(14) ADSORPTION EQUILIBRIA OF MULTICOMPONENT ORGANIC MIXTURES OF UNKNOWN COMPOSITION

組成未知の多成分系原水中有機物の平衡吸着特性に関する研究

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Abstract; Batch experiments on activated carbon adsorption of background organics of unknown composition were conducted. A few specific characteristics of the adsorption equilibria, such as the dependence of the overall isotherms on the overall initial concentrations, were demonstrated. Accordingly, a new approach was developed to mathematically describe the overall adsorption isotherms. This method consists of an overall adsorption isotherm expression derived from the ideal adsorbed solution theory (IAST) and a technique of fractionating the background organics into a multicomponent mixture in terms of the adsorptive strength described by the Freundlich parameters. Once the composition was determined by fitting the calculated overall isotherms to experimental data, the distribution of organics in both the liquid and the solid phases was calculated, and its relationship with the characteristic behavior of the overall adsorption isotherms was discussed.

Key words; adsorption equilibria, composition, activated carbon, competitive adsorption, isotherms, multicomponent mixtures

1. INTRODUCTION

Organics contained in waters and wastewaters are a mixture of organics. Some of them can never be identified and quantified. The coexistence results in a decrease of the removal of certain specific organics that must be removed, because some other organics compete with them for adsorption sites and blockade their way to the pores that are most effective for them [1], when activated carbon adsorption was applied to treat such solutions. Therefore, to investigate the adsorbability of target organics singled out from the organic mixtures, the behavior of the remaining organics, generally defined as the background organics, in adsorption has to be clarified.

In many researches, the background organics were treated as a single component for equilibrium and kinetic studies, where the concentration of the background organics is measured on an overall basis, such as total organics carbon (TOC) or ultraviolet absorbance (UV absorbance). With such a method, the competitive interactions between the constituting components are generally neglected, and the influence of the experimental conditions such as the initial overall concentration is not considered.

Frick and Sontheimer [2] developed a technique, namely the sorption analysis, to evaluate the adsorption equilibria for humic acid solutions and a groundwater. Similar procedures were also used by Crittenden, *et al.*[3] to a contaminated groundwater. In their researches, a theoretical component concept was applied in IAST or SCAM (a simplified com-

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petitive adsorption model) calculations to account for the competitive effects of the unknown mixture on a tracer component.

Focusing on the behavior of background organics in batch adsorption, Yuasa[4] developed a few dimensionless overall isotherm models to eliminate the influence of the initial overall concentrations. Besides, by conducting simulations for imaginary raw waters containing organics of different composition, he concluded that [5], no matter whether the Freundlich exponent ($1/n$) for each constituting component was the same or not, there was a characteristic value of $1/n$ that represented the behavior of the total background organics.

In this study, a new approach was developed to mathematically describe the overall adsorption isotherms of the background organics of unknown composition. The description was based on an overall adsorption isotherm expression derived from IAST-Freundlich equation, and a technique of fractionating the background organics into a multicomponent mixture in terms of the adsorptive strength described by the Freundlich constant k and the exponent $1/n$. The effectiveness of this approach was verified experimentally for two types of background organics by the overall quality indexes of TOC and E260 (UV-absorbance at 260nm). After the concentration ratios and the Freundlich parameters for all fractionated components are determined, which represent a pseudo-composition that shows an overall adsorption behavior equivalent to that of the real background organics, the changing tendency of the distribution of organics in both the liquid and the solid phases was then calculated to further investigate the behavior of multicomponent mixtures in batch adsorption.

2. MATERIALS AND METHODS

2.1 Working solutions

A biological process effluent of a collected night soil treatment plant, and the effluent of the coagulation, sedimentation and sand filtration treatment following the biological process (simply referred as the coagulation process effluent, hereafter) were used as raw waters. The coagulation post-treatment removed a great extent (about 70%) of the background organics remaining in the biological process effluent. Each water was diluted with distilled water to prepare the working solutions of three different initial concentrations, and the electrical conductivity and the value of pH were adjusted [6,7]. All solutions were filtrated through membrane filters of 0.2μm before experiments. The characteristics of the raw water and the working solutions are summarized in Table 1.

Table 1 Characteristics of raw water and working solutions

Items	TOC (mg/L)	E260 (1/cm)	pH	Conductivity (mS/m)
Biological Process Effluent				
Raw water	105.7	2.295	8.1	464.0
WS No.1	5.79	0.122	7.0	92.8
WS No.2	10.1	0.222	7.0	92.8
WS No.3	20.1	0.445	7.0	92.8
Coagulation Process Effluent				
Raw water	31.1	0.642	6.0	562.0
WS No.4	5.97	0.114	7.0	399.0
WS No.5	10.99	0.229	7.0	399.0
WS No.6	20.84	0.454	7.0	399.0

[WS denotes the working solution diluted from each raw water]

2.2 Activated carbon

Pulverized particles with a diameter below 47μm from the representative samples of granular activated carbon (Filtrasorb 400, Calgon Corporation, USA) were used in experiments. They were rinsed with distilled water to remove fines and dried at 105°C before use.

2.3 Experimental procedures

Carbon samples ranging from 0.2 to 2000mg were added to flasks that were then filled with the working solution of 200mL to make the carbon doses from 1 to 10,000mg/L. After reaching equilibrium through shaking for seven days at 20°C, the carbon particles were removed by filtrating the water samples through 0.45μm membrane filters, and the liquid phase concentration was determined in terms of TOC and E260.

3. APPROACH

3.1 Basic equations

The following equations in IAST [8] are used to describe multicomponent interactions:

$$C_i = \frac{q_i}{\sum_{j=1}^{N} q_j} C_i^o \quad (i = 1, 2, \cdots\cdots, N) \qquad (1)$$

$$\sum_{j=1}^{N}\frac{q_j}{q_j^o}=1 \tag{2}$$

$$\pi A/RT=\int_0^{C_i^o}\frac{q_i^o}{C_i^o}dC_i^o \tag{3}$$

where, C_i and q_i : liquid and solid phase concentrations for component i; C_i^o and q_i^o : single component liquid and solid phase concentrations for component i; π : spreading pressure; A : Surface area of adsorbent per unit mass; R : universal gas constant; T : absolute temperature; N : the total number of components.

If the Freundlich isotherm equation (4) is used to represent single component behavior, following equations [9] can be obtained from equations (1)-(3).

$$q_i^o=k_i\left(C_i^o\right)^{1/n_i} \tag{4}$$

$$C_i=\frac{q_i}{\sum_{j=1}^{N}q_j}\left(\frac{\pi A/RT}{n_ik_i}\right)^{n_i} \tag{5}$$

$$\pi A/RT=n_iq_i^o=\sum_{j=1}^{N}\left(n_jq_j\right) \tag{6}$$

where, k_i : Freundlich constant; n_i : Freundlich exponent, for component i.

Combining equations (5) and (6) yields the following equation, which describes the behavior of each component in batch adsorption of multicomponent mixtures.

$$C_i=\frac{q_i}{\sum_{j=1}^{N}q_j}\left[\frac{\sum_{j=1}^{N}n_jq_j}{n_ik_i}\right]^{n_i}\quad(i=1,2,\cdots\cdots N) \tag{7}$$

IAST was originally formulated on a basis of molar concentration for C_i and q_i. However, as the determination of the molar concentration of the natural background organics is impossible, the overall water quality indexes TOC and E260 were used in this study.

3.2 Overall adsorption isotherm expression

Under equilibrium conditions in batch adsorption, the following mass balance equations exist for each component and for the total components.

$$q_i=\left(C_{i0}-C_i\right)\frac{V}{M} \tag{8}$$

$$q_T=\left(C_{T0}-C_T\right)\frac{V}{M} \tag{9}$$

Supposing the value of Freundlich exponent $1/n_i$ is the same for all components, the combination of equations (7), (8) and (9) gives the following equation.

$$\frac{q_i}{q_T}\left(\frac{{q_T}^n}{{k_i}^nC_{T0}}+1-\frac{C_T}{C_{T0}}\right)-\frac{C_{i0}}{C_{T0}}=0 \tag{10}$$

At any equilibrium point, as the following relation [equation (11)] exists, the equation (10) can be modified to the form of equation (12).

$$\sum_{i=1}^{N}\frac{q_i}{q_T}=1 \tag{11}$$

$$\sum_{i=1}^{N}\frac{C_{i0}/C_{T0}}{\left(q_T/k_i\right)^n\cdot\left(1/C_{T0}\right)+1-\left(C_T/C_{T0}\right)}=1 \tag{12}$$

where, V : volume of solution; M : mass of activated carbon; C_{i0} : initial liquid phase concentration of component i; and,
C_{T0} : initial total liquid phase concentration; C_T : total liquid phase concentration; q_T : total solid phase concentration, described as follows:

$$C_{T0}=\sum_{i=1}^{N}C_{i0};\quad C_T=\sum_{i=1}^{N}C_i;\quad q_T=\sum_{i=1}^{N}q_i$$

The equation (12) describes the overall batch adsorption isotherm represented by the relationship between q_T and C_T. To solve this non-linear equation, the single component Freundlich parameters of k_i and n, and the initial concentration ratio of C_{i0}/C_{T0} have to be known.

3.3 Definition of the composition of background organics

The overall background organics were divided into 21 (N=21) adsorbable components with specific single component behavior and one non-adsorbable component. For all adsorbable components, the $1/n$ was assumed to be identical based on the findings of Yuasa [5]. The logarithmic normal distribution was supposed to represent the frequency distribution of k as follows.

$$f\left(\log_{10}k\right)=\frac{1}{\sqrt{2\pi}\sigma}e^{-\left(\log_{10}k-\mu\right)^2/2\sigma^2} \tag{13}$$

where, μ and σ : the mean and the standard deviation of $\log_{10}k$, respectively.

$$\mu = \overline{\log_{10} k} = \frac{\sum_{i=1}^{N} \log_{10} k_i}{N} \quad (14)$$

$$\sigma^2 = \frac{\sum_{i=1}^{N} (\log_{10} k_i - \mu)^2}{N} \quad (15)$$

The average value of k_i is described as follows.

$$K_M = 10^{\mu} \quad (16)$$

The values of k_i for the adsorbable components can be described as follows.

$$\log_{10} k_i = \mu + (i - 11)\cdot\Delta \quad (17)$$

or $$k_i = 10^{\mu+(i-11)\cdot\Delta} \quad (18)$$

where: Δ is the increment of $\log_{10}k$ and is given as follows.

$$\Delta = [(\mu + 3\sigma) - (\mu - 3\sigma)]/N = 6\sigma/21 \quad (19)$$

Accordingly, the initial concentration ratio of each component can be determined as follows.

$$C_{i0}/C_{T0} = f(\log_{10} k_i)\cdot\Delta \quad (20)$$

From above equations, it is obvious that once the parameters μ and σ are given, the values of k_i and C_{i0}/C_{T0} for each component can then be calculated using equations (18) and (20).

These two parameters, along with the Freundlich exponent $1/n$, were searched to give the best fit of the calculated overall batch adsorption isotherms by using the equation (12) to the experimental data.

The choice of the distribution pattern of k values of the hypothetical or imaginary components shown above is arbitrary and other various distribution patterns may exist to describe the experimental overall batch adsorption isotherm. However, preliminary tests showed that the assumption of the normal distribution of k values resulted in a very poor fit to the experimental overall batch adsorption isotherm data. The choice of the logarithmic normal distribution of k is based on the following aspects. (1) A wide range distribution of k value is given. (2) The mathematical expression is very simple. Only two parameters (μ and σ) are needed. (3) The simulation results can fit fairly well to the experimental overall batch adsorption isotherm data as shown later.

4. RESULTS AND DISCUSSION

4.1 Adsorption isotherm of E260

The overall adsorption isotherms of the background organics contained in working solutions of both the biological process effluent and the coagulation process effluent on the basis of E260 are shown in Figs.1 and 2, respectively. The experimental data are given by marks and the calculations that best fit the experimental data are represented by solid lines.

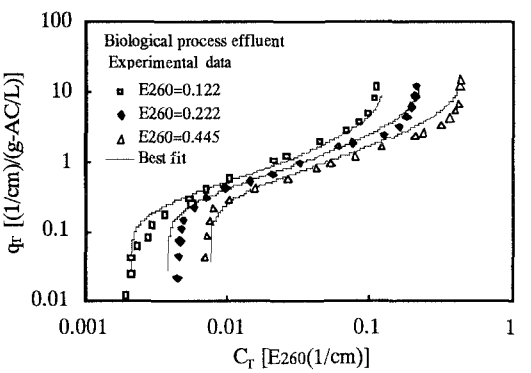

Fig.1 The overall batch adsorption isotherms (E260) of the biological process effluent

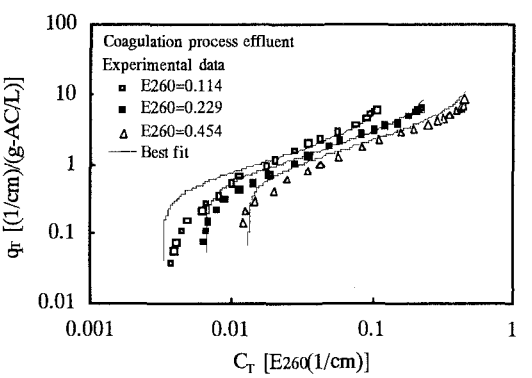

Fig.2 The overall batch adsorption isotherms (E260) of the coagulation process effluent

For the background organics examined, there are a few characteristics. The first characteristic is the great dependence of the overall isotherms on the initial overall concentrations. The position of the isotherms shifts regularly in a direction from the right to the left as the initial concentration decreases. The second characteristic is that the shape of the isotherms can not be simply described by the Fre-

undlich expression. The isotherms can be represented by nearly three regions. The first region is the one observed near the initial concentration, i.e., at the equilibrium points obtained with very low carbon doses, where the adsorptive capacity increases steeply. The second region is represented by the flat part of the isotherm, which seems to be able to be approximated as a linear line described by the Freundlich expression for each working solution. A steep descending part is the third region, which indicates the existence of nonadsorbable fraction of organics, which are determined to be 1.75 and 2.95% of the total organics for the biological process effluent and the coagulation process effluent, respectively, as will be shown later in Table 2.

These characteristics are representative of the behavior of multicomponent mixtures in batch adsorption, although some mixtures may not contain the nonadsorbable fraction of organics. Therefore, it is obvious that, to fully display the equilibrium behavior of background organics of multicomponent solutions in batch adsorption experiments, the carbon doses should cover a great range and the influence of the overall initial concentration has to be considered.

Besides, as one of the most important objectives of this study, the effectiveness of the developed approach to mathematically describe the overall adsorption equilibria of background organics of unknown composition is confirmed, as can be seen from these figures that, the calculated isotherms agree fairly well with the corresponding experimental data. The major parameters determined and then used for these calculations will be discussed later.

4.2 Adsorption isotherm of TOC

Figs. 3 and 4 show the overall adsorption isotherms of the background organics contained in working solutions of both the biological process and the coagulation process effluent on the basis of TOC.

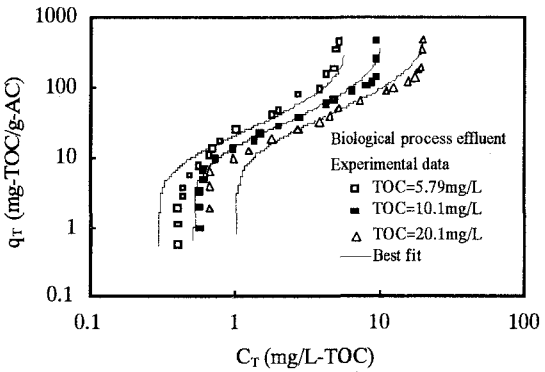

Fig.3 The overall batch adsorption isotherm (TOC) of the biological process effluent

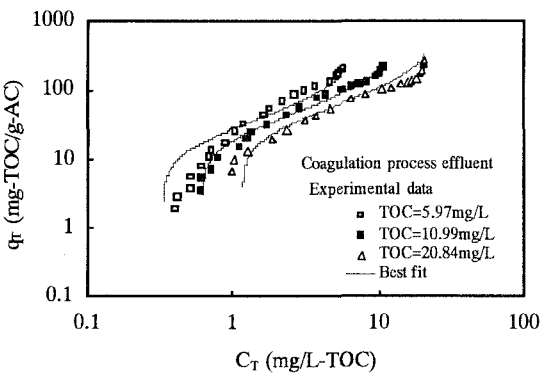

Fig.4 The overall batch adsorption isotherms (TOC) of the coagulation process effluent

Table 2 Parameters of the composition of the background organics

Biological process effluent	Non-adsorbable fraction (%)	Adsorbable components				
		μ	σ	k_i	K_M	1/*n*
E260	1.75	0.75	0.42	0.36-89.72	5.66	0.33
TOC	5.25	1.64	0.44	2.39-810.72	43.98	0.35
Coagulation process effluen	Non-adsorbable fraction (%)	Adsorbable components				
		μ	σ	k_i	K_M	1/*n*
E260	2.95	0.84	0.32	0.84-58.35	6.99	0.34
TOC	5.64	1.69	0.35	4.94-486.32	49.0	0.37

[note: K_i, K_M : (1/cm)/(g-AC/L) for E260 basis, or mg-TOC/g-AC for TOC basis]

Similar characteristics to that of E260 are observed, and good agreement of the calculated isotherms to the experimental data is achieved. This further verifies the effectiveness of the approach proposed.

With this approach, the adsorption equilibria of the background organics of unknown composition at any initial overall concentration can be predicted, and a more reasonable and reliable theoretical analysis of the behavior of background organics in fixed bed adsorbers can be realized [10]. This approach should also be beneficial to the investigation or estimation of the behavior of certain target trace organic compounds of special interest singled out from the total organics of unknown composition.

4.3 Composition parameters

The best searched parameters and some other relative indexes for the background organics in both the biological process effluent and the coagulation process effluent are displayed in Table 2. The Freundlich constant k_i and the concentration ratio C_{i0} / C_{T0} of each component in the biological process effluent on the basis of E260 are summarized in Table 3 as an example.

The Freundlich constant k differs greatly with the components for both the quality indexes of TOC and E260, no matter which effluent is concerned. The coagulation treatment removed a great extent of the background organics over the wide range of k_i, and results in a narrower distribution of k_i and a slight increase of K_M (the average of k_i) for the adsorbable components.

4.4 Effect of C_{T0} on the distribution of organics in liquid and solid phases at constant C_T / C_{T0}

Based on the parameters shown in Table 3, the liquid and the solid phase distribution of each component (E260 basis) contained in the biological process effluent at constant overall residual ratio of C_T / C_{T0} was calculated by using the equation (7).

Figs. 5 and 6 show the results plotted on the concentration bases of C_i and q_i versus the Freundlich constant k_i of each component at an overall residual ratio 0.9 (C_T / C_{T0} = 0.9). The results plotted on the concentration ratio bases of C_i / C_T and q_i / q_T versus the Freundlich constant k_i of each component at the overall residual ratios 0.9, 0.5 and 0.25 (C_T / C_{T0} = 0.9, 0.5, 0.25) are shown in Fig.7. Although the absolute values of C_i and q_i for each

Table 3 Distribution of the adsorbable components of the background organics

i	k_i	C_{i0} / C_{T0}	i	k_i	C_{i0} / C_{T0}
1	0.357	0.0019	12	7.463	0.1094
2	0.471	0.0042	13	9.838	0.0968
3	0.621	0.0084	14	12.969	0.0789
4	0.818	0.0154	15	17.096	0.0593
5	1.079	0.0262	16	22.537	0.0411
6	1.422	0.0411	17	29.709	0.0262
7	1.875	0.0593	18	39.165	0.0154
8	2.471	0.0789	19	51.629	0.0084
9	3.258	0.0968	20	68.060	0.0042
10	4.294	0.1094	21	89.721	0.0019
11	5.661	0.1140	Total		1.0000

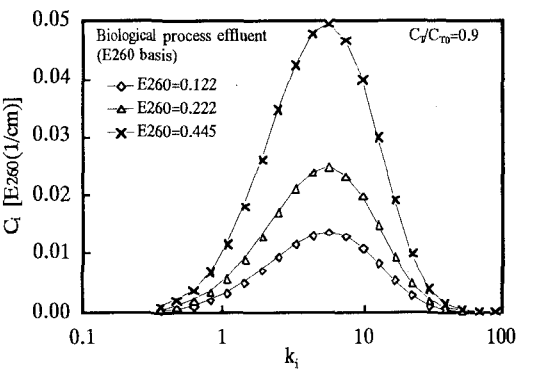

Fig. 5 Liquid phase distribution of components at C_T/C_{T0}=0.9

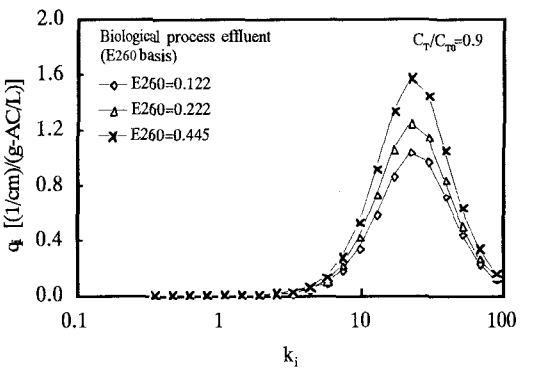

Fig. 6 Solid phase distribution of components at C_T/C_{T0}=0.9

component change with the change of the initial overall concentrations as shown in Figs. 5 and 6, the distribution of organics in either the liquid or the solid phase on the concentration ratio basis is identical when the overall residual ratio C_T / C_{T0} is the same, showing a tendency independent of the initial overall concentrations as shown in Fig. 7. It can be also observed that, with the decrease of the overall residual ratio, i.e, the increase of the carbon dose, the occupation ratios (C_i / C_T) of the components

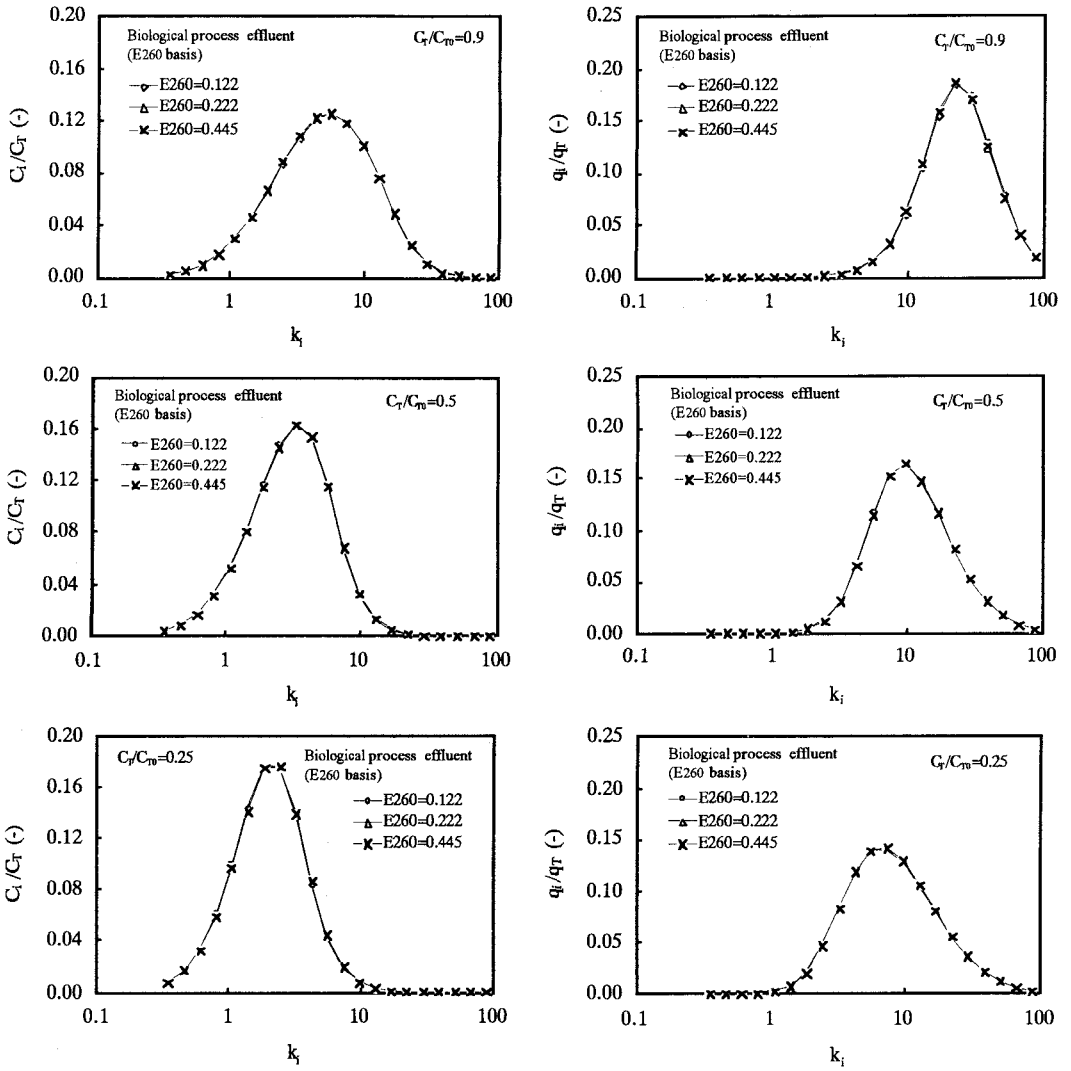

Fig. 7 Distribution of components in both the liquid and the solid phases at constant values of C_T/C_{T0}

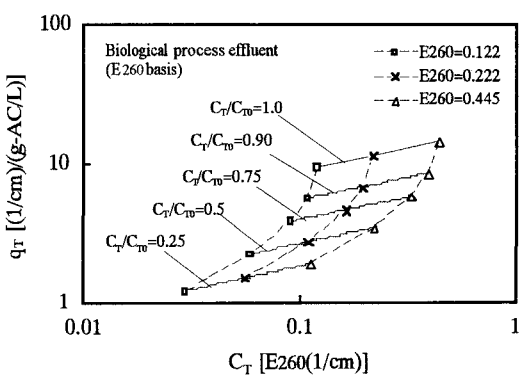

Fig. 8 The overall batch adsorption isotherm at constant values of C_T/C_{T0}

Table 4 Freundlich parameters of the isotherms shown in figure 8

C_T/C_{T0}	K_T	$1/n_T$
0.25	3.961	0.343
0.5	5.782	0.342
0.75	8.233	0.321
0.9	11.407	0.324
1.0	18.764	0.333
Average		0.333

[note: K_T : (1/cm)/(g-AC/L) for E260 basis]

with greater k_i decrease and that of components with smaller k_i increase.

The result indicates that, batch adsorption of multicomponent mixtures takes place in such a manner that components with stronger adsorbability are removed from solutions in preference to those with weaker adsorbability. It is the preferential adsorption of these components that attributes to the steep increase of the adsorptive capacity at the equilibrium concentration near the initial overall concentration, as indicated in Figs. 1-4.

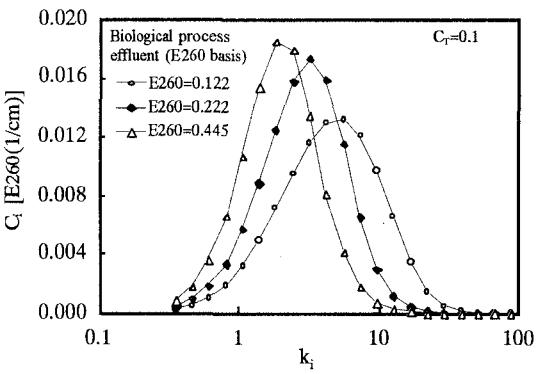

Fig. 9 Liquid phase distribution of components at C_T=0.1

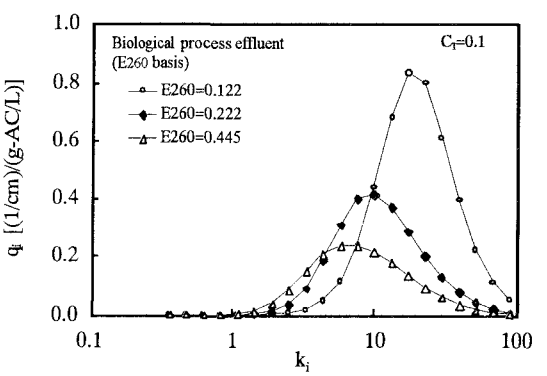

Fig. 10 Solid phase distribution of components at C_T=0.1

The result also implies that, the composition of background organics remaining in batch adsorption is determined by the overall residual ratio rather than by the initial overall concentration. In other words, the overall adsorptive capacity is not only a function of the overall liquid phase concentration, but also a function of the composition. As can be seen from Fig. 8, which shows the adsorption isotherms at constant overall residual ratios, as the liquid phase composition at the same ratio does not change with the change of the initial overall concentration, the adsorption isotherms at different values of C_T / C_{T0} can all be described by the Freundlich expression. It is also interesting to note that, the values of 1/n for all these isotherms are the same, as summarized in Table 4. This further verifies the finding of Yuasa [5] that there is a characteristic value of 1/*n* that exists in batch adsorption of multicomponent mixtures.

4.5 Effect of C_{T0} on the distribution of organics in liquid and solid phases at constant C_T

Based on the parameters shown in Table 3, the liquid and the solid phase distribution of each compo-

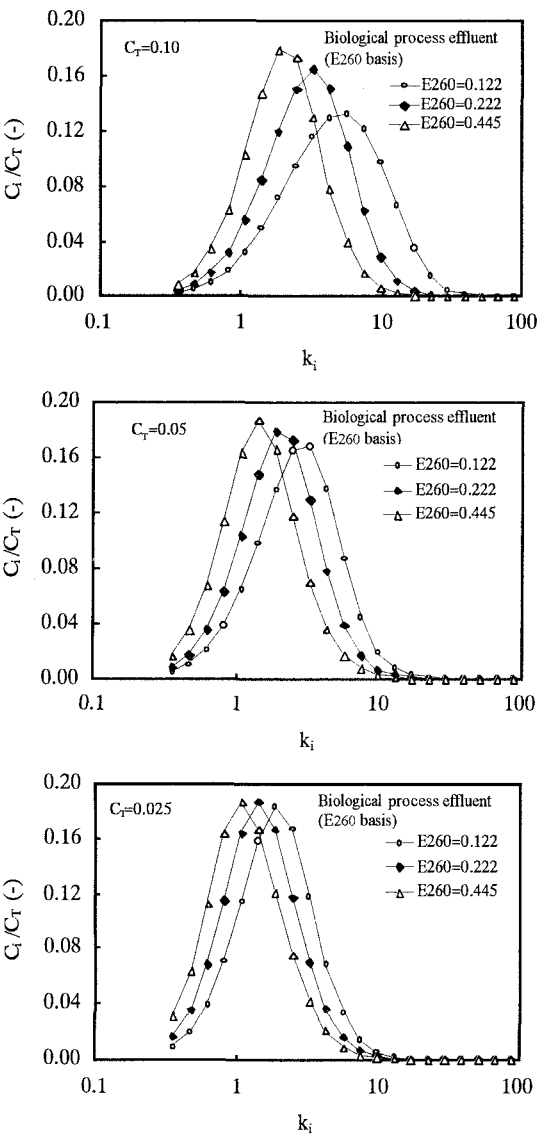

Fig.11 Liquid phase distribution of components at constant values of C_T

nent (E260 basis) contained in the biological process effluent at constant overall equilibrium concentration of C_T was also calculated.

Figs. 9 and 10 show the results plotted on the concentration bases of C_i and q_i versus the Freundlich constant k_i of each component at an overall equilibrium concentration of 0.1 (C_T = 0.1). The results plotted on the concentration ratio bases of C_i / C_T and q_i / q_T versus the Freundlich constant k_i of each component at the overall equilibrium concentration of 0.1, 0.05 and 0.025 (C_T = 0.1, 0.05, 0.025) are shown in Figs.11 and 12 respectively.

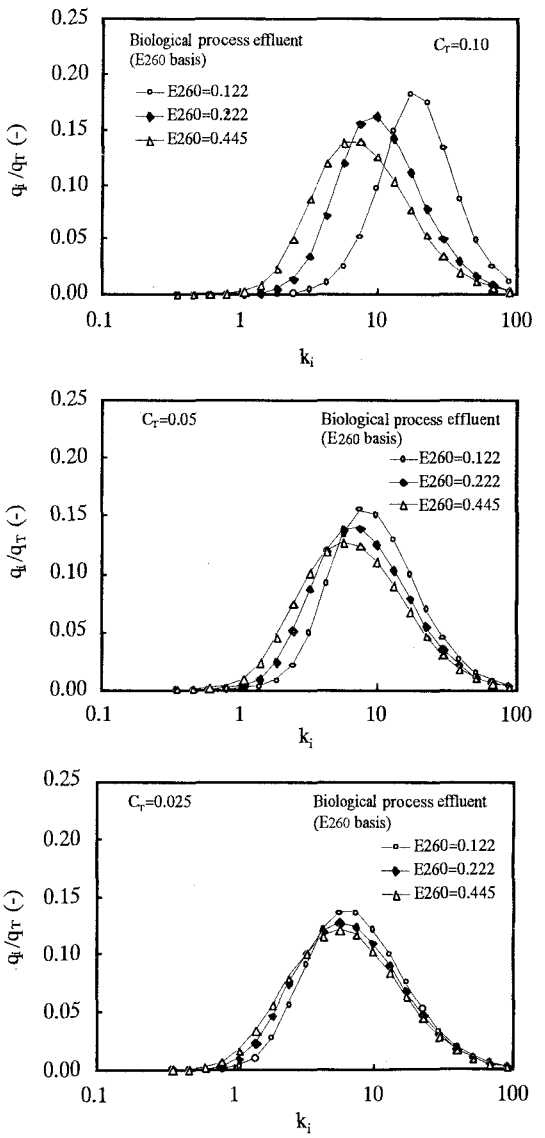

Fig.12 Solid phase distribution of components at constant values of C_T

At the same value of C_T, both the liquid and the solid phase concentrations of components with greater k_i are higher, for the working solution of lower initial overall concentration, than that of higher initial overall concentration as shown in Figs.9 and 10. Besides, it is obvious that, at the same value of C_T the distribution of organics on the concentration ratio bases is different with the difference of the initial overall concentration. The working solution with the lower initial overall concentration has higher ratios for the components with stronger adsorbability in both the liquid and the solid phases. It is this kind of adsorption behavior that leads to the shift of the overall adsorption isotherms in a direction from the right to the left as the initial concentration decreases, with the activated carbon performing better for the solution with the lower initial overall concentration, as displayed in Figs.1-4.

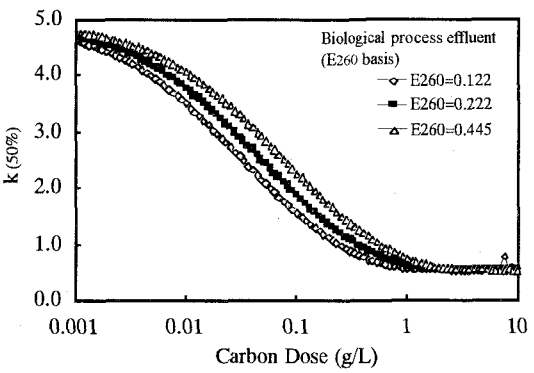

Fig.13 Changing tendency of the median values of the adsorptive strength vs. carbon doses

Besides, with the decrease of C_T , i.e., the increase of the carbon dose, the distribution narrows. The components that possess weaker adsorbability constitute the major portion of the total organics remaining in the liquid phase. This could be reflected in Fig. 13, which displays a gradual decrease of the median value of k (the k when the cumulative concentration ratio versus k_i reaches 50% of the total organics remaining at a certain dose), described as *K(50%)*, with the increase of the carbon doses. This is also a result of the preferential adsorption of the components with the greater adsorptive strength.

5. CONCLUSIONS

1) The overall adsorption isotherms of the background organics of unknown composition are a

set of non-unique isotherms, which are greatly affected by the initial overall concentrations.

2) An approach to fractionate the background organics into a multicomponent mixture in terms of the adsorptive strength, and therefore to mathematically describe the adsorption equilibria using an expression derived from IAST-Freundlich equation is proposed. The effectiveness of this approach was verified for two types of background organics on the overall quality indexes TOC and E260.

3) With this approach, the adsorption equilibria of background organics of unknown composition at any initial overall concentration can be predicted. This approach should also be beneficial to a more reasonable and reliable theoretical analysis of the behavior of background organics or certain target organic compounds of special concern in fixed bed adsorbers.

4) Batch adsorption of multicomponent mixtures takes place in such a manner that the components with stronger adsorbability are preferentially adsorbed.

5) The adsorptive capacity is not only influenced by the overall liquid phase concentration, but also by the composition of organics remaining. At the same overall equilibrium concentration ratio, the composition distribution of organics in either the liquid or the solid phase is identical, which is independent of the initial overall concentration.

6) A characteristic value of the Freundlich exponent (1/n) of a multicomponent mixture can be obtained by a series of batch adsorption isotherm tests. Use of the same value of 1/n for all fractionated components simplifies the analytical procedure and facilitates to search other parameters needed to describe the overall batch adsorption equilibria of the background organics of unknown composition.

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