Adsorption Characterization for Multi-Component Organic Matters by Titanium Oxide (TiO$_2$) in Wastewater

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ABSTRACT

In this study, an experimental and analytical study on adsorption and adsorption kinetics of organic matters in titanium oxide (TiO$_2$, 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 TiO$_2$ 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 TiO$_2$. 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

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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 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 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 adsorption phase of organic matter on TiO_2 is a determining stage in the process of photodegradation [12-14], a few researches are studied in the adsorption of TiO_2 [14-15]. It is thus important to

evaluate the performance of TiO_2 in terms of the better understanding of the adsorption phenomenon.

Adsorption technology has been used for removal of organic contaminants from wastwater. 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 adsorption equilibrium of organic matters helps design and simulation of the adsorption system in removing those contaminants from wastewater [17-20]. The most common approach for 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.

Characteristic distribution of Langmuir coefficient was applied for a useful concept to describe 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 multi-component adsorption equilibrium. [26, 27]

To understand the phenomenon of adsorption in detail, it is necessary to know the range of 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 adsorption equilibrium, batch kinetics adsorption systems because finite number of pseudospecies can be systematically assigned by a binomial concentration distribution function.

In this study, the effect of fundamental adsorption on TiO_2 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 TiO_2 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 sulfornate, sodium lauryle 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.

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Titanium oxide

The photocatalyst, TiO₂, used in this study was Degussa P25, ca. surface area 50 m^2/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 flask. In each flask, a known concentration of wastewater was mixed with the known amount of 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 ℃. The adsorbed amount (q) and removal efficiency (RE) of SOMs were calculated by following equation.

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

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

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 (%).

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

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

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

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

$$P = M_w / M_n \tag{5}$$

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 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 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].

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

The initial concentrations are given by

$$C_{io} = x_{io}C_{To}, \ i = 0, \ 1, \ 2, \ \cdots, \ N \qquad (7)$$

Where C_{To} is the total TOC concentration of the solution and x_{io} is the initial TOC fraction of the i-th species. The species, i=0, means a 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:

$$C_i = C_i^o z_i \qquad (8)$$

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

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

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

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:

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

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

$$\pi = \pi_1 = \pi_2 = \cdots = \pi_N \qquad (13)$$

To simply the subsequent computation work required in both the characterization and the adsorption calculations, one may assume that all the pseudospecies adsorption isotherm 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.

$$q_i^o = k_i C_i^{o^{1/n}} \qquad (14)$$

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

$$\prod = \pi_i A / RT = n k_i C_i^{o^{1/n}} \ \text{ or } \ n q_i^o \qquad (15)$$

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

$$C_i^o = \left(\Pi / nk_i\right)^n \tag{16}$$

$$q_i^o = \Pi / n \tag{17}$$

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

$$q_T = q_1 = q_2 = \cdots = q_N = \Pi / n \tag{18}$$

Eq. (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:

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

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

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

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 jth species in the original solution is represented as follows:

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

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

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

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).

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

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 overall mass transfer coefficient unchanged during experiments is the following Eq. (24).

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

where R = radius of adsorbent (m), 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 TiO$_2$ 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 TiO_2 adsorption isotherm was investigated in the range of 0.01 to 2 g/L of TiO_2 at initial concentration of 11.04 mg/L in synthetic wastewater. Figure 1 shows removal of different organic sizes. At lower concentration of TiO_2, 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 TiO_2. Table 3 shows MW values after TiO_2 adsorption in terms of number-averaged MW and weight-averaged MW. The initial weight-averaged MW was 33200 dalton. The weight-averaged MW was similar to that at lower concentration of TiO_2. On contrary, the weight-averaged MW from more than 0.5 g/L of TiO_2 was significantly decreased up to 1200 dalton. This can be concluded that TiO_2 adsorption preferentially removed the large MW.

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 unfavorable tendency at low 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 TiO_2. 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 TiO_2 surface. For these reasons, a characterization procedure depending on different concentrations to interpret the adsorption equilibrium data and 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 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. 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 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 Figure 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 Figure 3 was that a nonadsorable species existed with ca. 0.25 fraction of TOC in case of Freundlich constant $k^{1/2} = 0$, major components number for adsorption was around 5.

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This nonadsorable portion of TOC fratcion was related to extremely unfavorable tendency at 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 LDFA kinetic equation, assuming that 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 experimental data.

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 increased, 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 increased pseudospecies number.

Figure 6 shows predicted curves in various TiO_2 loading by LDFA kinetics equation. The necessary time of equilibrium increased with increased TiO_2 loading. The amount of SOMs adsorbed increased with increased TiO_2 loading. This may be due to the increase in adsorbent surface area of the sorbent.

CONCLUSIONS

In this study, the removal of SOMs by TiO_2 adsorption was experimentally and analytically investigated. A detailed characterization of SOMs was made in terms of the TOC removal, MW distribution and adsorption characterization model. The results obtained led to the following conclusions.

● The weight-averaged MW (33200 dalton) of initial synthetic wastewater was similar to that at lower concentration of TiO_2. However, the weight-averaged MW from more than 0.5 g/L of TiO_2 was significantly decreased up to 1200 dalton. As such, TiO_2 adsorption preferentially removed the majority of large MW.

● The characterization results obtained from different sets of equilibrium data were similar regardless of initial TOC concentration. The characterization procedure was suitable for the synthetic wastewater to provide information on the concentration distribution of TOC fraction.

● A non-adsorable species existed with ca. 0.25 fraction of TOC and major components number for adsorption was around 5 from characterization procedure. This non-adsorable portion of TOC fraction is likely to relate 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 characterization procedure.

● As the pseudospecies number increased, 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 in SOMs as the pseudospecies number increased.

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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 lauryle sulphate	0.94	0.1438	0.042
Arabic gum powder	4.7	0.7233	0.213
Arabic acid	5.0	0.5300	0.156
$(NH_4)_2SO_4$	7.1	0	0
K_2HPO_4	7.0	0	0
NH_4HCO_3	19.8	0	0
$MgSO_4 \cdot 7H_2O$	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

Table 3. MW values of organic matter after adsorption isotherm by TiO_2

	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

Table 4. Characterization results of synthetic wastewater on TiO_2.

Characterization results with 5.25 mg/L TOC

k_s	N	n	s	F(%)
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

k_s	N	n	s	F(%)
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

k_s	N	n	s	F(%)
1.0	8	0.62	0.14	6.69
	10	0.61	0.13	4.90
	12	0.60	0.11	4.50

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

(a)

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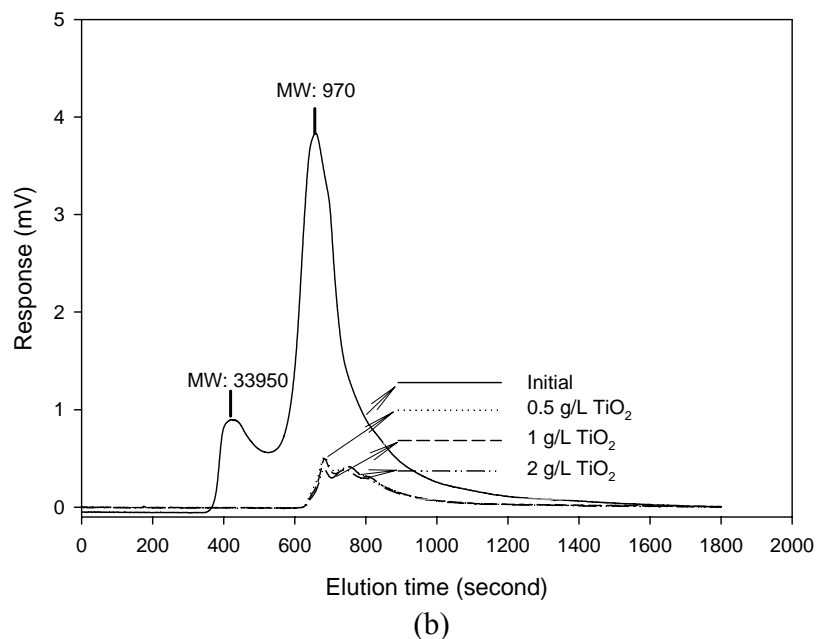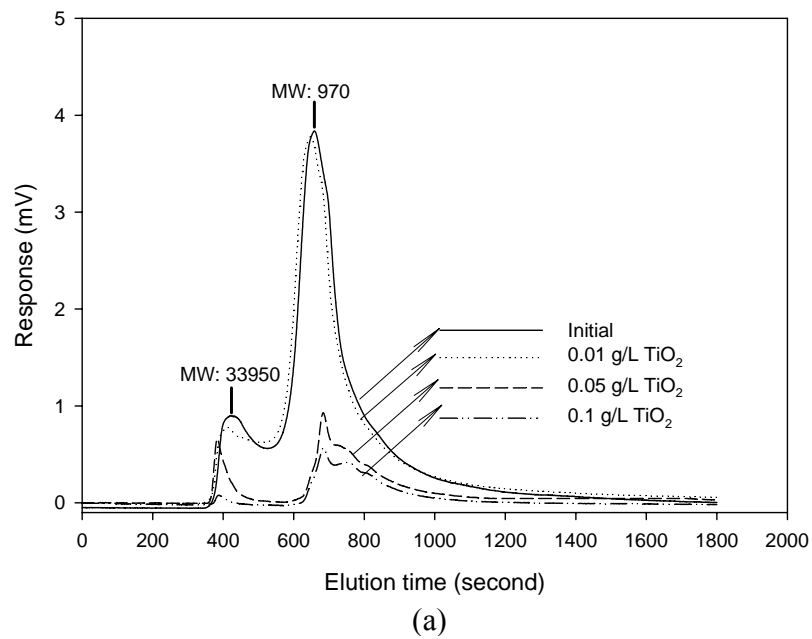
Figure 1. MW distribution after TiO_2 adsorption isotherm by P25 TiO_2 in batch reactor in range of (a) 0.01 – 0.1 g/L and (b) 0.5 - 2 g/L at initial concentration of 11.04 mg/L. (temperature = 25 °C; mixing speed = 100 rpm)
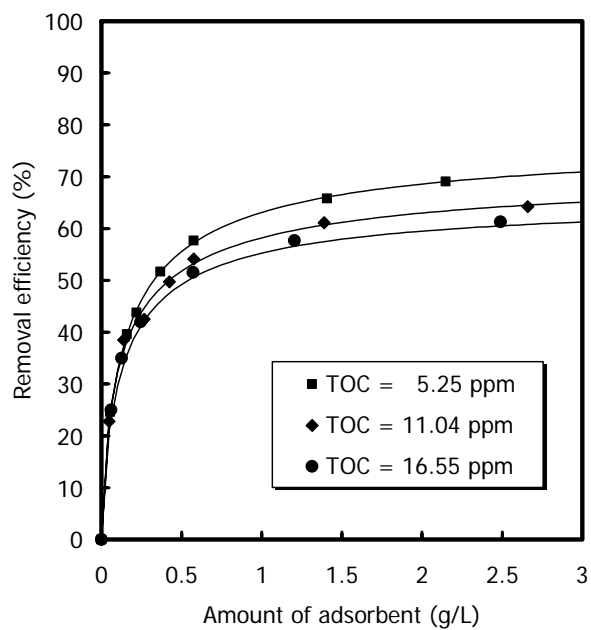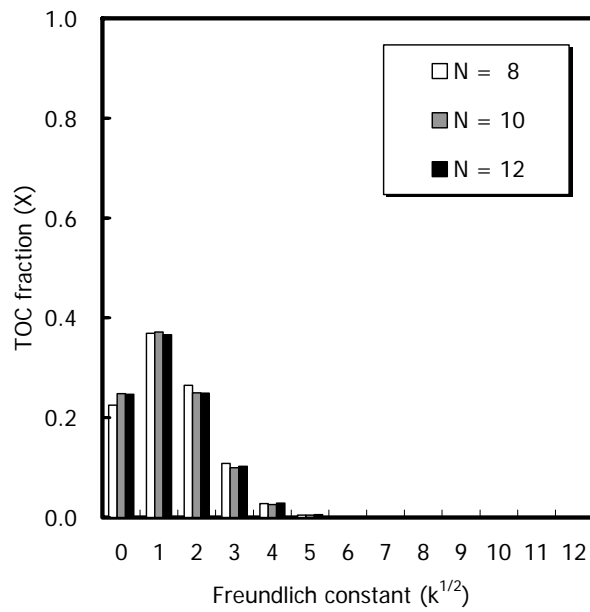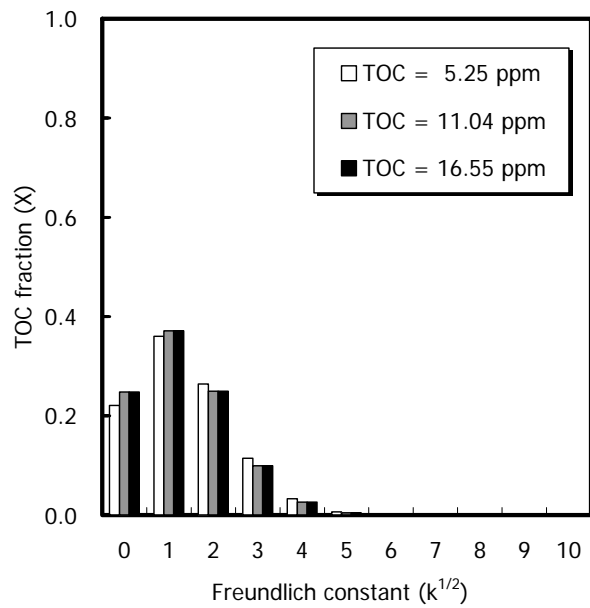
(a)
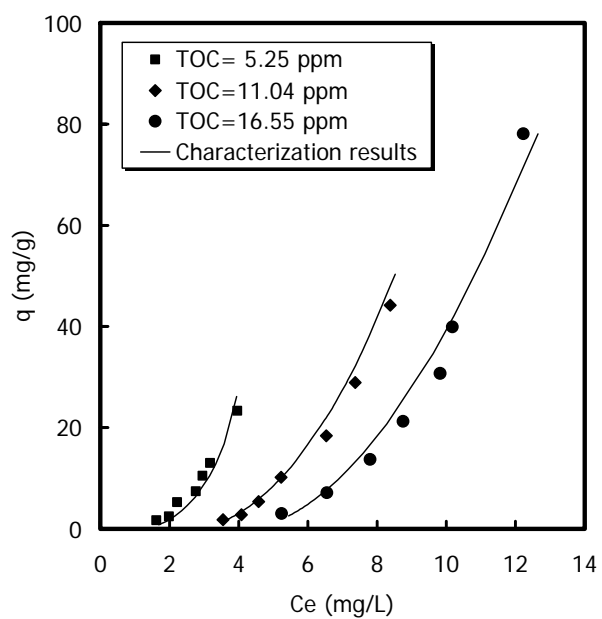
(b)

Figure 2. Removal efficiency depending on (a) the amount of adsorbent and (b) overall adsorption isotherms of SOMs on TiO_2. (initial concentration of SOMs =5.25, 11.04, 16.55 mg/L)
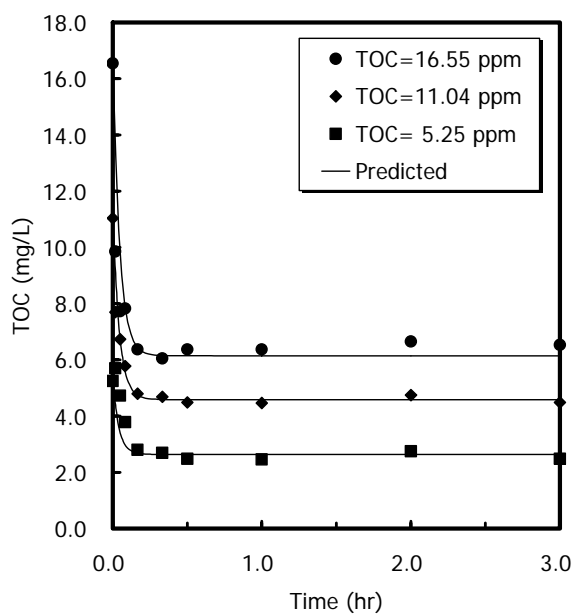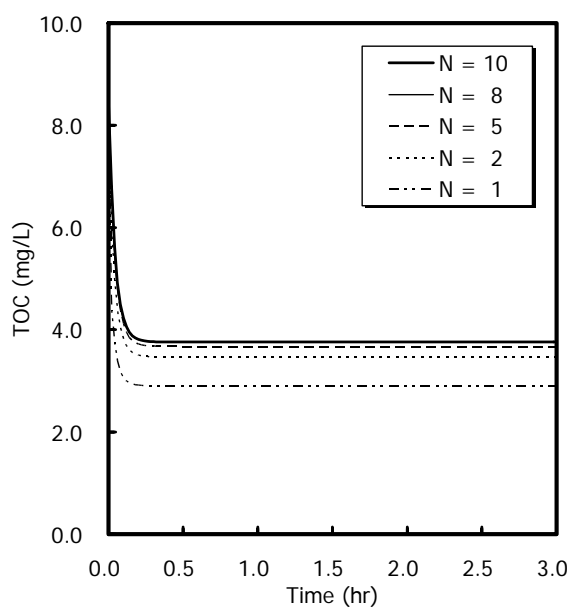
(a)

(b)

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)
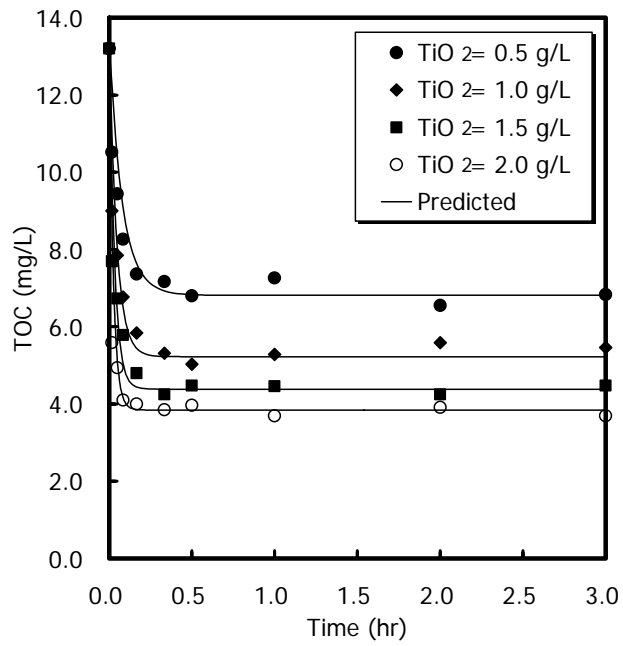
Figure 4. Effect of initial SOM concentration on kinetics of TiO$_2$ adsorption by TiO$_2$ at 25.0 °C (mixing speed = 100 rpm, adsorbent amount = 1 g/L, concentrations of SOMs = 5.25, 11.04 and 16.55 mg/L)

Figure 5. Effect of pseudospecies number on kinetics of TiO$_2$ adsorption.

(concentration of SOMs =11.04 mg/L, adsorbent amount = 1 g/L, mixing speed = 100 rpm)

Figure 6. Effect of TiO$_2$ loading on kinetics of TiO$_2$ adsorption at 25.0 $^{\circ}$C.
(concentration of SOMs =13.20 mg/L, mixing speed = 100 rpm)