a dense distribution at lower values. The use of Eq. (17) could be assured by a series of sample calculations.

2. Optimization-search procedure

According to the statement above, one needs to determine three quantities, n, s, and k_s, to complete the characterization of an unknown solution in which N pseudospecies are assumed to be present. There is no adequate principle to assign the number of pseudospecies in representing the solution. Thus, one can assign the number according to a tradeoff between the accuracy of the representation and the required computational complexity. In this study, the number of species less than 10 was employed, considering the practical application to fixed-bed adsorption calculations. Consequently, three quantities for characterizing a solution should be determined by minimizing the object function, F, defined by

$$F=\frac{100}{M}\left\{\sum_{m=1}^{M}\left[(c_{T\,exp}-c_{T\,cal})/c_{T\,exp}\right]_m\right\} \tag{18}$$

subject to the constraint that the sum of the pseudospecies concentration is equal to the total adsorbate concentration c_T. The requirement, that the calculated value agrees with the corresponding experimental value measured by contacting the solution with a known amount of adsorbent under the same condition, provides a basis for the optimization-search procedure. Thus, the object function stands for the average percent fitting error in the characterization step.

Since k_s represents only the magnitude of the k value, it can be easily determined through a trial-and-error method by characterizing the solution in question several times with different k_s. Subsequently one needs to decide two quantities, n and s, to identify all the pseudospecies according to the proposed procedure while the Frick's method [14] required determining 3N-1 quantities and the Jayaraj-Tien procedure [5], N-1 quantities for a solution with N pseudospecies.

RESULTS AND DISCUSSIONS

1. Test of characterization scheme

Generally speaking, a perfect characterization should identify all the adsorbates in the solution and their concentrations. However, it is impossible to develop a procedure which can withstand such a requirement. The proposed procedure as outlined above is based on a binomial distribution of TOC fraction so that a solution can be represented by a number of discrete pseudospecies. In order to test the characterization scheme, a sample characterization was carried out in detail. Kage and Tien [8] measured the total adsorbate concentration data by contacting aqueous solutions containing multiple organic adsorbates with activated carbon (Filtrasorb 400, Calgon Co.). Experi-

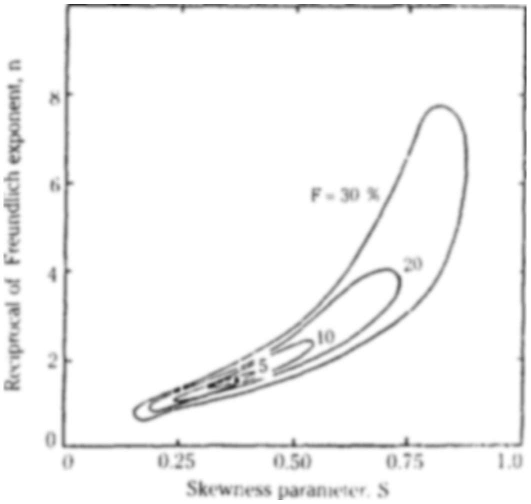

Fig. 1. Contour map of the object function F for Kage and Tien's Solution II with N = 8 and k_s = 1.0.

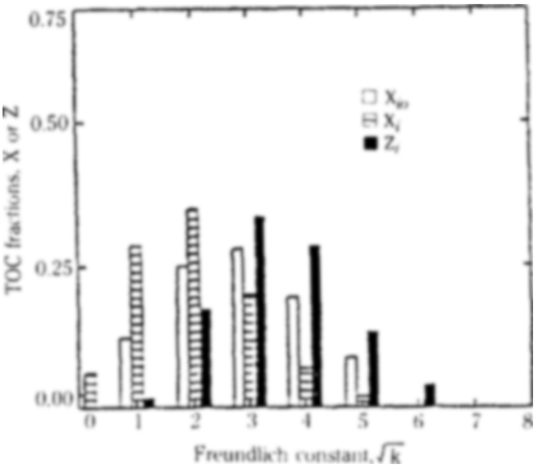

Fig. 2. Distribution of TOC fraction of Solution II (x_i and z_i are equlibrium TOC fractions at m/V = 1.0 kg/m^3 and N = 8).

Table 1. Characterization results (1)

Source : Kage and Tien (1987)
Adsorbates: Mixed organic chemicals
Type : IAE data with C_{TO} = 216 ppm

k_s	N	n	s	F(%)
1.0	6	1.44	0.422	3.82
	8	1.51	0.359	3.84
	10	1.55	0.301	3.87

mental data of Solution II with C_{TO} = 216 ppm TOC among their results were chosen as a set of sample data. The number of adsorbable pseudospecies was chosen to be 8 as a matter of convenience. Since there is a nonadsorbable species with k = 0 in the solution, the actual number of pseudospecies is N + 1. According to a trial-and-error manner mentioned in the previous section, the scale factor of the k value, k_s, was determined to be 1.0. Once N and k_s are given, the characterizing parameters, n and s, can be determined from the optimization-search procedure. Fig. 1 shows a contour map of the object function F for Solution II with c_{TO} = 216 ppm TOC when N = 8 and k_s = 1.0. Each closed solid line represents a contour with the same value of F and the star represents the optimum point at which the object function is minimum in the n-s domain. For Solution II, the parameters, n and s, at the optimum point are 1.51 and 0.359, respectively. The most valuable feature of the proposed procedure is to give a unique optimum point while the Jayaraj-Tien procedure have multiple optimum points. The value of F at the optimum point is 3.84% which is quite comparable with the result based on the Jayaraj-Tien procedure, 3.04%. Fig. 2 shows the distribution of equilibrium TOC fraction in the solution and adsorbed phases for Solution II at m/V = 1.0 kg/m^3. The initial TOC fractions, x_{iO}, are represented by white bars. This stands for the binomial distribution with N = 8, k_s = 1.0 and s = 0.359.

2. Application to aqueous solutions

In principle, the characterization has been conducted based on the total adsorbate concentration, c_T, obtained by using an original solution. The validity of characterization then was tested by predicting c_T obtained by using diluted solutions which had the same distribution of TOC fraction but at lower concentration levels. On the other hand, the characterization result obtained by using the differential adsorption equilibrium (DAE) data was used in predicting the other differential or integral adsorption equilibrium (IAE) data. In order to demonstrate the applicability of the proposed procedure, three different aqueous solutions, including a wastewater, were characterized by the procedure. Table 1 shows the characterization results of Solution II in terms of the number of pseudospecies N. As N increases, the value of n increases while that of s decreases. However, the values of F are nearly the same regardless of the number of pseudospecies. This means that there is a compensation effect between two characterization parameters in representing the solution. Since the TOC fraction with higher k values increases with the increase of the skewness parameter s, the corresponding n value must decrease for the same adsorption equilibrium data to give the same magnitude of affinity. Fig. 3 shows the cumulative distributions of TOC fraction with different N. This figure reveals that all the distributions are nearly identical. In

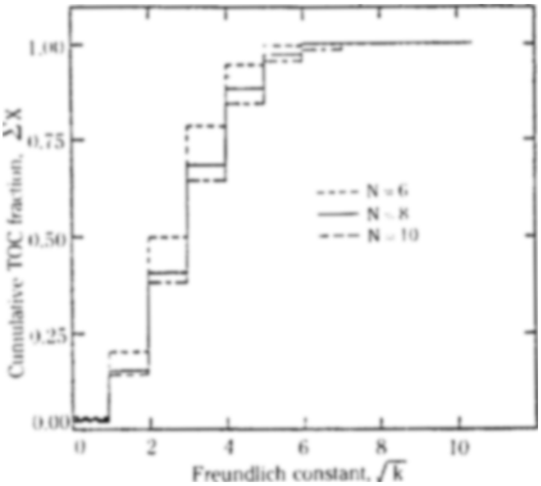

Fig. 3. Cumulative distribution of TOC fraction of Solution II with different N.

Table 2. Characterization results (2)

Source : Hubele (1985)
Adsorbates : Humic substances extracted from soil
Type : IAE data with C_{T0} = 7.97 ppm DOC

k_s	N	n	s	F(%)
1.0	6	1.26	0.581	3.77
	8	1.38	0.460	3.79
	10	1.48	0.381	3.80

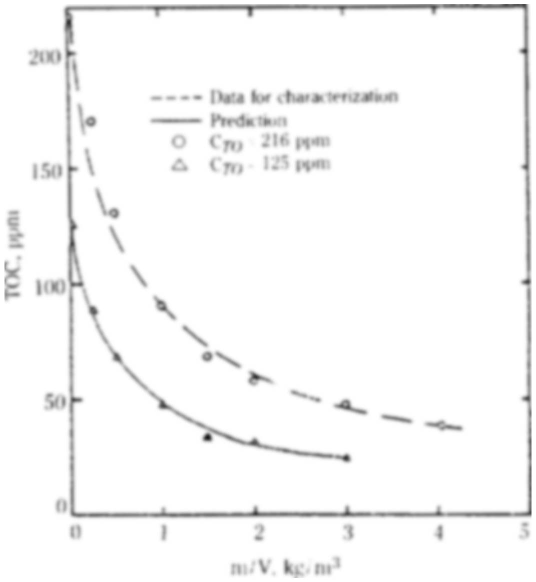

Fig. 4. Calculated and experimental IAE data of Solution II.

Table 1, it should be noted that the value of F with N = 10 is slightly higher than that with N = 6. In principle, the accuracy of representation by the characterization result must be better with the number of the pseudospecies used in the representation. However, the result in Tables 1 and 2 shows that the argument is not always true in assigning the number of pseudospecies. In this study, the number of pseudospecies for adsorption calculations was assigned to be 8 regardless of fitting errors, considering the resonable representation of actual adsorption behavior and the calculation efficiency as mentioned in previous sections. Figure 4 shows the comparison between calculated and experimental data of Solution II [8]. The broken line represents a fitting curve by the characterization and the solid line presents a prediction curve for a diluted version with c_{T0} = 125 ppm TOC. As shown in Fig. 4, predictions based on the characterization results agree closely with the experimental data within the accuracy of experiment. As a further demonstration of the utility of the proposed procedure, the experimental data reported by Hubele ("Isotherm B" p. 170 in ref. [7]) was characterized by using the proposed procedure. He conducted the adsorption of humic substances from aqueous solutions. Humic substances, whose constituents are difficult to identify, are often found in soil and natural water. The characterization results of this aqueous solution are listed in Table 2. The scale factor of the k value was determined to be 1.0 and the optimum values of n and s were 1.38 and 0.460, respectively when the number of pseudospecies is assumed to be 8. The value of F at the optimum point was 3.79%. Fig. 5 shows the fitted IAE curve with the experimental data. Unfortunately, the prediction could not be done because there was no experimental data by using a diluted solution. However, the result proved that the aqueous solution containing humic substances can be successfully characterized by the proposed procedure.

The utilization of the proposed procedure can be proven more rigorously by applying the procedure to Okazaki et al.'s data [4]. They measured the total adsorbate concentration data by two different methods, the integral and differential contacting measurements. The integral contacting measurement was also used by Kage and Tien [8] and Hubele [7]. The differential contacting measurement has been usually used to reveal the interactions among adsorbates at different concentration levels. At first, a small amount of adsorbent is added to a given volume of solution. After equilibrium is reached and the total adsorbate concentration in the solution phase is determined, the saturat-

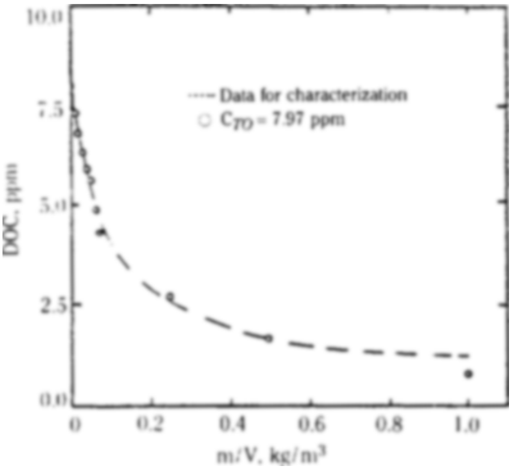

Fig. 5. Calculated and experimental IAE data of aqueous solution containing humic substances.

Table 3. Characterization results (3)

Source : Okazaki et al. (1981)
Adsorbates: Industrial wastewater (Molasses)
Type : IAE data with C_{TO} = 18.5 mol/m³

k_s	N	n	s	F(%)
0.01	6	1.53	0.602	1.76
	8	1.52	0.450	1.71
	10	1.41	0.351	1.68

Type : DAE data with C_{TO} = 18.5 mol/m³

k_s	N	n	s	F(%)
0.01	6	1.55	0.605	5.17
	8	1.75	0.499	5.01
	10	1.87	0.421	4.88

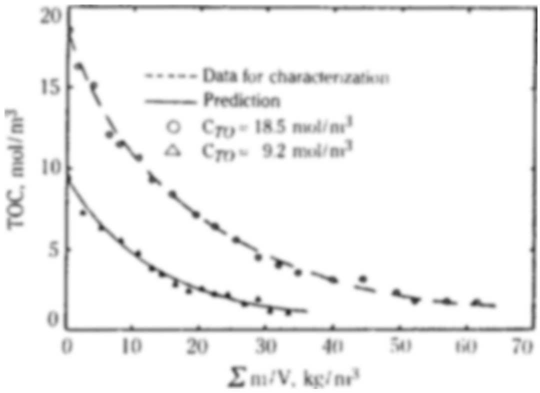

Fig. 6. Calculated and experimental DAE data of Okazaki et al.'s Wastewater V.

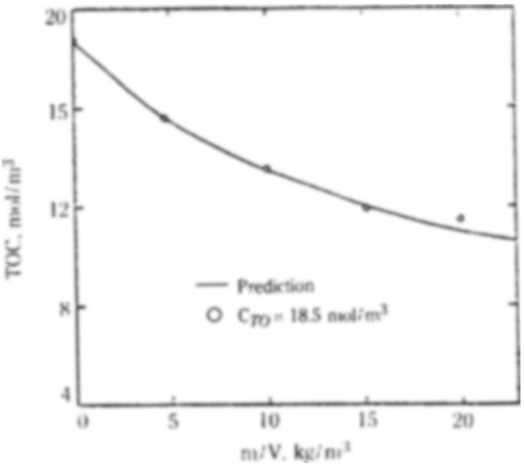

Fig. 7. Prediction of IAE data of Wastewater V.

ed adsorbent is removed and a new amount of fresh adsorbent is added. The differential contacting measurement can be done by repeating this procedure. In this study, experimental data of Wastewater V with C_{TO} 18.5 mol TOC/m³ [4], obtained by the differential contacting measurement, was characterized and the result was used as the basis for predicting other experimental data of the same solution at a different concentration level. This solution is an industrial wastewater which contains molasses as a major component with a lot of background species. Table 3 shows the characterization results of Wastewater V. To compare the results obtained by two different contacting measurements, two independent characterizations were carried out. The scale factor of the k value was determined to be 0.01 and the values of n and s were 1.52 and 0.450 for IAE data and 1.75 and 0.499 for DAE data, respectively when the number of pseudo-species is assumed to be 8. The value of F for IAE data at the optimum point was 1.71 and that for DAE data was 5.01. The reason for the difference in F may be explained by scattering of experimental data measured at low concentrations. Fig. 6 shows the comparison between calculated and experimental data measured by the differential contacting measurement. A comparison between predictions of the integral contacting measurement and experiments is shown in Fig. 7. Figs. 6 and 7 show that predictions using the characterization results are quite satisfactory. Based on the results above, it was proven that the procedure proposed in this study successfully characterizes various aqueous solutions. The values of F for different predictions are tabulated in Table 4. The prediction errors

Table 4. Prediction errors from characterization results

Data Source	Data for Characterization	Data for Prediction	F(%)	F(%)
Kage and Tien	IAE data with C_{TO} 216 ppm	IAE data with C_{TO} 125 ppm	6.88	4.99
Hubele	IAE data with C_{TO} 7.97 ppm	—	3.79	9.97
Okazaki et al.	DAE data with C_{TO} 18.5 mol/m^3	DAE data with C_{TO} 9.2 mol/m^3	8.84	9.38
		IAE data with C_{TO} 18.5 mol/m^3	1.93	4.20

Based on the Jayaraj-Tien procedure (1985)
Characterization errors

are in the range of 2-9%. However, considering the errors in experiments, the degree of prediction accuracies based on the proposed procedure is quite acceptable. Prediction errors based on the Jayaraj-Tien procedure are added in Table 4 for comparisons. The result shows that the proposed procedure gives more accurate predictions than the Jayaraj-Tien procedure for Wastewater V.

CONCLUDING REMARKS

Based on the characterization results and the predictions, it is proven that the characterization procedure proposed in this study is extremely simple and advantageous. All the aqueous solutions encountered here can be represented by the binomial distribution of TOC fraction in terms of the Freundlich coefficient, k. The most valuable feature of the proposed procedure is to give a unique characterization result unlike other procedures which used a complex algorithm as the optimization-search method [5,8]. The fitting and prediction errors are quite comparable with those obtained by using the Jayaraj-Tien procedure. According to the property of the distribution function, the proposed procedure has a potential application for characterizing solutions, in which a dominant species exists with various background substances, like most of industrial wastewater. Furthermore, the characterization result can be easily incorporated into solving the fixed-bed adsorption problem, namely the calculation of breakthrough curves based on local equilibrium assumption.

ACKNOWLEDGEMENT

This research was performed under grant No. 881-1005-015-2, Korea Science and Engineering Foundation.

NOMENCLATURE

A : area of the solution-solid interface, [m^2]
c : concentration in solution, [ppm or mol/m^3]
c_T : total adsorbate concentration in solution, [ppm or mol/m^3]
F : object function or averaged error defined in Eq. (18)
k : Freundlich constant
k : scale factor of k value
m : mass of adsorbent, [kg]
M : number of data
n : reciprocal of Freundlich exponent
N : number of pseudospecies
q : concentration in the adsorbed phase, [ppm or mol/kg]
q_T : total adsorbate concentration in the adsorbed phase, [ppm or mol/kg]
R : gas constant
s : skewness factor
T : temperature, [K]
V : volume of solution, [m^3]
x : TOC fraction in solution
z : TOC fraction in the adsorbed phase

Greek Letters

π : spreading pressure
Π : modified spreading pressure defined in Eq. (10)

Superscripts

o : single species state
: equilibrium

Subscripts

i,j : the i-th or j-th species
o : initial value

Abbreviations

DAE : differential adsorption equilibrium
DOC : dissolved organic carbon

IAE : integral adsorption equilibrium
TOC : total organic carbon

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