Korean J. Chem. Eng., **19**(5), 888-894 (2002)

Characterization Procedure for Adsorption of DOC (Dissolved Organic Carbon) from Synthetic Wastewater

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(*Received 5 June 2002 • accepted 26 July 2002*)

Abstract−A characterization method to evaluate the composition of background organic matters in terms of adsorbability was presented and applied to synthetic and domestic wastewater. The binomial distribution of DOC (Dissolved Organic Carbon) fraction in relation of a characterizing variable, the Freundlich coefficient, k, was proposed to describe the initial composition of wastewater by a finite number of pseudospecies. This method was tested for removal of DOC by using granular and powdered activated carbons. These experiments enable us to get information on the distribution function of species in the solution. From the results obtained in this work, kinetic experimental data were predicted on the assumption that the diffusion coefficients were unchanged during the experiments. It was confirmed to be effective in determining the initial composition and describing the equilibria of the DOC. From the experiments, it was found that this synthetic solution has a sigmoid type isotherm on activated carbons. This implies that there are two different adsorption regions in a system, favourable and unfavourable cases, depending on the solution concentration. This unfamiliar problem can be solved by using a characterization method based on IAST-Freundlich model.

Key words: DOC (Dissolved Organic Carbon), Adsorption, Synthetic Wastewater, GAC (Granular Activated Carbon), PAC (Powdered Activated Carbon), Characterization

INTRODUCTION

DOC (Dissolved Organic Carbon) in water and wastewater is a mixture of organic compounds with different physical and chemical properties. The identities and concentrations of organic substances to be removed by adsorption are often unknown since wastewater encountered has a series of unidentified organic matters in applying carbon adsorption for treating natural water and wastewater [Matsui et al., 1998].

Therefore, it is a very fundamental and important task to characterize the solution before any adsorption process is applied to the system. The characterization result supplies information on adsorption equilibrium of organic matters on carbon in designing and simulating the adsorption system for removing those contaminants from natural water and wastewater. The most common approach for characterization of unknown solutions is to group several components together as a single pseudospecies according to similarity of their physical and chemical properties. That is why a single surrogate quantity such as biological oxygen demand (BOD), dissolved organic carbon (DOC), or total organic carbon (TOC) has been used in representing the total contaminant in the target solution. The presence of a variety of substances with different adsorption affinity in an aqueous solution also requires that one must consider the competitive interaction among them after characterizing the solution into several pseudospecies.

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Some researchers suggested a useful concept, the characteristic distribution of Freundlich coefficient, to describe adsorption equilibrium of wastewater in which many unknown species exist [Yuasa et al., 1996a, b]. The wastewater encountered can then be characterized by its concentration frequency function assuming that the number of pseudospecies is infinite [Okazaki et al., 1981]. However, it is very difficult to implement this concentration frequency function in simulating batch and fixed bed adsorption systems while conceptually simple and elegant. Considering this point, Jayaraj and Tien [1985] proposed a characterization procedure with a finite number of pseudospecies based on the concept of species grouping suggested by Calligaris and Tien [1982]. They assumed that all the pseudospecies obey the Freundlich expression and the IAST (ideal adsorbed solution theory) is valid in describing multicomponent adsorption equilibrium [Maria et al., 1994]. A simple procedure for the characterization was made by using a binomial distribution of composition in terms of a characterizing variable, namely one of the adsorption constants. This characterization procedure was very convenient and suitable for natural water and wastewater treatments using batch and fixed-bed adsorption systems because finite number of pseudospecies can be systematically assigned by a binomial function. In this work, the simple characterization procedure was further tested for a synthetic solution in which organic and inorganic compounds exist together. From equilibrium experiments, it was found that this synthetic solution has a sigmoid type isotherm on activated carbons. This implies that there are two different adsorption regions in a system, favorable and unfavorable, depending on the solution concentration. In this case, any conventional iso-

Table 1. Synthetic wastewater constituents

Compounds	Weight (mg/L)	Species
Glucose	16.50	Organic compounds
Yeast extract	1.75	
Peptone	1.75	
$MnSO_4$	0.13	Inorganic compounds
$CaCl_2$	0.93	
$NaHCO_3$	0.88	
NaCl	2.50	
$MgSO_4 \cdot 7H_2O$	3.75	
KH_2PO_4	1.25	
$(NH_4)_2 \cdot SO_4$	3.50	

therm equation cannot be applied suitably. This unfamiliar problem can be solved by using a characterization method based on IAST-Freundlich model [Moon et al., 1991]

EXPERIMENTS

Synthetic wastewater was made to multiple proportional concentrations as the original synthetic wastewater components to avoid errors of the dilution effects by working with different initial concentrations. The working solution as a synthetic wastewater was prepared by dissolving several organic matters such as glucose, yeast extract, and peptone in addition to some typical inorganic compounds that normally exist in domestic wastewater. Organic and inorganic wastewater constituents are listed in Table 1. Since all individual components cannot be separately analyzed, a surrogate quantity, DOC, was used in measuring the concentration of the solution.

In this study, two different activated carbons, GAC (granular activated carbon) and PAC (powdered activate carbon), were used in removing DOC from the synthetic wastewater. Table 2 shows major physical properties of GAC and PAC.

Equilibrium experiments were conducted in stirred batch reactors. After a given amount of PAC or GAC was added into a batch reactor that contains 1 liter of the synthetic solution, the concentration of the solution was monitored with time. It was found that biological degradation generally occurred after 8 hours. Therefore, all equilibrium experiments were finished before 8 hours to avoid the effect of biodegradation on the removal of DOC. The samples from the batch reactor were filtered through 0.45 μm filters to remove carbon particles prior to measuring DOC values with a UV-persulfate TOC analyzer (Dohrmann Phoenix 8000). As a mixture like the synthetic solution encountered in this study has a somewhat ambiguous adsorption equilibrium character, equilibrium data obtained from different initial concentrations does not match even at the same equilibrium concentration. This comes from the difference in adsorption affinities of individual species that exist in the solution. In this work, three different initial DOC concentrations were used in order to show this phenomenon which would never be expected from any single species adsorption system. Experimental equilibrium data were measured at different PAC and GAC loading in the batch reactor while the initial DOC value was fixed. Those data will be used in the characterization of the synthetic solution.

Table 2. Physical properties of GAC and PAC

Specification	GAC	PAC
Bed density, kg/m^3	840	350-500
Surface area, m^2/g	1001.2	1200
Mean pore dia., Å	22.55	30.41
Micropore vol., cc/g	0.269	0.067
Mean dia., μm	750	34.15

THEORETICAL APPROACH

The characterization procedure proposed in this study was to assume a simple discrete distribution function to represent a number of pseudospecies with the same Freundlich exponent. The initial concentration of each pseudospecies can be assigned by a binomial function in terms of the Freundlich constant [Kim et al., 2000; Moon et al., 1991; Kage et al., 1987]. Furthermore, the competitive adsorption between species was estimated by a conventional equilibrium theory such as IAST (the ideal adsorbed solution theory). Assuming that the individual isotherm follows the Freundlich equation with the same exponent, n,

$$q_i^o = k_i C_i^{o^{1/n}} \tag{1}$$

Multicomponent equilibrium can be described by the following set of equations based on the IAST.

$$C_T = \sum_{i=1}^{N} C_i \tag{2}$$

$$C_i = Z_i(\Pi/nK_i)^n \tag{3}$$

$$Z_i = \frac{C_{io}}{[(\Pi/nK_i)^n + (M/V)(\Pi/n)]} \tag{4}$$

$$\sum_{i=1}^{N} \frac{C_{io}}{(\Pi/nK_i)^n + (M/V)(\Pi/n)} - 1 = 0 \tag{5}$$

Here the superscript 0 represents its single-species state and q_T is the total adsorption amount of the mixture. z_i is the mole fraction of the i-th species in the adsorbed phase corresponding to C_i. q_i^o is the equilibrium concentration corresponding to C_o^i in its single-species state. Since the spreading pressure should be the same for all species at equilibrium as represented by Eq. (7), it should be evaluated at a given equilibrium condition using Newton's method. The individual spreading pressure, π_i, at equilibrium can be calculated from Eq. (5). Once the spreading pressure for the mixture is known, the equilibrium values, C_i and q_i, for the mixture can be calculated from the set of equations above.

With n, K_i, C_{io}, M and V known, Π can be calculated from Eq. (5). After the Z_i and Π known, one can readily determine C_i (i=1, 2, …, N), the sum of which gives C_T. A pseudospecies number of N is assumed and values of n and s are determined from the minimization of F for significantly different values of k_s. Once k_s is found, one can conduct the second step of search for optimum values of n and s for different values of N.

In order to determine exponential n of the Freundlich isotherm, it is necessary that most of the solutes must be adsorbable and exhibit favorable adsorption in their pure-component adsorption isotherm data. In cast of unfavorable isotherm, the condition should be n<0.5.

The value of s in Eq. (6) determines the skewness of the pseudospecies concentration distribution and is within the range 0<s<1.0, with s=0.5 corresponding to a normal distribution type.

The adsorption affinity of a specified species depends on both of its Freundlich constants. However, in this work, only the Freundlich coefficient was used to identify a couple of pseudospecies as a matter of convenience. Therefore, one has the freedom to assign an arbitrary value to the Freundlich exponent, n, regardless of species. This value can be determined by taking an average value from preliminary results obtained by an optimization-search procedure. Once the exponent value is properly assigned for a given system, the characterization can be carried out straightforwardly based on a binomial distribution. Then the DOC fraction of the j-th species in the original solution may be represented as follows:

$$x_j=\sum_{j=1}^{N} s^j(1-s)^{N-j},\ j=0,\ 1,\ 2,\ \ldots,\ N \qquad (6)$$

Here each species, j, is specified by a Freundlich coefficient, k_j, which is assigned by the following equation.

$$k_j=k_s j^2 \qquad (7)$$

where k_s is the scale factor which represents the order of magnitude of the lowest k value for the solution in question. Eq. (9) was used since the range of the k value should be wide enough to cover all species, having a dense distribution at lower values.

It should be noted that there is a non-adsorbable species assigned by j=0 in the binomial distribution in Eq. (8).

In carrying out the characterization of a given solution, one can use a proper optimization technique to obtain optimum results. In this work, a simplex program was used to determine characterization results from equilibrium data obtained from different initial concentrations by minimizing its corresponding object function. The objective function, F, is defined as

$$F=\frac{100}{ND}\sum_{m=1}^{ND}[(C_{Texp}-C_{Tcal})/C_{Texp}]_m \qquad (8)$$

The batch adsorption of a solution containing several unknown species was represented by a concentration density function, $f(C_{io})$. When the volume of the solution is V and the mass of fresh adsorbent is M, 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.

$$C_i+(M/V)q_i=C_{i0} \qquad (9)$$

The initial concentration may be given from its characterization result as follows.

$$C_{i0}=x_{i0}C_{T0},\ i=0,\ 1,\ 2,\ \ldots,\ N \qquad (10)$$

Where C_{T0} is the total DOC concentration of the solution and x_{io} is the initial DOC fraction of the i-th species.

The mass transfer rate between liquid and solid phases represented by the LDFA (Linear Driving Force Approximation) model is the following, Eq. (11).

$$\frac{dq}{dt}=\frac{3\times k_f}{R\times\rho_p}(c_i-c_s)=k_m(q_s-q) \qquad (11)$$

where R=radius of adsorbent, k_f=overall mass transfer coefficient (m/s), ρ_p=density of particle (kg/m^3), k_m=mass transfer coefficient (1/s).

The adsorption rate of adsorbate by a PAC grain is linearly proportional to a driving force using the LDFA model, defined as the difference between the surface concentration and the average adsorbed-phase concentration. The IAE (Integral Adsorption Experi-

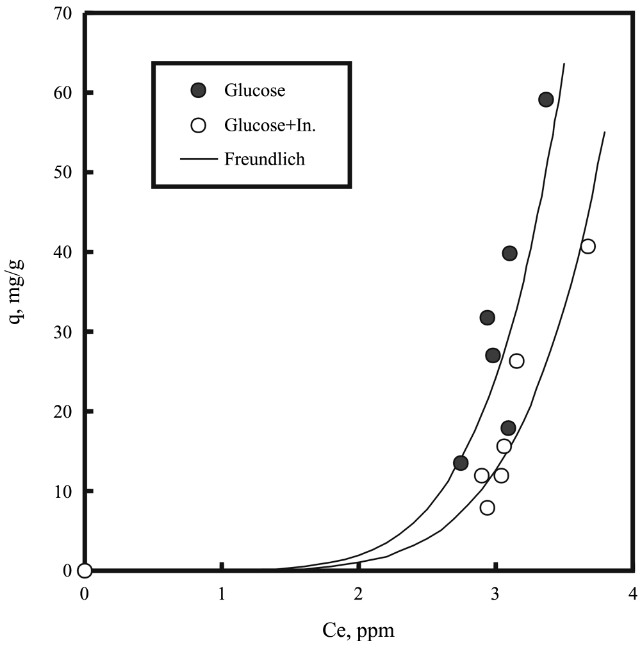

Fig. 1. Equilibrium data of glucose on PAC with and without inorganic compounds.

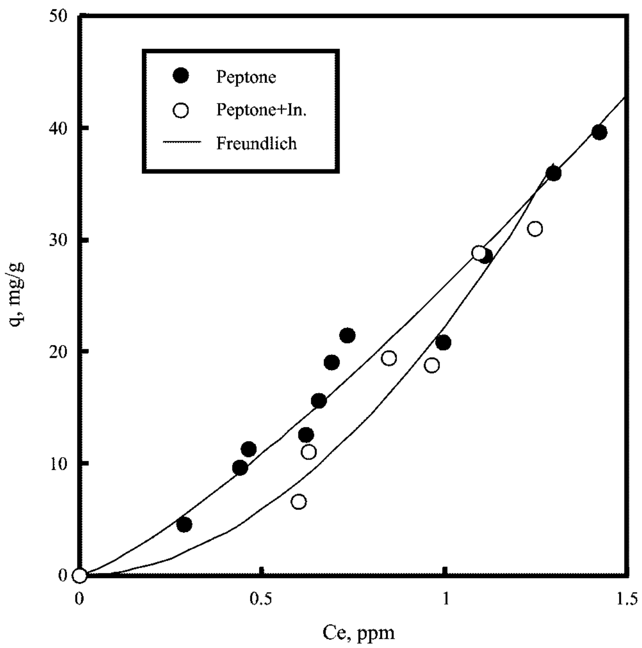

Fig. 2. Equilibrium data of peptone on PAC with and without inorganic compounds.

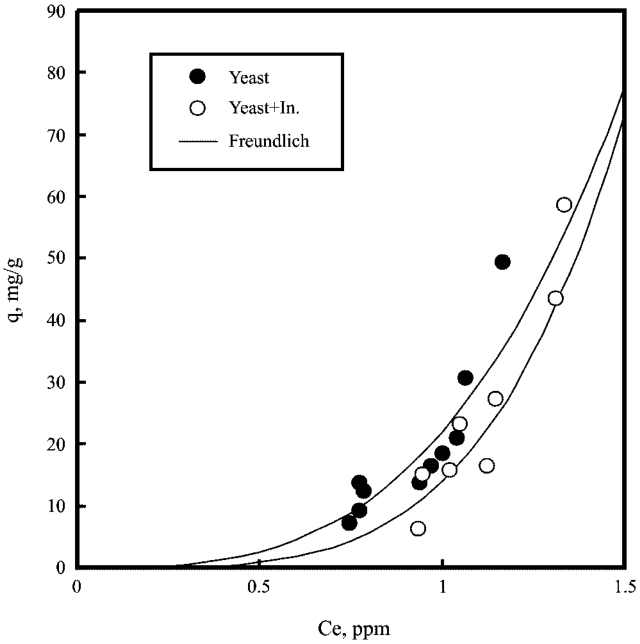

Fig. 3. Equilibrium data of yeast on PAC with and without inorganic compounds.

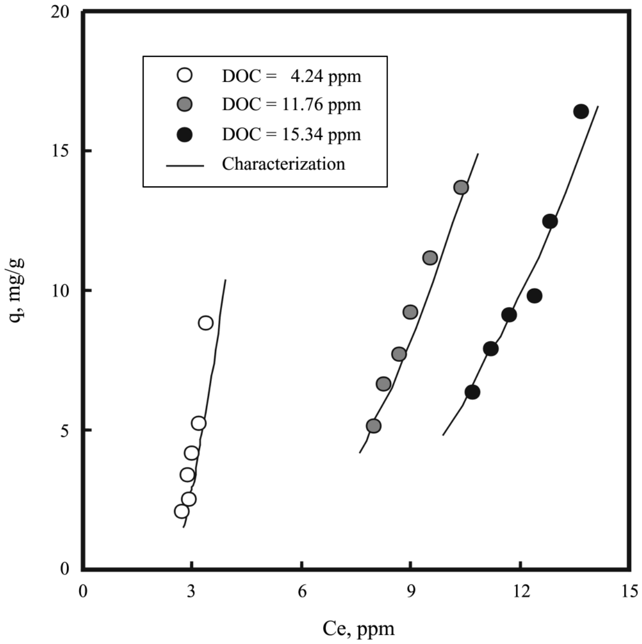

Fig. 4. Equilibrium isotherm data of synthetic wastewater on PAC.

ment) used batch adsorption data as the basis for characterizing solutions of unknown compositions.

RESULTS AND DISCUSSION

Equilibrium experiments for single organic compounds such as glucose, peptone, and yeast extract on PAC were conducted in a batch reactor with and without inorganic compounds that normally exist in domestic wastewater. As shown in Figs. 1-3, most equilibrium adsorption data show unfavorable tendency in the range of low concentrations around 1-3 ppm. One possible explanation for this unfavorable tendency is the change in the zeta potential of the solution or the net charge on PAC surface. All sets of data are fitted to Freundlich equation and their isotherm parameters are listed in Table 3. It is also confirmed that yeast extract and glucose organic compounds encountered here are unfavorable to PAC form their Freundlich exponents given in Table 3, showing values much less than unity.

On the other hand, Fig. 4 shows three sets of equilibrium data of the synthetic wastewater of which constituents are listed in Table 1. Each set of data was obtained with a given initial concentration such as 4.24, 11.76, and 15.34 ppm DOC by varying the PAC loading.

Table 3. Freundlich isotherm parameters of organics with and without inorganic compounds

	Without inorganic compounds		With inorganic compounds	
	k	n	k	n
Glucose	2.53×10^{-2}	0.16	1.31×10^{-2}	0.16
Peptone	25.84	0.8	22.24	0.53
Yeast	21.88	0.32	13.98	0.25

These data also show a highly unfavorable tendency at low concentration ranges. However, it also shows that the adsorption is quite possible over certain concentration levels. The most interesting feature in Fig. 4 is that three different sets of data do not match together. This implies that there is strong competitive adsorption between adsorbing components on PAC [Yuasa et al., 1996a, b]. In many cases which contain different organic matters like natural and domestic wastewater, similar equilibrium behavior can be expected from mutual interactions between species. The equilibrium data of a mixture showed a very unfavorable case below a certain concentration and then dramatically changed to a favorable case over that concentration [Yuasa et al., 1996a, b]. One possible explanation for this phenomenon is the change in the zeta potential of the solution or the net charge on PAC surface that depends on the solution concentration. In this case, the phenomenon might be interpreted as coagulation rather than adsorption.

The other possible explanation for the change in adsorption affinity depending on the concentration is to use the concept of mutual competition between adsorbing species on the surface. For this purpose, one can try a characterization procedure. As mentioned in the previous section, the simple characterization technique was proposed to be further tested for the synthetic wastewater prepared in this study [Moon et al., 1991]. The same procedure was used for three sets of equilibrium data on PAC and their results are listed in Table 4. From preliminary characterizations, the scale factor of k was chosen as 1.0. As shown in Table 4, the Freundlich exponent value was obtained in the range of 1.1-1.3 and the skewness of the binomial distribution function, s, is decreasing with the assigned number of species. It should be noted that the assigned number of pseudospecies could not improve the object function, F, or the average percent deviation in Table 4. This result can be more strongly confirmed by looking at the characterization results shown in Fig. 5. Characterization results obtained from different experimental sets are very similar and pseudospecies assigned by k values more than

Table 4. Characterization results of synthetic wastewater on PAC

ks	N	n	s	F (%)
IAE data with C_{T0}=4.24 ppm DOC				
1.0	6	1.1	0.20	5.65
	8	1.1	0.11	5.64
	10	1.0	0.10	5.40
C_{T0}=11.76 ppm DOC				
1.0	6	1.2	0.17	1.92
	8	1.2	0.13	1.80
	10	1.2	0.10	1.93
C_{T0}=15.34 ppm DOC				
1.0	6	1.1	0.14	1.48
	8	1.1	0.11	0.98
	10	1.3	0.10	1.16

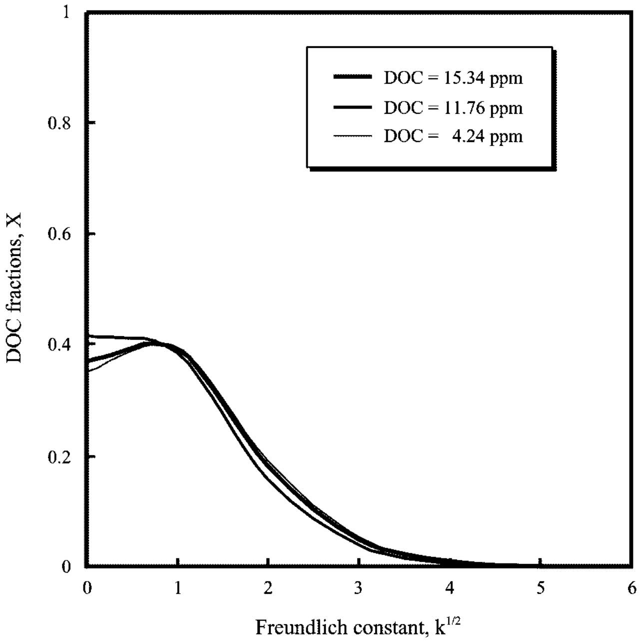

Fig. 5. Concentration distribution for synthetics wastewater on PAC.

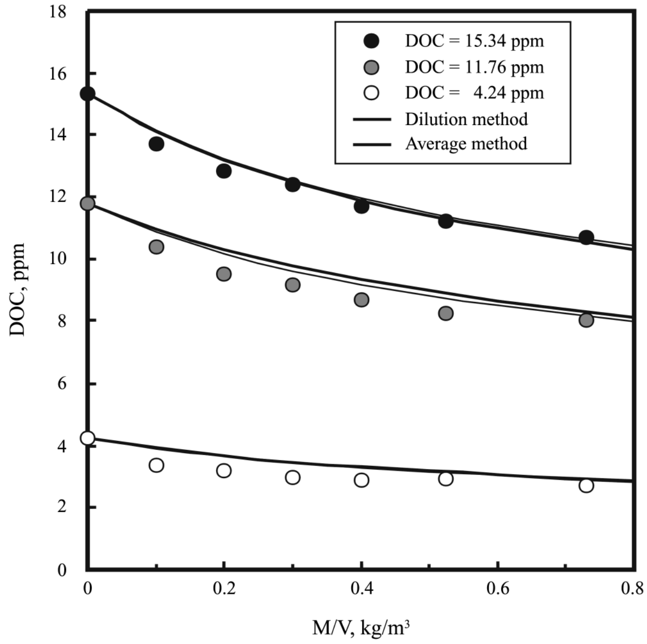

Fig. 6. Calculated and experimental IAE data for synthetic wastewater on PAC.

Table 5. Characterization results of synthetic wastewater on GAC

ks	N	n	s	F(%)
IAE data with C_{T0}=4.62 ppm DOC				
1.0	6	2.0	0.15	3.70
	8	2.3	0.11	3.10
	10	2.0	0.09	3.26
C_{T0}=11.30 ppm DOC				
1.0	6	2.2	0.12	0.92
	8	2.3	0.09	0.86
	10	2.3	0.07	1.11
C_{T0}=16.46 ppm DOC				
1.0	6	2.2	0.10	1.23
	8	2.2	0.08	1.90
	10	2.2	0.06	1.34

4 do not contribute to the distribution function at all. The most interesting result in Fig. 5 is that a nonadsorbable species exists with about 0.4 fraction of DOC. This portion of DOC fraction is likely to relate to extremely unfavorable tendency at low concentration levels. After average fractions were taken from three binomial distribution functions shown in Fig. 4, all sets of equilibrium data in Figs. 4 and 6 were predicted. According to these results, it can be concluded that predictions based on the characterization procedure are in good agreement with experimental data. The prediction by the dilution method given in Fig. 6 means that all predictions were done by the characterization result using data obtained from the highest initial DOC concentration, namely 15.34 ppm.

To check the applicability of the characterization procedure, it was also tested for equilibrium data of the same synthetic wastewater on GAC. The results for GAC are very similar to those for PAC as shown in Table 5 and Figs. 7-9. However, it should be understood that there are two different things to point out from the results for GAC. One thing is that very similar distribution functions for GAC were obtained compared to those for PAC even though their properties are quite different as listed in Table 2. Since any characterization is to give information on the target solution rather than adsorbent, the characterization should be similar for a given wastewater whatever adsorbent was used. This result implies that the procedure used here is quite suitable in characterizing the synthetic wastewater. The other thing to point out from results above is the difference in the Freundlich exponent values for PAC and GAC.

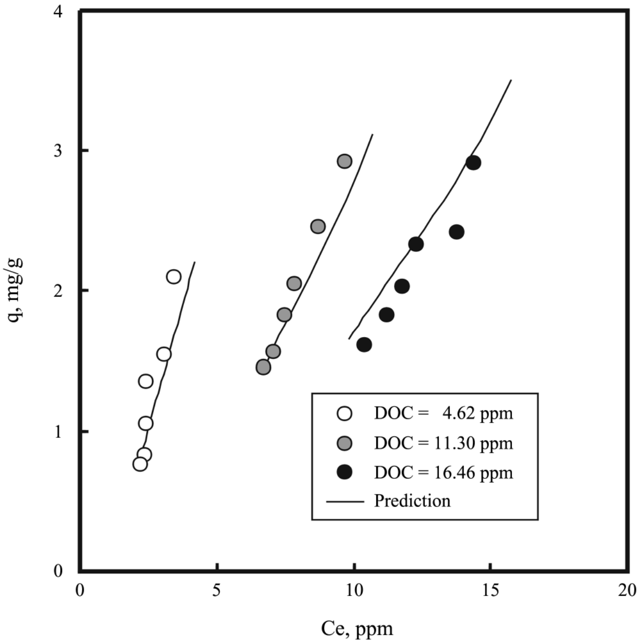

Fig. 7. Equilibrium isotherm data of synthetic wastewater on GAC.

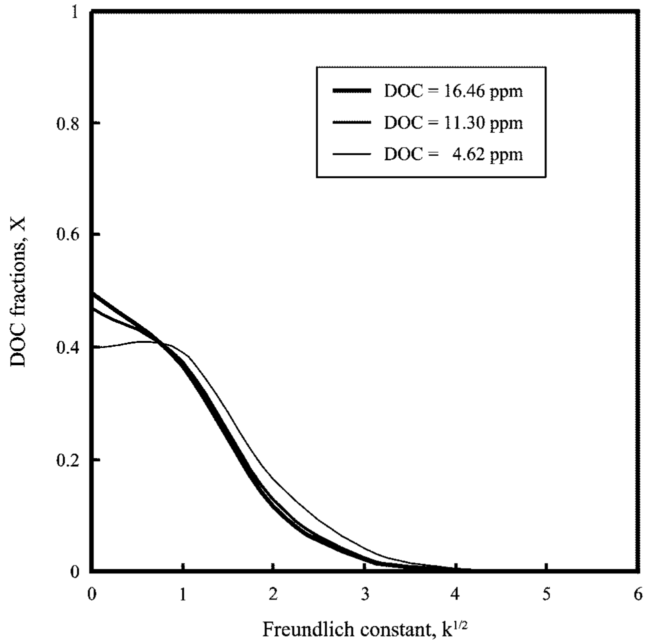

Fig. 9. Concentration distribution for synthetic wastewater on GAC.

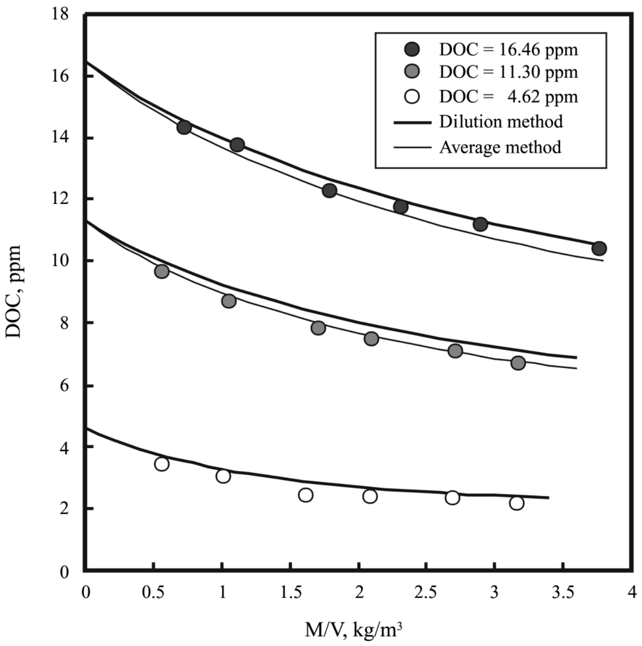

Fig. 8. Calculated and experimental IAE data for synthetic wastewater on GAC.

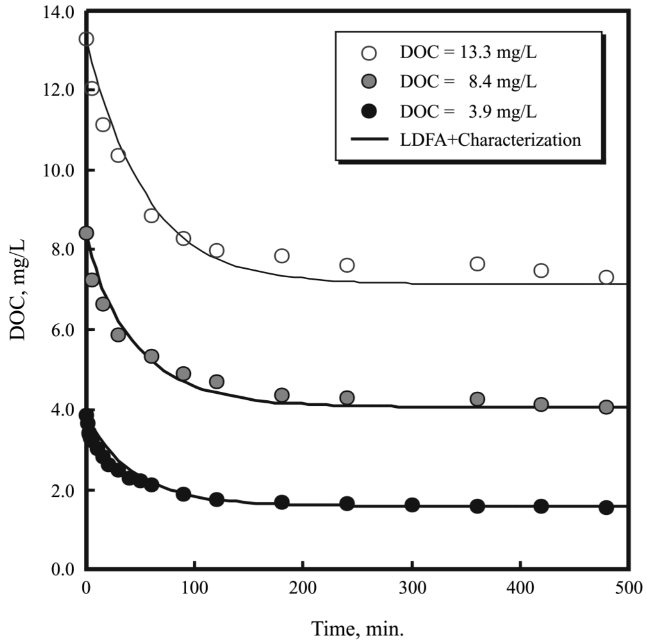

Fig. 10. Effect of organic concentration on mass transfer rate (GAC=5 g/L, RPM=100).

The value of n for GAC is about 2.2, which is much larger than those for PAC. In fact, the higher exponent value in the Freundlich equation represents relatively the higher adsorption affinity. Therefore, one may say that GAC used here has higher adsorption affinity than PAC to the synthetic wastewater encountered in this work. Fig. 10 shows the effect of organic concentration on mass transfer rate. Predictions based on this characterization procedure with LDFA model were in good agreement with experimental data. According to these results, it can be concluded that predictions based on the characterization procedure are in good agreement with experimental data.

CONCLUSIONS

A simple characterization procedure proposed in this study was further tested for a synthetic wastewater that contains organic and inorganic matter together in removing DOC using PAC and GAC. Even though this adsorption system has a highly complex adsorption behavior, the characterization results obtained from different sets of equilibrium data are quite similar regardless of initial DOC concentration or type of activated carbon. This implies that the characterization procedure is quite suitable for the synthetic wastewater to get information on the initial distribution of DOC fraction. From the results obtained in this work, it seems that the application of the characterization procedure will be very beneficial in designing and simulating any adsorption process systematically to remove DOC from natural water and wastewater.

ACKNOWLEDGEMENT

This work was supported by ARC (Australia) - KOSEF (Korea) joint research fund.

NOMENCLATURE

C : concentration in soultion [ppm or mg/L]
C_T : total adsorbate concentration in solution [ppm or mg/L]
F : object function or average error defined on Eq. (1)
k : Freundlich isotherm coefficient
k_f : overall mass transfer coefficient [m/s]
k_m : mass transfer coefficient [1/s]
k_s : scale factor of k value
M : mass of adsorbent [kg]
n : Freundlich isotherm exponent
N : number of pseudospecies
ND : number of data
q : concentration in adsorbed phase [ppm or mg/L]
q_T : total adsorbate concentration in adsorbed phase [ppm or mg/L]
R : radius of adsorbent
s : skewness of binomial distribution function
V : volume of solution [L]
x : TOC fraction in solution
z : TOC fraction in adsorbed phase

Greek Letters

π : spreading pressure
Π : modified spreading pressure defined in Eq. (5)
ρ_p : density of particle [kg/m^3]

Abbreviations

DOC : dissolved organic carbon
IAE : integral adsorption equilibrium
TOC : total organic carbon
BOD : biological oxygen demand
COD : chemical oxygen demand
IAST : ideal adsorbed solution theory
GAC : granular activated carbon
PAC : powdered activated carbon

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