

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

Adsorption Characterization for Multi-Component Organic Matters by Titanium Oxide (TiO₂) in Wastewater

Seoung-Hyun Kim^a; H. K. Shon^a

^a Faculty of Engineering, University of Technology, Sydney, Australia

To cite this Article Kim, Seoung-Hyun and Shon, H. K.(2007) 'Adsorption Characterization for Multi-Component Organic Matters by Titanium Oxide (TiO₂) in Wastewater', *Separation Science and Technology*, 42: 8, 1775 – 1792

To link to this Article: DOI: 10.1080/01496390701310470

URL: <http://dx.doi.org/10.1080/01496390701310470>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Adsorption Characterization for Multi-Component Organic Matters by Titanium Oxide (TiO₂) in Wastewater

Seung-Hyun Kim and H. K. Shon

Faculty of Engineering, University of Technology, Sydney, Australia

Abstract: In this study, an experimental and analytical study on adsorption and adsorption kinetics of organic matters in titanium oxide (TiO₂, Degussa P25) with synthetic wastewater was investigated. In order to understand the removal of different organic sizes in detail molecular weight (MW) distribution of organics matters was examined in terms of number and weight-average MW. The large MW (33950 dalton) of synthetic organic matters (SOMs) was significantly removed by TiO₂ adsorption and the slight decrease of the small MW (970 dalton) occurred with time. A characterization method was applied to evaluate the composition of SOMs in terms of adsorbability by adsorption of TiO₂. Several adsorption equilibrium and batch kinetics experiments were conducted with different initial concentrations of SOMs and different amounts of adsorbent. A binomial distribution(s) of SOM fraction with the Freundlich coefficient (*k*) was obtained. The synthetic wastewater was explained by a finite number of pseudospecies (*N*) identified with a Freundlich isotherm constant (*k*) value. These parameters were determined by the characterization procedure, together with ideal adsorbed solution theory (IAST) with the pseudospecies number method. Prediction of adsorption isotherm and kinetics derived from a binomial concentration distribution of the characterization procedure were in good agreement with experimental data conducted.

Keywords: Characterization, titanium oxide, overall adsorption, adsorbability, molecular weight distribution, synthetic organic matter, competitive adsorption, wastewater treatment

Revised 1 September 2006, Accepted 26 January 2007

Address correspondence to H. K. Shon, Faculty of Engineering, University of Technology, P. O. Box 123, Broadway, Sydney NSW 2007, Australia. Tel.: +61-2-9514-2629; Fax: +61-2-9514-2633; E-mail: hkshon@eng.uts.edu.au

INTRODUCTION

The composition of organic matter in wastewater is a combination of those of natural organic matter (NOM), soluble microbial products, and trace harmful chemicals. Most of the NOM originates from drinking water, which is one of the major components in wastewater, while soluble microbial products come from biological treatment with the wastewater treatment plant and non-biodegradable organic matter. Of particular interest are recalcitrant organic chemicals which are resistant to biodegradation, and thus challenging to remove during typical wastewater treatment. Some micro-contaminants associated with wastewater effluent may cause adverse impacts to aquatic and human health if the compounds are present in recycled water. Some of the compounds of concern include disinfection by-products, *N*-nitrosodimethylamines, pesticides, herbicides, pharmaceuticals, and endocrine disrupting chemicals (1). As such, it is important to remove organic matter from wastewater.

In the sewage treatment process, organic matter in wastewater is reduced by physical, chemical, and biological means (2). Treatment methods, where the application of physical force predominates, are known as physical unit operations. Physical treatments include screening, sedimentation, and filtration. Chemical treatment involves the removal or conversion of contaminants by the addition of chemicals or by indirect chemical reactions. Flocculation, adsorption, ion exchange, and disinfection are the most common chemical treatment methods. Biological treatment using microbes to biodegrade organic matter is important to select an appropriate treatment to remove specific compounds found in organic matter. In order to remove these compounds, it is necessary to understand the roles and mechanisms of different treatment processes.

Application of photocatalysis in removing organic matter in wastewater has increasingly been of major concern (3–5). It is well known that photocatalysis with TiO_2 can significantly remove organic matter (6–10). It was reported that organic removal by a photocatalysis hybrid system was similar to that by nanofiltration (11). Although the adsorption phase of organic matter on TiO_2 is a determining stage in the process of photodegradation (12–14), a few researches have studied the adsorption of TiO_2 (14, 15). It is thus important to evaluate the performance of TiO_2 in terms of better understanding of the adsorption phenomenon.

Adsorption technology has been used for the removal of organic contaminants from wastewater. In applying adsorption technology on TiO_2 in treating organic matters in wastewater, the identities and concentrations of organic substances to be removed by TiO_2 adsorption are unknown since wastewater has a series of unidentified organic matters (16–21). A few pseudospecies to handle such a mixture according to the multi-component adsorption calculation method for unknown species in

wastewater can be determined. It is a fundamental approach to characterize the solution before any adsorption process is applied to the system. Information on the adsorption equilibrium of organic matters helps the design and simulation of the adsorption system in removing those contaminants from wastewater (17–20). The most common approach for the characterization of unknown solutions is to group several components together with a single pseudospecies according to similarity of their physical and chemical properties because a single surrogate quantity such as biological oxygen demand, dissolved organic carbon, or total organic carbon (TOC) has been used in representing the total contaminant in the target solution (22–24). The presence of a variety of substances with adsorption affinity in an aqueous solution also requires that the competitive interaction among them after characterizing the solution into several pseudospecies should be considered.

A characteristic distribution of Langmuir coefficient was applied for a useful concept to describe the adsorption equilibrium of wastewater in which many unknown species exist (25). The wastewater encountered can then be characterized by its concentration frequency function, assuming that the number of pseudospecies is infinite. While conceptually simple and elegant, it is difficult to implement this concentration frequency function in simulating batch kinetics adsorption systems. Considering this point, some researchers proposed a characterization procedure with a finite number of pseudospecies based on the concept of species grouping. They assumed that all the pseudospecies are fitted with the Freundlich expression and the ideal adsorbed solution theory (IAST) can describe the multi-component adsorption equilibrium (26, 27).

To understand the phenomenon of adsorption in detail, it is necessary to know the range of the molecular weight (MW) distribution of organic matter removed from the wastewater (28). A polydisperse composition of organic matter present in natural surface water was investigated in terms of MW and activated carbon adsorbabilities (17). The fictive component method was used to analyze the activated carbon adsorbabilities (17–21). Recently, a simple procedure for the characterization was devised using a binomial distribution of composition in characterizing variable, namely adsorption constants (29, 30). This characterization procedure was convenient and suitable for wastewater treatments using the adsorption equilibrium, batch kinetics adsorption systems because a finite number of pseudospecies can be systematically assigned by a binomial concentration distribution function.

In this study, the effect of the fundamental adsorption on TiO₂ was investigated in terms of TOC and MW distribution of organic matters from synthetic wastewater. The experimental adsorption and the adsorption kinetics of organic matters by TiO₂ in wastewater were also investigated. The simple characterization procedure was used for SOMs in which organic and inorganic compounds existed together.

EXPERIMENTAL

Synthetic Wastewater

The composition of the synthetic wastewater used in this study is presented in Table 1. This synthetic wastewater represents effluent organic matter generally found in the biologically treated sewage effluent (31). Tannic acid, sodium lignin sulfonate, sodium lauryl sulfate peptone, and arabic acid contributed to the large MW size organic matter, while the natural organic matter from tap water, peptone, beef extract, and humic acid consisted of the small MW organic matters. The MW of the mixed synthetic wastewater ranged from 970 dalton to about 33950 with the highest fraction at 970 dalton.

Titanium Oxide

The photocatalyst, TiO₂, used in this study was Degussa P25, ca. surface area 50 m²/g, 6.9 nm mean pore size obtained from Degussa Company (Germany). Table 2 shows the characteristics of TiO₂ used.

Batch Test Procedure

Batch adsorption experiments were performed at 100 rpm with TiO₂ adsorbents. The batch reactors were 1 L conical glass flasks. In each flask, a known concentration of wastewater was mixed with the known amount of

Table 1. Constituents of SOMs in wastewater used in this study

Compounds	Concentration (mg/L)	Concentration (TOC, mg/L)	Fraction by TOC
Beef extract	1.8	0.2204	0.065
Peptone	2.7	0.4688	0.138
Humic acid	4.2	0.2777	0.082
Tannic acid	4.2	0.8042	0.237
Sodium lignin sulfonate	2.4	0.2266	0.067
Sodium lauryl sulphate	0.94	0.1438	0.042
Arabic gum powder	4.7	0.7233	0.213
Arabic acid	5.0	0.5300	0.156
(NH ₄) ₂ SO ₄	7.1	0	0
K ₂ HPO ₄	7.0	0	0
NH ₄ HCO ₃	19.8	0	0
MgSO ₄ · 7H ₂ O	0.71	0	0

Table 2. Characteristics of Degussa P25 photocatalytic powdered used

Specification	Degussa P25 TiO ₂ photocatalyst
Structure	Non-porous
Components	65% anatase, 25% rutile, 0.2% SiO ₂ , 0.3% Al ₂ O ₃ , 0.3% HCl, 0.01% Fe ₂ O ₃
Average aggregate particle diameter	Non-porous
Primary crystal size	3 μm
Mean pore diameter	6.9 nm
Band gap	3.03 (from 500 to 300 nm) with UV-Vis
Apparent density	130 kg/m ³
Surface area	42.32 ± 0.18 m ² /g
Type	Powdered
Product code	Degussa P25, Frankfurt am Main, Germany

adsorbent. The purpose of these experiments is to investigate the SOM removal with time and to find the equilibrium TOC concentration. All experiments were carried out at a temperature of 25°C. The adsorbed amount (q) and removal efficiency (RE) of SOMs were calculated by the following equations

$$q = \frac{V(C_i - C_e)}{M} \quad (1)$$

$$RE = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$

Where q is the adsorbed amount (mg/g), V is the volume (L) of solution, C_i is the initial TOC concentration of SOMs (mg/L), C_e is the equilibrium TOC concentration (mg/L), M is the amount of adsorbent TiO₂ (g), and RE is the removal efficiency of SOMs (%). All experiments were investigated at pH 4 because the pH value was found to be the optimum pH in removing SOM.

Analytical Methods to Measure Organic Matter

Total Organic Carbon (TOC)

TOC was measured by using the UV-persulphate TOC analyzer. All samples were filtered through 0.45 μm membrane prior to the TOC measurement.

Molecular Weight (MW) Distribution

The synthetic wastewater was subjected to MW distribution measurement. High pressure size exclusion chromatography (HPSEC, Shimadzu, Corp.,

Japan) with a SEC column (Protein-pak 125, Waters, Milford, USA) was used to determine the MW distributions of organic matter. Standards of MW of various polystyrene sulfonates (PSS: 210, 1800, 4600, 8000, and 18000 daltons) were used to calibrate the equipment. The details on the measurement methodology are given elsewhere (32). The MW can be classified into three groups: i) number-average molecular weight, ii) weight-average molecular weight, and iii) polydispersity.

The number-average MW (M_n) called "median", can be calculated as follows:

$$M_n = \frac{\sum_{i=1}^n (N_i M_i)}{\sum_{i=1}^n (N_i)} \quad (3)$$

The weight-average MW (M_w) and polydispersity (P), can be calculated from the following equation:

$$M_w = \frac{\sum_{i=1}^n (N_i M_i^2)}{\sum_{i=1}^n (N_i M_i)} \quad (4)$$

$$P = M_w / M_n \quad (5)$$

where N_i is the number of molecules having a molecular weight M_i and i is an incrementing index over all molecular weight present.

THEORETICAL APPROACH

The main modification in the characterization procedure proposed was to assume a simple discrete distribution function to represent a number of pseudospecies with the same Freundlich exponent (29, 30). Similar to the continuous function (33), the initial concentration of each pseudospecies was assigned by a binomial function in terms of the Freundlich constant. The competitive adsorption between species was estimated by a conventional equilibrium theory, namely the ideal adsorbed solution theory (IAST).

When a quantity of the adsorbent of mass M , initially free of any adsorbates, is added to a volume of solution V containing pseudospecies species N , the solution and adsorbed phase concentration C_i and q_i of the i -th species at equilibrium are related by the following mass balance equation (34).

$$C_i + (M/V)q_i = C_{i0} \quad (6)$$

The initial concentrations are given by

$$C_{i0} = x_{i0} C_{T0}, \quad i = 0, 1, 2, \dots, N \quad (7)$$

Where C_{T0} is the total TOC concentration of the solution and x_{i0} is the initial TOC fraction of the i -th species. The species, $i = 0$, means a non-adsorbable

species in the solution. If the multi-component equilibrium can be described by the IAST, the relationships among concentrations are given by the following set of equations:

$$C_i = C_i^o Z_i \quad (8)$$

$$q_i = q_T z_i \quad (9)$$

$$q_T = \left[\sum_{i=1}^N z_i / q_i^o \right]^{-1} \quad (10)$$

$$\pi_i = (RT/A) \int_0^{C_i^o} q_i^o / C_i^o dC_i^o \quad (11)$$

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 the 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:

$$\sum_{i=1}^N z_i = 1.0 \quad (12)$$

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

$$\pi = \pi_1 = \pi_2 = \dots = \pi_N \quad (13)$$

To simplify the subsequent computation work required in both the characterization and the adsorption calculations, one may assume that all the pseudospecies adsorption isotherms obey the Freundlich expression with a constant exponent, $1/n$, as follows. In general, a Freundlich exponential value n of <1.0 means unfavorable adsorption.

$$q_i^o = k_i C_i^{o1/n} \quad (14)$$

The integration of Eq. (11) and Eq. (13) yield as follows:

$$\Pi = \pi_i A / RT = nk_i C_i^{o1/n} \quad \text{or} \quad nq_i^o \quad (15)$$

The following relationships are obtained from Eqs. (14) and (15).

$$C_i^o = (\Pi / nk_i)^n \quad (16)$$

$$q_i^o = \Pi / n \quad (17)$$

The following relationship is obtained by substituting Eq. (16) into Eq. (10).

$$q_T = q_1 = q_2 = \dots = q_N = \Pi / n \quad (18)$$

Equation (19) represents that the total adsorption amount is equal to the adsorption amount of individual species at the single-species state. Substituting

Eqs. (8), (9), (16), and (18) into the material balance equation yields the mole fraction in the adsorbed phase as follows:

$$z_i = \frac{C_{io}}{(\Pi/nk_i)^n + (M/V)(\Pi/n)} \quad (19)$$

The following relationship is obtained from Eq. (12).

$$\sum_{i=1}^N \frac{C_{io}}{(\Pi/nk_i)^n + (M/V)(\Pi/n)} - 1 = 0 \quad (20)$$

Since the spreading pressure (Π) should be the same for all species at equilibrium, it should be evaluated at a given equilibrium condition using the Newton iteration method (35, 36). Once the spreading pressure for the mixture is known, the equilibrium values C_i and q_i for the multi-component can be calculated from the set of equations above.

The adsorption affinity of a specified species depends on both Freundlich constants. However, in this study, only the Freundlich coefficient was used to identify a couple of pseudospecies as a matter of convenience. Therefore, one has a 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 straightforwardly carried out on a binomial distribution. The value of s in Eq. (21) determines the skewness of the pseudo species concentration distribution and is within the range $0 < s < 1.0$, with $s = 0.5$ corresponding to a normal distribution type. Then the TOC fraction of the j^{th} species in the original solution is represented as follows:

$$x_j = \sum_{j=1}^N s^j (1-s)^{N-j}, \quad j = 0, 1, 2, \dots, N \quad (21)$$

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

$$k_j = k_s j^2 \quad (22)$$

where k_s is the scale factor which represents the order of magnitude of the lowest k value for the solution in question.

One can use a proper optimization technique to obtain optimum results can be used in carrying out the characterization of a given solution. In this study, a simple 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 Eq. (23).

$$F = \frac{100}{ND} \sum_{m=1}^{ND} \left[|C_{T\text{exp}} - C_{T\text{cal}}| / C_{T\text{exp}} \right]_m \quad (23)$$

where the superscripts “exp” and “calc” are the experimental and calculated values and ND is the total number of experimental data point.

The mass transfer rate between liquid and solid phases represented by the LDFA model, assuming that the overall mass transfer coefficient unchanged during experiments is the following Eq. (24).

$$\frac{dq}{dt} = \frac{3 \times k_f}{R \times \rho_p} (c_i - c_s) = k_m (q_s - q) \quad (24)$$

where R = radius of adsorbent (m), k_f = overall mass transfer coefficient (m/s), ρ_p = density of particle (kg/m³), k_m = mass transfer coefficient (1/s).

The adsorption rate of adsorbate by a TiO₂ particle 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 (37–39).

RESULTS AND DISCUSSION

Molecular Weight (MW) Distribution of Organic Matter by Adsorption

Synthetic wastewater has a number of known compounds at a known concentration. The MW distribution of each component in SOMs of synthetic wastewater can be found elsewhere (40). The MW of the mixed synthetic wastewater ranged from 970 dalton to 33950 with the highest fraction of 970 dalton. MW distribution of SOMs after TiO₂ adsorption isotherm was investigated in the range of 0.01 to 2 g/L of TiO₂ at initial concentration of 11.04 mg/L in synthetic wastewater. Figure 1 shows removal of different organic sizes. At lower concentration of TiO₂, the large (33950) and small (970) MWs of SOMs still remained. However, the majority of the large MW of SOMs was removed from 0.5 g/L of TiO₂. Table 3 shows MW values after TiO₂ adsorption in terms of number-averaged MW and weight-averaged MW. The initial weight-averaged MW was 33200 dalton. The weight-averaged MW of the influent was similar to that at low concentration of TiO₂. On contrary, the weight-averaged MW from more than 0.5 g/L of TiO₂ was significantly decreased up to 1200 dalton. Thus it can be concluded that the TiO₂ adsorption preferentially removed the large MW.

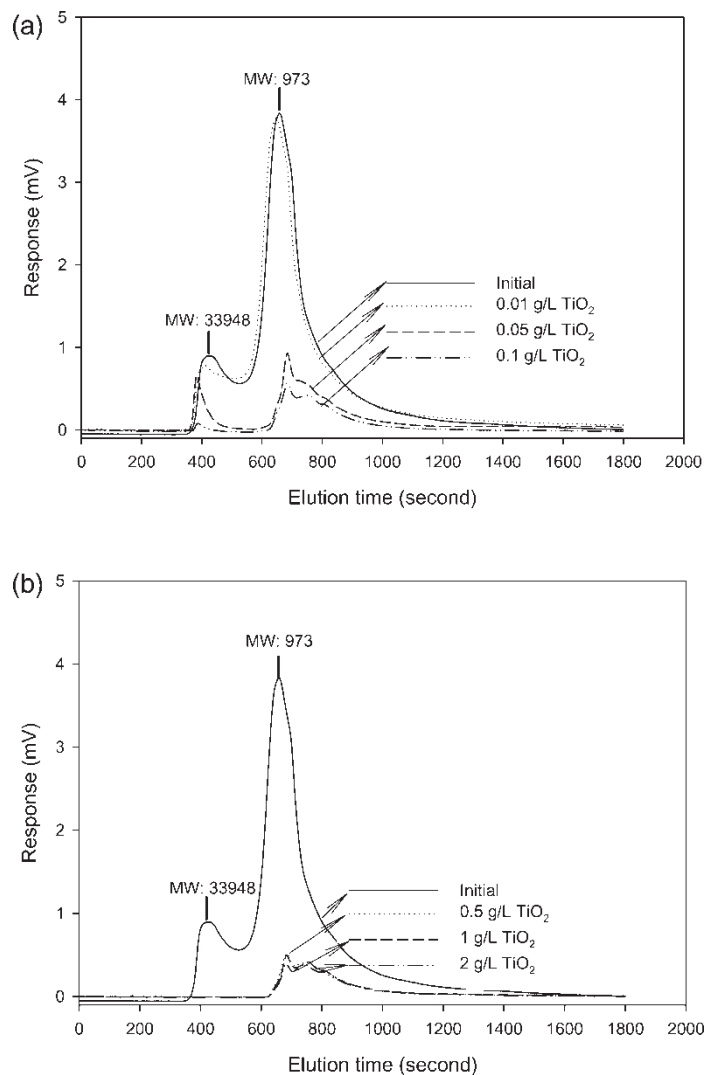


Figure 1. MW distribution after TiO_2 adsorption isotherm by P25 TiO_2 in batch reactor in range of (a) 0.01–0.1 g/L and (b) 0.5–2 g/L at initial concentration of 11.04 mg/L. (temperature = 25°C; mixing speed = 100 rpm).

Effect of Initial TOC Concentration in Adsorption Equilibrium

Figure 2 shows three sets of removal efficiency and overall adsorption equilibrium data of the SOMs. Each set of data was obtained with a known initial TOC concentration of 5.25, 11.04, and 16.55 mg/L using different concentrations of TiO_2 . The results indicated an unfavorable tendency at low

Table 3. MW values of organic matter after adsorption isotherm by TiO₂

	M _n (dalton)	M _w (dalton)	P
Initial	12800	33200	2.6
After 0.01 g/L TiO ₂ adsorption	12300	32000	2.6
After 0.05 g/L TiO ₂ adsorption	11900	30600	2.6
After 0.1 g/L TiO ₂ adsorption	11500	28300	2.5
After 0.5 g/L TiO ₂ adsorption	1090	1200	1.1
After 1.0 g/L TiO ₂ adsorption	1090	1200	1.1
After 2.0 g/L TiO ₂ adsorption	1000	1100	1.1

concentration ranges. However, it shows that the adsorption is quite possible over certain concentration levels. The interesting result was that three different sets of data did not match together. This implies that there was strong competitive adsorption between adsorbing components on TiO₂. The similar equilibrium behavior can be expected from mutual interactions between various species of organic matters in the wastewater depending on the nature and sources of wastewater such as domestic wastewater. The equilibrium data of a mixture showed a unfavorable case below a concentration and then dramatically changed to a favorable case over that concentration. This may be due to the change in adsorption affinity depending on the concentration with the concept of mutual competition between adsorbing species on the TiO₂ surface. For these reasons, a characterization procedure depending on different concentrations to interpret the adsorption equilibrium data and

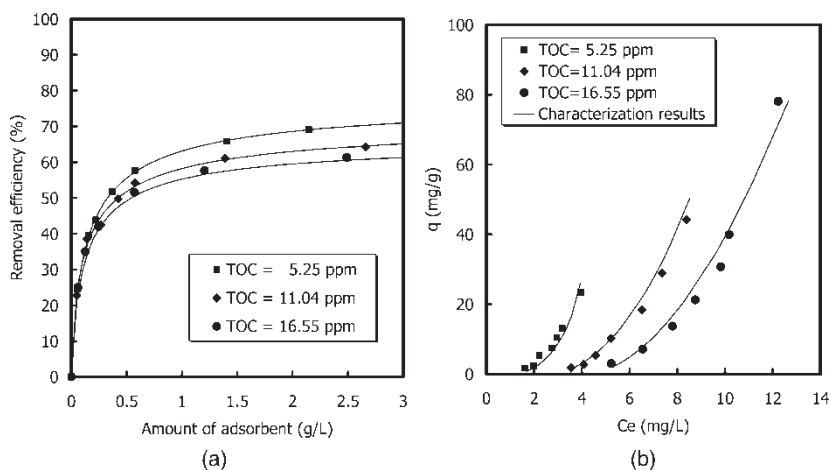


Figure 2. Removal efficiency depending on (a) the amount of adsorbent and (b) overall adsorption isotherms of SOMs on TiO₂. (initial concentration of SOMs = 5.25, 11.04, 16.55 mg/L).

adsorption kinetics was explored. The simple characterization procedure and technique were investigated for the adsorption of SOMs on TiO_2 .

Concentration Distribution of Wastewater

Figure 3 shows the distribution of the TOC fraction with different pseudospecies number N and various TOC concentrations. All the distributions were nearly identical for a binomial concentration distribution with $k_s = 1.0$ depending on pseudospecies number. Table 4 shows the characterized results of synthetic wastewater with TiO_2 adsorption in terms of the number of pseudospecies (N). As the number of pseudospecies number (N) increased, the values of n were in the range of 0.61~0.63, while that of s decreased. The values of F were nearly the same regardless of the number of pseudospecies and TOC concentrations. This indicated that there was a compensational effect between two characterization parameters in representing the solution. In this study, the F value was obtained at an optimum point in the conditions of pseudospecies number 12 and initial MM concentrations. The F values at the optimum points were 5.09%, 5.98%, and 4.50%, respectively. The smaller value of F indicates the good fit between the experimental and predicted data. Predictions based on the characterization were well fitted with the experimental data in the range from 4.5 to 7.5. Since the TOC fraction with higher k values increased with the increase of the skewness parameter(s), the corresponding n value decreased for the same adsorption equilibrium data to give the same magnitude of affinity. It should

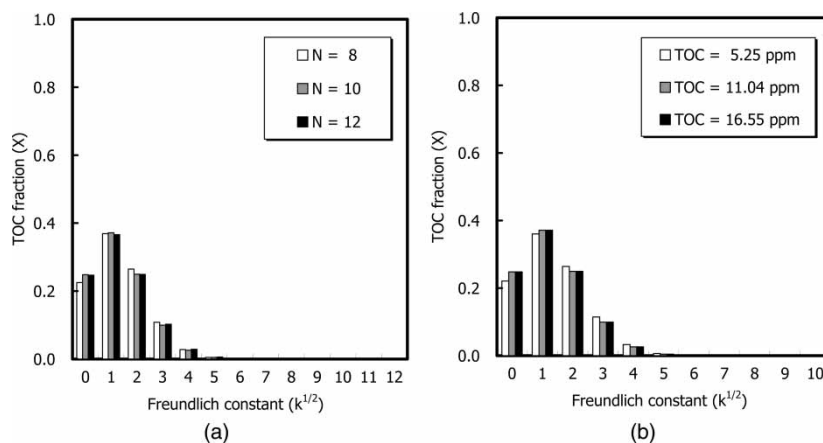


Figure 3. A binomial concentration distribution depending on (a) pseudospecies number and (b) TOC concentration on TiO_2 ((a) $N = 8, 10, 12$, TOC = 11.04 mg/L (b) TOC = 5.25, 11.04 and 16.55 mg/L).

Table 4. Characterization results of synthetic wastewater on TiO₂

k_s	N	n	s	F(%)
Characterization results with 5.25 mg/L TOC				
1.0	8	0.62	0.17	7.50
	10	0.61	0.14	6.20
	12	0.60	0.12	5.09
Characterization results with 11.04 mg/L TOC				
1.0	8	0.62	0.17	6.39
	10	0.61	0.13	6.23
	12	0.60	0.11	5.98
Characterization results with 16.55 mg/L TOC				
1.0	8	0.62	0.14	6.69
	10	0.61	0.13	4.90
	12	0.60	0.11	4.50

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 was confirmed by the characterization results shown in Fig. 2. Characterization results obtained from different experimental sets were similar and pseudospecies assigned by k values more than 11 did not contribute to the binomial distribution function as shown in Table 5. The average concentration distribution was used in order to apply the results to adsorption simulation. The interesting result in Fig. 3 was that a non-adsorbable species existed with ca. 0.25 fraction of TOC in case of the Freundlich constant $k^{1/2} = 0$, major components number for adsorption was around 5. This non-adsorbable portion of the TOC fraction was related to an extremely unfavorable tendency at a lower concentration.

Effect of Initial TOC Concentration in Batch Kinetics

Figure 4 shows the kinetics of adsorption at different initial concentrations of SOMs. The rate of adsorption was rapid in the initial minutes of solution-adsorbent contact and after ~ 20 min it became equilibrium state. The amount of SOMs adsorbed increases with increased initial concentration. The necessary time of equilibrium increased with increased initial concentration of SOMs. It was successfully predicted in various concentrations of SOMs by the LDFA kinetic equation, assuming that the overall mass transfer value of each component in wastewater had the same value. From 3.0×10^{-4} m/s to 7.0×10^{-4} m/s of mass transfer coefficients from batch experimental data was obtained to predict the kinetics data. It can be concluded that characterization predictions were in good agreement with the experimental data.

Table 5. Concentration distribution results of wastewater on the characterization procedure depending on pseudospecies number in TOC = 11.04 mg/L

Pseudospecies number (N)	k_i	X_i			Average (X)
		N = 8	N = 10	N = 12	
0	0	0.225034	0.248167	0.246691	0.239964
1	1	0.368965	0.371119	0.366215	0.368766
2	4	0.264668	0.249744	0.249173	0.254528
3	9	0.108487	0.099594	0.10275	0.103610
4	16	0.027793	0.026064	0.02860	0.027486
5	25	4.56E-03	4.68E-03	5.66E-03	4.97E-03
6	36	4.67E-04	5.83E-04	8.17E-04	6.22E-04
7	49	2.73E-05	4.98E-05	8.66E-05	5.46E-05
8	64	7.0E-07	2.8E-06	6.7E-06	3.4E-06
9	81		9.0E-08	3.7E-07	2.3E-07
10	100		1.0E-08	1.0E-08	6.7E-09
11	121			0	0
12	144			0	0
F(%)		6.39	6.23	5.98	6.20

Effect of Pseudospecies Number and Adsorbent Loading in Batch Kinetics

Figure 5 shows the kinetics simulation based on the characterization procedure with the pseudospecies number. As the pseudospecies number

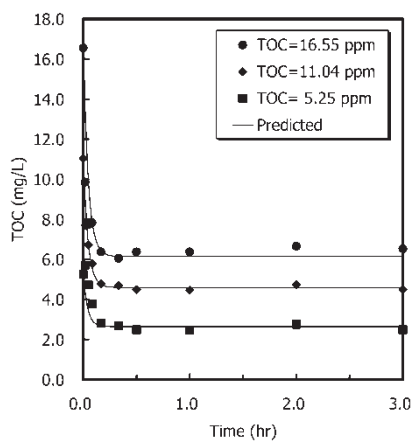


Figure 4. Effect of initial SOM concentration on kinetics of TiO_2 adsorption by TiO_2 at 25.0°C (mixing speed = 100 rpm, adsorbent amount = 1 g/L, concentrations of SOMs = 5.25, 11.04 and 16.55 mg/L).

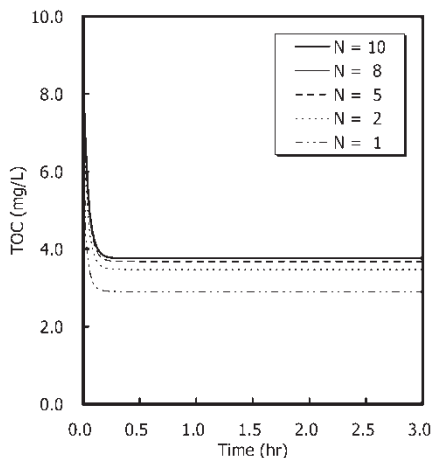


Figure 5. Effect of pseudospecies number on kinetics of TiO₂ adsorption. (concentration of SOMs = 11.04 mg/L, adsorbent amount = 1 g/L, mixing speed = 100 rpm).

increased, the adsorption capacity of SOMs decreased. The amount of SOMs adsorbed increased with decreased pseudospecies number. This suggested that there was competitive adsorption in multi-component SOMs as the pseudospecies number increased. The necessary time of equilibrium increased with the increased pseudospecies number.

Figure 6 shows predicted curves in various TiO₂ loading by LDFA kinetics equation. The necessary time of equilibrium increased with

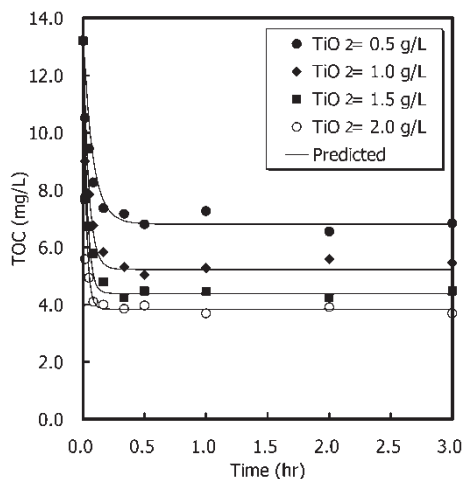


Figure 6. Effect of TiO₂ loading on kinetics of TiO₂ adsorption at 25.0°C. (concentration of SOMs = 13.20 mg/L, mixing speed = 100 rpm).

increased TiO₂ loading. The amount of SOMs adsorbed increased with increased TiO₂ loading. This may be due to the increase in the adsorbent surface area of the sorbent.

CONCLUSIONS

In this study, the removal of SOMs by TiO₂ adsorption was experimentally and analytically investigated. A detailed characterization of SOMs was made in terms of the TOC removal, MW distribution, and the adsorption characterization model. The results obtained led to the following conclusions.

- TiO₂ adsorption preferentially removed the majority of large MW of SOMs.
- The characterization results obtained from different sets of equilibrium data were similar regardless of the initial TOC concentration. The characterization procedure was suitable for the synthetic wastewater to provide information on the concentration distribution of the TOC fraction.
- A non-adsorbable species existed with ca. 0.25 fraction of TOC and major components number for adsorption was around 5 from characterization procedure. This non-adsorbable portion of the TOC fraction is likely to relate an unfavorable tendency at low concentration levels.
- Batch kinetics results were successfully predicted in various concentrations of SOMs by the LDFA kinetic equation with a binomial concentration distribution in the characterization procedure.
- As the pseudospecies number increased, the adsorption capacity of SOMs decreased. The amount of SOMs adsorbed increased with the decreased pseudospecies number. This suggested that there was competitive adsorption in multi-component in SOMs as the pseudospecies number increased.

ACKNOWLEDGEMENTS

This research was funded by the Korea Research Foundation by the Korean Government (MOEHRD) (KRF-2006-214-D00027) and a UTS Chancellor's postdoctoral research fellowship grant.

REFERENCES

1. Shon, H.K., Vigneswaran, S., and Snyder, S.A. (2006) Effluent organic matter (EfOM) in wastewater: constituents, effects and treatment. *Crit. Rev. Env. Sci. Tec.*, 36 (4): 327.

2. Tchobanoglous, G. and Burton, F.L. (1991) *Wastewater Engineering: Treatment, Disposal, and Reuse*, 3rd Edn.; McGraw-Hill: New York.
3. Jianfeng, F., Min, J., Yaqian, Z., and Lizhang, W. (2006) Kinetics of aqueous photocatalytic oxidation of fulvic acids in a photocatalysis-ultrafiltration reactor (PUR). *Sep. Purif. Technol.*, 50 (1): 107.
4. Alexander, G., Bea, T., Valeria, P., and Gianluca, L.P. (2006) Photocatalytic oxidation of herbicides in single-component and multicomponent systems: Reaction kinetics analysis. *Appl. Catal. B: Environ.*, 65 (1–2): 1.
5. Shon, H.K. et al. (2005) Chemical coupling of photocatalysis with flocculation and adsorption in the removal of organic matter. *Water Res.*, 39: 2549.
6. Thiruvenkatachari, R., Kwon, T.O., and Moon, I.S. (2005) Application of slurry type photocatalytic oxidation-submerged hollow fiber microfiltration hybrid system for the degradation of bisphenol A (BPA). *Sep. Sci. Technol.*, 40 (14): 2871.
7. Mehrab, M. and Sarah, H.V. (2005) Photocatalytic treatment of linear alkylbenzene sulfonate (LAS) in water. *J. Environ. Sci. Heal. A: Toxic/Hazard. Sub. Environ. Eng.*, 40 (5): 1003.
8. Sha, J. and Fumihide, S. (2004) Photocatalytic activities enhanced for decompositions of organic compounds over metal-photodepositing titanium dioxide. *Chem. Eng. J.*, 97 (2–3): 203.
9. Al-Rasheed, R. and Cardin, D.J. (2003) Photocatalytic degradation of humic acid in saline waters part2. Effect of various photocatalytic materials. *Appl. Catal. A-Gen.*, 246: 39.
10. Sagawe, G. et al. (2003) Photocatalytic reactors for treating water pollution with solar illumination. I: a simplified analysis for batch reactors. *Chem. Eng. Sci.*, 58: 2587.
11. Shon, H.K. et al. (2005) Comparison of nanofiltration with flocculation – microfiltration — photocatalysis hybrid system in dissolved organic matter removal. *Filtration J.*, 5 (3): 215–221.
12. Jose Pedro, S.V., Pedro, M.P., and Ariovaldo, O.F. (2006) Studies on the adsorption and kinetics of photodegradation of a model compound for heterogeneous photocatalysis onto TiO₂. *Chemosphere.*, 64 (7): 1128.
13. Bizani, E.K.F., Poullos, I., and Tsiroidis, V. (2006) Photocatalytic decolorization and degradation of dye solutions and wastewaters in the presence of titanium dioxide. *J. Hazard. Mater.*, 136 (1): 85.
14. Bekkouche, S. et al. (2004) Study of adsorption of phenol on titanium oxide (TiO₂). *Desalination*, 166: 355.
15. Paritam, K.D. et al. (2004) Adsorption of arsenate and arsenite on titanium dioxide suspensions. *J. Colloid. Interf. Sci.*, 278: 270.
16. Matsui, Y., Yuasa, A., and Li, F. (1999) Overall adsorption isotherm of natural organic matter. *J. Env. Eng.*, 1099.
17. Fusheng, Li et al. (2003) Storm impacts upon the composition of organic matrices in Nagara River—A study based on molecular weight and activated carbon adsorbability. *Water Res.*, 37: 4027.
18. Yuasa, A., Li, F., Matsui, Y., and Ebie, K. (1996) Adsorption equilibria of multi-component organic mixtures of unknown composition. *Proc. of Environ. Eng. Res.*, 33: 123.
19. Yuasa, A. et al. (1996) Evaluation of the overall adsorption isotherm of background organics on activated carbon. *Proc. of 10th IWSA-ASPAC Regional Conf. and Exhib.*, 2: 542.

20. Pelekani, C. and Snoeyink, V.L. (2003) Competitive adsorption in natural water: role of activated carbon pore size. *Water Res.*, 33: 1209.
21. Akio, I. et al. (2002) Characterization of dissolved organic matter in effluents from wastewater treatment plants. *Water Res.*, 36: 859.
22. Feggig, J. and Sontheimer, H. (1987) Kinetics of adsorption on activated carbon: III. Natural organic matter. *J. Environ. Eng.*, 113: 795.
23. Digiano, F.A. et al. (1978) A simplified competitive equilibrium adsorption model. *Chem. Eng. Sci.*, 33: 1667.
24. Smith, E.H. (1994) Bench-scale tests and modelling of adsorption of natural organic matter by activated carbon. *Water Res.*, 28: 1693.
25. Okazaki, M. et al. (1981) Approximate description of multisolute adsorption equilibrium in organic aqueous solution. *J. Chem. Eng. Jpn.*, 26: 14.
26. Jayaraj, K. and Tien, C. (1985) Characterization of adsorption affinity of unknown substances in aqueous solutions. *Ind. Eng. Chem. Process Design Devel.*, 24: 1230.
27. Calligaris, M.B. and Tien, C. (1982) Species grouping in multicomponent adsorption calculations. *Can. J. Chem. Eng.*, 60: 772.
28. Tandanier, C.J., Berry, D.F., and Knocke, W.R. (2000) Dissolved organic matter apparent molecular distribution and number-average apparent molecular weight by batch ultrafiltration. *Environ. Sci. Technol.*, 34 (11): 2348.
29. Kim, S.H. et al. (2002) Characterization procedure for adsorption of DOC (Dissolved Organic Carbon) from Synthetic Wastewater. *Korean J. Chem. Eng.*, 19 (5): 888.
30. Kim, S.H. et al. (2002) Application of characterization procedure in water and wastewater treatment by adsorption. *Korean J. Chem. Eng.*, 19 (5): 895.
31. Seo, G.T., Ohgaki, S., and Suzuki, Y. (1997) Sorption characteristics of biological powdered activated carbon in BPAC-MF (biological activated carbon-microfiltration) system for refractory organic removal. *Water Sci. Technol.*, 35 (7): 163.
32. Her, N.G. (2002) Identification and characterization of foulants and scalants on NF membrane, University of Colorado: Ph. D. Dissertation.
33. Kage, H. and Tien, C. (1987) Further development of the adsorption affinity characterization procedure for aqueous solutions with unknown compositions. *Ind. Eng. Chem. Res.*, 26: 284.
34. Gordon, M. (1996) *Use of Adsorbents for the Removal of Pollutants from Wastewaters*; CRC Press: Boca Raton, FL.
35. Froment, G.F. and Bischoff, K.B. (1990) *Chemical Reactor Analysis and Design*; John Wiley & Sons: New Jersey.
36. Minceva, M. and Rodrigues, A.E. (2003) Influence of the transfer line dead volume on the performance of an industrial scale simulated moving bed for p-xylene separation. *Sep. Sci. Technol.*, 38 (7): 1463.
37. Lee, S.H., Vigneswaran, S., and Moon, H. (1997) Adsorption of phosphorus in saturated slag media columns. *Sep. Purif. Technol.*, 12: 109.
38. Tien, C. (1994) *Adsorption Calculations and Modelling*; Butterworth-Heinemann: Boston, MA.
39. Simone, C., Carlos, A.G., and Alirio, E.R. (2005) Separation of methane and nitrogen by adsorption on carbon molecular sieve. *Sep. Sci. Technol.*, 40: 2721.
40. Shon, H.K. et al. (2005) Is semi-flocculation effective as pretreatment to ultrafiltration in wastewater treatment? *Water Res.*, 39 (1): 147.