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**ADSORPTIVE SEPARATION OF HEAVY METALS
FROM AQUEOUS ENVIRONMENT
BY INORGANIC AND ORGANIC ADSORBENTS**

BY

HIDESHI SEKI

A DISSERTATION
SUBMITTED IN PARTIAL FULFILLMENT OF
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ABSTRACT

PART I

ADSORPTION OF METAL IONS ON A HYDROUS METAL OXIDE

For the recovery of valuable metals or the removal of toxic metals from aqueous environments, a fundamental study of the adsorption of metal ions onto a hydrous metal oxide adsorbent was carried out. In Chapter 2, equilibrium adsorption of divalent metal ions onto hydrous titanium(IV) oxide (HTO) is dealt with. Based on three equilibrium reactions, that is, hydrolysis of metal ions to hydroxides, deprotonation of hydroxyl groups (adsorption sites) on HTO's surface and complexation of the hydroxides with the deprotonated sites, a general adsorption isotherm is derived. Two parameters of the isotherm enable us to give useful information about the adsorption capacity and adsorption strength of adsorbent for target metal ions. The theoretical adsorption isotherm was confirmed by several experiments carried out under acidic or basic conditions using uranium, lead, cadmium and zinc ions as adsorbates. The adsorption model completely explained the experimental results. It was found that the used HTO had the available sites of 7.15×10^{-4} (mole $\cdot$ g $^{-1}$) for all the divalent ions dealt with in this work, and the adsorption strength between the metal ions and the surface sites was in the order of $\text{Zn}^{2+} < \text{Cd}^{2+} < \text{Pb}^{2+} < \text{UO}_2^{2+}$. The model could be applied to uranium-carbonate-HTO system and it was revealed that the active species in uranium adsorption on

HTO was not uranyl carbonates but free uranyl ion, even in carbonate solutions.

In Chapter 3, HTO with various moisture contents were prepared. Equilibrium and kinetic experiments of uranium adsorption onto them were conducted. The equilibrium data were analyzed with the above adsorption model. The results showed that the amount of available sites for uranium was remarkably decreased with the decrease of moisture content, although the adsorption constants were not changed. On the other hand, the kinetic data were examined by another simple mathematical model for adsorption kinetics, and it was revealed that the pore size in HTO was greatly influenced by the moisture content. The used HTO had two kinds of available sites for uranium, that is, macro-pore and meso-pore sites. The macro-pore sites adsorbed uranium very rapidly, whereas the adsorption process onto the meso-pore sites proceeded in a considerably slow rate.

PART II

APPLICATIONS OF HUMIC ACID TO AQUEOUS-PHASE

SEPARATION OF METAL IONS

Application of humic acid to the aqueous-phase separation of metal ions was dealt with. For this purpose, a new adsorbent of immobilized humic acid, HA-gel, was developed in Chapter 2. Humic acid has an excellent complexing ability with heavy metals, while it easily dissolves in water. In HA-gel, humic acid is immobilized by the gel network of calcium alginate or by adsorption on

activated carbon powder(ACP). The conditions for preparing HA-gel were experimentally examined. The results showed that the discharge of humic acid from the gel was almost completely prevented by the addition of the humic acid's weight in ACP. The spherical HA-gel was formed in 0.1M CaCl_2 solution. This immobilization technique enabled the preparation of an adsorbent containing about 50 wt% humic acid on dry-weight basis.

A fundamental study of the recovery of lead from acidic solution by HA-gel was carried out in Chapter 3. To understand the adsorption mechanism of lead on the adsorbent(HA-gel), a simple model for complexation between divalent metal ions and acidic groups on organic polymers was proposed. The model was confirmed by two kinds of experiments in which humic and alginic acids in liquid state were used as adsorbents. The results show that the complexation of humic acid was not influenced by immobilization. However, the alginate gel used as an immobilizing agent affected the rate of adsorption to a remarkable extent.

In Chapter 4, a membranous HA-gel (HA-M) was developed in order to increase the adsorption rate and the humic acid content on a wet-weight basis. Static adsorption data of lead-HA-M system were compared with the complexation model proposed in Chapter 3. Results indicated that the complexation constants and the complexation capacities of lead-humic acid and lead-alginic acid systems were not influenced by immobilization. On a wet-weight basis, HA-M had twice as much lead adsorption capacity as the HA-gel particle. Results of the kinetic adsorption experiments showed that the rate of lead adsorption by the HA-M was much faster than that of the HA-gel

particle. HA-M was rapidly regenerated by washing with 0.1M HNO₃.

In Chapter 5, another HA insolubilized by heating treatment (IHA) was employed for the recovery of cadmium and lead from dilute solution. A general complexation model for the complexation of divalent metal ions on organic polymers with acidic groups was proposed. The theoretical complexation isotherm was confirmed by several experiments carried out in the range of about pH3 to pH6.5 using lead and cadmium as adsorbates. Using the metal-complexation model, the adsorption characteristics of insolubilized humic acid (IHA) was compared with those of HA. The results showed that two different types of acidic groups were present on HA and the insolubilization process scarcely influenced on the metal complexation constant of acidic groups, however, the number of available metal binding sites on IHA was decreased to some extent.

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CONTENTS

PART I

ADSORPTION OF METAL IONS ON A HYDROUS METAL OXIDE

	page
1 General Introduction	13
2 Adsorption equilibrium of Divalent Metal Ions onto Hydrous Titanium(IV) Oxide	16
2.1 Introduction	16
2.2 Theoretical Derivation of Adsorption Isotherm	17
2.3 Experimental	19
2.3.1 Adsorbent	19
2.3.2 Titration of HTO Suspension	19
2.3.3 Adsorption Experiments	20
2.4 Results and Discussion	21
2.4.1 Determination of N_H and $K_H(n)$	21
2.4.2 Adsorption of Uranium, Lead, Cadmium and Zinc in Acidic Solutions	23
2.4.3 Adsorption of Uranium in Basic (Carbonate) Solutions	28

2.5 Conclusions	41
2.6 Nomenclature	41
3 Influence of Dehydration Process of Hydrous Titanium(IV) Oxide on its Uranium Adsorption Characteristics	43
3.1 Introduction	43
3.2 Experimental	44
3.2.1 Adsorbent	44
3.2.2 Conductometric Titration of HTO	44
3.2.3 Adsorption Experiment of Uranium on HTO	46
3.3 Results and Discussion	46
3.3.1 Influence of Dehydration of HTO on the Amount of Available Sites for Uranium	46
3.3.2 Adsorption Kinetics of HTO	57
3.3.3 Pore Shrinkage of HTO by Dehydration	57
3.4 Conclusions	64
3.5 Nomenclature	65
4 General Conclusions	66
5 References	67

PART II
APPLICATIONS OF HUMIC ACID TO AQUEOUS-PHASE
SEPARATION OF METAL IONS

1 General Introduction	71
2 Immobilization of Humic Acid in Calcium Alginate Gel	74
2.1 Introduction	74
2.2 Experimental	75
2.2.1 Materials	75
2.2.2 Immobilization of HA	75
2.2.3 Conductometric Titration	75
2.2.4 Effectiveness of Immobilization	76
2.3 Results and Discussion	76
2.3.1 Number of Acidic Groups	76
2.3.2 Entrapping Effect of Calcium Alginate	78
2.3.3 Entrapping Effect of Activated Carbon Powder	81
2.3.4 Effect of CaCl_2 Concentration and Gelation Time	83
2.4 Conclusions	83
3 Adsorption of Lead Ions on Humic Acid Immobilized by Calcium Alginate Particle	87
3.1 Introduction	87

3.2 A Simple Organo-Metallic Complexation Model	87
3.3 Experimental	90
3.3.1 Adsorbent	90
3.3.2 Complexation between Lead and Humic or Alginic Acid	90
3.3.3 Adsorption of Lead on HA-gel	92
3.4 Results and Discussion	92
3.4.1 Organo-metallic Complexation	92
3.4.2 Adsorption of Lead Ions on HA-gel	99
3.4.3 Estimation of the Amount of Lead Adsorbed on HA-gel	103
3.5 Conclusions	104
3.6 Nomenclature	106
 4 Adsorption of Lead Ions on Humic Acid Immobilized by Calcium Alginate Membrane	 107
4.1 Introduction	107
4.2 Experimental	108
4.2.1 Adsorbent	108
4.2.2 Adsorption of Lead on HA-M	108
4.2.3 Desorption of Lead from HA-M	108
4.3 Results and Discussion	109
4.3.1 Entrapping Effect of Calcium Alginate	109
4.3.2 Entrapping Effect of Activated Carbon Powder	109
4.3.3 Influence of Immobilization on Metal-HA Complexation	112

4.3.4 Influence of Alginate Concentration on Adsorption Rate	113
4.3.5 Desorption of Lead from HA-M	121
4.4 Conclusions	121
4.5 Nomenclature	124
 5 Adsorption of Metal Ions on insolubilized Humic Acid	 125
5.1 Introduction	125
5.2 Experimental	126
5.2.1 HA Calcium Salt	126
5.2.2 Insolubilization	126
5.2.3 Effectiveness of Insolubilization	127
5.2.4 Potentiometric Titration of HA and IHA	127
5.2.5 Complexation between HA and Metal Ions	127
5.2.6 Adsorption of Metal Ions on IHA	128
5.3 Results and Discussion	128
5.3.1 Conditions for Preparing IHA	128
5.3.2 Dissolution Characteristics of IHA	131
5.3.3 Influence of Insolubilization on Acid-Base Properties of HA	131
5.3.4 Influence of Insolubilization on Metal-HA Complexation	140
5.4 Conclusions	150
5.5 Nomenclature	151

6 General Conclusions	152
7 References	154
List of Figures	157
List of Tables	167

PART I

ADSORPTION OF METAL IONS ON A HYDROUS METAL OXIDE

1. GENERAL INTRODUCTION

Separation of metal ions from aqueous-phase have attracted much attention in relation to the recovery of valuable elements or the removal of toxic metal contaminants, and has become very important subject for various engineering fields(4,21,23,24,28,30,34,35,37). For this purpose, "adsorption" would be considered as one of the most promising technique, because of; a) low energy requirement, b) no requirement for complicated equipment, c) selectivity for specific metal ions. Ability of adsorbent has been evaluated with their "selectivity for target metal ions", "adsorption capacity" and "adsorption kinetics". Selectivity of adsorbent for target metal ions is mainly dependent on the nature of adsorbent material and it can be quantitatively evaluated with adsorption constant. In order to make the best choice of adsorbent for a target metal ion, the adsorption constant between the adsorbent and the target metal ion must be determined. The cost performance of adsorption process is largely dependent on the capacity and kinetics of the adsorption system. Therefore, the study of adsorption mechanism is very important for development of excellent adsorbent and determination of the optimal operating condition.

Many studies about adsorption mechanism of heavy metal ions onto hydrous metal oxides have been carried out in relation to various engineering fields, e.g. the recovery of uranium from sea water (9,12,13,16,22,29,36), the operation of nuclear reactors(33), and the other fields(14,15,17,18,19,27). Keen(22) and Yamashita et al.(36) reported that uranium was adsorbed by hydrous titanium(IV) oxide as UO_2^{2+} from sea water. On the contrary, Ogata et

al.(29) proposed that uranium was adsorbed probably as $\text{UO}_2(\text{CO}_3)_3^{4-}$. Ho and Miller(12) studied the adsorption of uranium on hematite in carbonate solution and suggested that more than one uranium species may be involved in the adsorption. They also suggested that the adsorbed species are negatively charged carbonate complexes such as $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$, from the fact that the uptake of uranium decreased abruptly with increasing solution pH and the decrease coincided with a decrease in the proportion of $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ present. Gupta and Venkataramani(9) investigated the uranium adsorption on various metal oxides in the absence of carbonate ions and proposed a model, named as surface hydrolysis model, which interpreted the uranium adsorption process as linking of uranyl ions with two adjacent free surface hydroxyl groups and formation of dimer-like structures on the surface.

For the design and optimal operation of industrial adsorption equipments, the establishment of a simple and generally applicable adsorption isotherm should be most important. In the following chapter, a general adsorption model for the adsorption of divalent metal ions onto hydrous metal oxide will be derived, based on three equilibrium reactions, that is, hydrolysis of metal ions, deprotonation of surface hydroxyl groups (adsorption sites) on the oxide and complexation of the hydroxides with the deprotonated sites. The theoretical adsorption isotherm will be confirmed by experiments carried out under acidic conditions using uranium, lead, cadmium and zinc ions as adsorbates. The two factors, which determine the adsorption ability such as the adsorption selectivity and the adsorption capacity, will be determined for the above adsorption system. Furthermore, the adsorption mechanism of uranium in

carbonate solutions will also be discussed based on the adsorption model.

On the other hand, inorganic adsorbents such as hydrous metal oxides are normally prepared through several steps including sol formation by precipitation (or crystallization), aging of the sol, solid-liquid separation and dehydration (or calcination) of the solid. The dehydration process should give a distinctive influence on pore structure that is closely related to the adsorbents' characteristics (adsorption capacity and kinetics). However, most previous studies have mainly dealt with the pore structure of well-dried sorbents (6,7,8,25) or its effect on gas-solid reaction (1,2,3,5,10,11,31). To develop more excellent adsorbents working in liquid media, it is much important to know quantitatively the changes in the amount of available sites for adsorbate metal ions and the kinetics by dehydration process.

In Chapter 2, the influence of the dehydration process on static and kinetic characteristics of uranium adsorption onto HTO, which have been often used as an adsorbent for uranium recovery from sea water, was investigated. HTO with various moisture contents were prepared, and equilibrium and kinetic experiments of uranium adsorption onto them were conducted. Based on two models, i.e., an equilibrium adsorption model mentioned above and a simple mathematical model for adsorption kinetics, the changes in the amount of micro-pore sites (inaccessible for uranyl ions), meso-pore sites (accessible for uranyl ions but has large diffusion resistance) and macro-pore sites (easily accessible for uranyl ions) during the dehydration process will be quantitatively discussed.

2. ADSORPTION EQUILIBRIUM OF DIVALENT METAL IONS ONTO HYDROUS TITANIUM(IV) OXIDE

2.1 Introduction

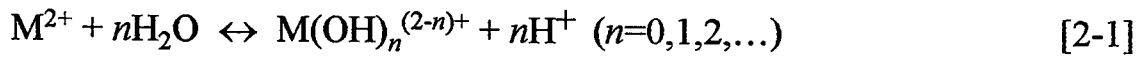
Hydrous metal oxide adsorbents have been used for the aqueous-phase separations of metal ions(23,24,28,30,34,35). In this field, the recovery of uranium from sea water has been a topic of intense research in recent years. For the development of excellent adsorbent and the determination of the optimal operating condition, many studies about adsorption mechanism of uranium onto hydrous metal oxides have been carried out and various adsorption mechanisms were proposed (9,12,13,16,22,29,36).

In this chapter, the adsorption of metal ions onto hydrous titanium(IV) oxide (HTO), which have been often used as an adsorbent for uranium recovery from sea water, was investigated. A general adsorption model for the adsorption of divalent metal ions onto hydrous metal oxide will be derived, based on three equilibrium reactions, that is, hydrolysis of metal ions, deprotonation of surface hydroxyl groups (adsorption sites) on the oxide and complexation of the hydroxides with the deprotonated sites. The theoretical adsorption isotherm will be confirmed by experiments carried out under acidic or basic conditions using uranium, lead, cadmium and zinc ions as adsorbates. The two factors, which determine the adsorption ability such as the adsorption selectivity and the adsorption capacity, will be determined for the above

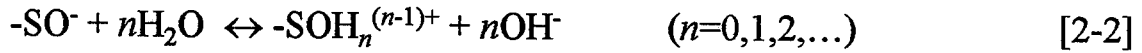
adsorption system. Furthermore, the adsorption mechanism of uranium in carbonate solutions will also be discussed based on the adsorption model.

2.2 Theoretical Derivation of Adsorption Isotherm

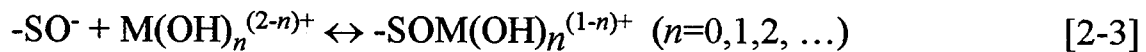
A divalent metal ion (M^{2+}) in water phase, as is well-known, is easily hydrolyzed as



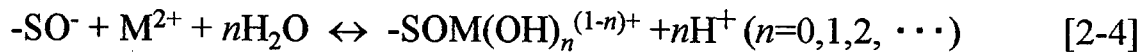
On the other hand, a surface adsorption site ($-SO^-$) also reacts with water molecules and is protonated as



That is, before adsorption occurs, the system contains various surface species ($-SO^-$, $-SOH$, $-SOH_2^+$, $-SOH_3^{2+}$, ...) and water phase species (H^+ , OH^- , M^{2+} , $M(OH)^+$, $M(OH)_2$, $M(OH)_3^-$, ...). Therefore, the combination of reactions between the two kinds of species may yield numerous surface complexes. For obtaining a simple and practical adsorption isotherm, however, minor complexes must be eliminated. In the present work the author assumes that the complexes of $-SOM(OH)_n^{(1-n)+}$ type are solely present on the surface. Then, the possible reactions in the system can be written as



Summarizing the reactions [2-1] and [2-3], the following equation is obtained



The equilibrium constants for Eqs.[2-2] and [2-4] are defined as

$$K_H(n) = \frac{\{-\text{SOH}_n^{(n-1)+}\}}{\{-\text{SO}^-\}[\text{H}^+]^n} \quad [2-5]$$

and

$$K_M(n) = \frac{\{-\text{SOM}(\text{OH})_n^{(1-n)+}\}[\text{H}^+]^n}{\{-\text{SO}^-\}[\text{M}^{2+}]} \quad [2-6]$$

respectively, where [] and { } represent the concentrations of water-phase species ($\text{mol}\cdot\text{dm}^{-3}$) and surface species ($\text{mol}\cdot\text{m}^{-2}$), respectively.

The amount of adsorbed metal ions, X_M ($\text{mol}\cdot\text{g}^{-1}$), can be expressed as

$$X_M = N_M \cdot \theta_M \quad [2-7]$$

where N_M ($\text{mol}\cdot\text{g}^{-1}$) and θ_M (-) represent the amount of adsorption sites available for the target metal ions and the fraction of sites complexated with the metal ions, respectively. As θ_M is written as

$$\theta_M = \frac{\sum \{-\text{SOM}(\text{OH})_n^{(1-n)+}\}}{\sum \{-\text{SOH}_n^{(n-1)+}\} + \sum \{-\text{SOM}(\text{OH})_n^{(1-n)+}\}} \quad [2-8]$$

An adsorption isotherm is given by

$$X_M = N_M \frac{[M^{2+}] \sum K_M(n) / [H^+]^n}{\sum K_H(n) [H^+]^n + [M^{2+}] \sum K_M(n) / [H^+]^n} \quad [2-9]$$

where Σ denotes the summation for $n=0$ to ∞ . In the subsequent part the applicability of this isotherm will be examined by adsorption experiments of uranium, lead, cadmium and zinc from aqueous solutions to hydrous titanium(IV) oxide surface as examples.

2.3 Experimental

2.3.1 Adsorbent

Hydrous titanium(IV) oxide (HTO) was prepared in the following manner. Into a titanium(IV) sulfate solution (ca. 1 mol·dm⁻³) under stirring at 25°C, an ammonia solution (ca 1 mol·dm⁻³) was added until the pH of the solution reached 8. After it had aged for 24 h, the precipitate was washed repeatedly with distilled water until the conductivity of the suspension was lowered below 50 (μS·cm⁻¹). Then, the precipitate was filtered and used as an adsorbent without further drying. The moisture content of the adsorbent was in the range of about 350 to 450% on the dry-weight basis. In this study, the amount of adsorbent is expressed by the terms of the weight of its ignition residue.

2.3.2 Titration of HTO suspension

For determining the total amount of surface sites on HTO and the

equilibrium constants defined by Eq.[2-5], acid-base titrations were carried out. 0.22g of HTO powder was suspended in 0.3 dm³ of a solution containing NaOH (3×10^{-3} mol) and NaNO₃ (0.1M) at 25 °C, and the suspension was titrated with a 0.1M HNO₃ solution; 0.5 ~ 2 cm³ aliquots of the acid were added to the suspension and the system was allowed to stand until there was no change in the pH. To eliminate CO₂, N₂ gas was continuously bubbled through the system.

2.3.4 Adsorption Experiments

Uranium adsorption experiments were conducted in either acidic or basic (carbonate) solution. Prior to the experiments, 1, 1.5 and 2×10^{-3} (mol·dm⁻³) uranium solutions of containing nitric acid or sodium hydrogencarbonate were prepared. A 0.27-dm³ suspension containing the adsorbent (ca 0.04 ~ 0.05 g) was stirred and thermally equilibrated in a water bath at 25°C. Then, 0.030 dm³ of the uranium solution was added to the suspension. After the adsorption equilibrium was reached, the pH of the suspension was measured with a pH meter (ORION RESEARCH 501). The suspension was filtered through a membrane filter (pore size = 0.2µm) and the uranium concentration of the filtrate was measured with a UVIDEC-220B spectrophotometer (Japan Spectroscopic Co., Ltd.), using Arsenazo III as a chromogenic reagent. The amount of uranium adsorbed was determined from the difference between the uranium initially added to the system and that remaining in solution at the equilibrium. The experiment was repeated, varying the concentration of nitric acid or sodium hydrogencarbonate.

Procedures of lead, cadmium and zinc adsorptions were similar to uranium, except that all the runs were performed only in acidic solutions. The experiments in weakly acidic media were conducted under nitrogen atmosphere to eliminate CO₂. Lead and cadmium were analyzed with an atomic absorption spectrophotometer (Hitachi A-1800), and the analysis for zinc was accomplished by a spectrophotometric method using xylenol orange (XO) as a chromogenic reagent.

2.4 Results and Discussion

2.4.1 Determination of N_H and $K_H(n)$

The results of acid-base titration are shown in Fig.2-1. The difference, Δx , between the amounts of H⁺ that must be added to achieve the same pH in the absence and in the presence of HTO is expressed by the following proton-balance equation (16):

$$\Delta x = \left(\frac{m \cdot N_H}{\gamma} \right) [\Sigma (n-1) \{-SOH_n^{(n-1)+}\} - \{-SO^-\}] \quad [2-10]$$

where $m(g)$, $N_H(\text{mol} \cdot g^{-1})$ and $\gamma(\text{mol} \cdot m^{-2})$ represent the weight of titrated HTO, the amount of surface hydroxyl groups available for proton and the surface density of hydroxyl groups, respectively. As γ is equal to $\Sigma \{-SOH_n^{(n-1)+}\}$, Eqs.[2-5] and [2-10] yield

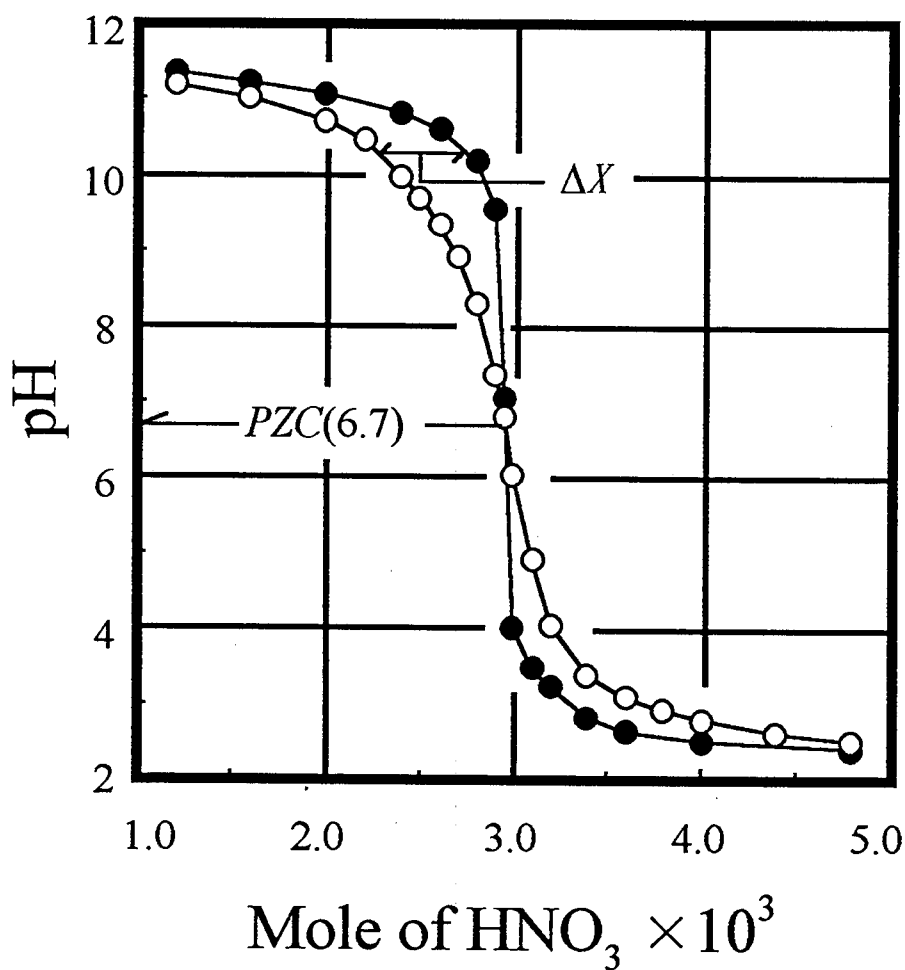


Fig.2-1. Titration curves for 300 cm³ of a solution containing 1.0×10^{-2} mol · dm⁻³ NaOH and 0.1 mol · dm⁻³ NaNO₃ in the absence (○) and in the presence (●) of 0.22g of hydrous titanium(IV) oxide at 25°C.

$$\Delta x = m \cdot N_H \frac{\sum (n-1) K_H(n) [H^+]^n - 1}{\sum K_H(n) [H^+]^n} \quad [2-11]$$

Provided that the solution is not so strongly acidic, it is reasonable to consider that the surface complexes of $n > 2$ (i.e., $-\text{SOH}_3^{2+}$, $-\text{SOH}_4^{3+}$, ...) are negligible. Then Eq.[2-11] is replaced by

$$\Delta x = m \cdot N_H \frac{K_H(2) [H^+]^2 - 1}{K_H(2) [H^+]^2 + K_H(1) [H^+] + 1} \quad [2-12]$$

As the intersecting point of two titration curves means the point of zero charge (pH=6.7), $K_H(2)$ was determined from Eq.[2-12] as 2.51×10^{13} ($= 10^{2 \times 6.7}$) ($\text{mol}^{-2} \cdot \text{dm}^6$). Further rearrangement of Eq.[2-12] leads to

$$K_H(2) [H^+] + 1/[H^+] = N_H \left(\frac{m}{\Delta x} \right) \left\{ K_H(2) [H^+] - \frac{1}{[H^+]} \right\} - K_H(1) \quad [2-13]$$

The replotted result of alkali data in Fig.2-1 by Eq.[2-13] is shown in Fig.2-2. From the slope and the intercept of straight line, N_H and $K_H(1)$ of the present HTO were determined as $2.39 \times 10^{-3} (\text{mol} \cdot \text{g}^{-1})$ and $1.70 \times 10^9 (\text{mol}^{-1} \cdot \text{dm}^3)$, respectively.

2.4.2 Adsorption of Uranium, Lead, Cadmium and Zinc in Acidic Solutions

Typical time-courses of uranium, lead, cadmium and zinc adsorptions are

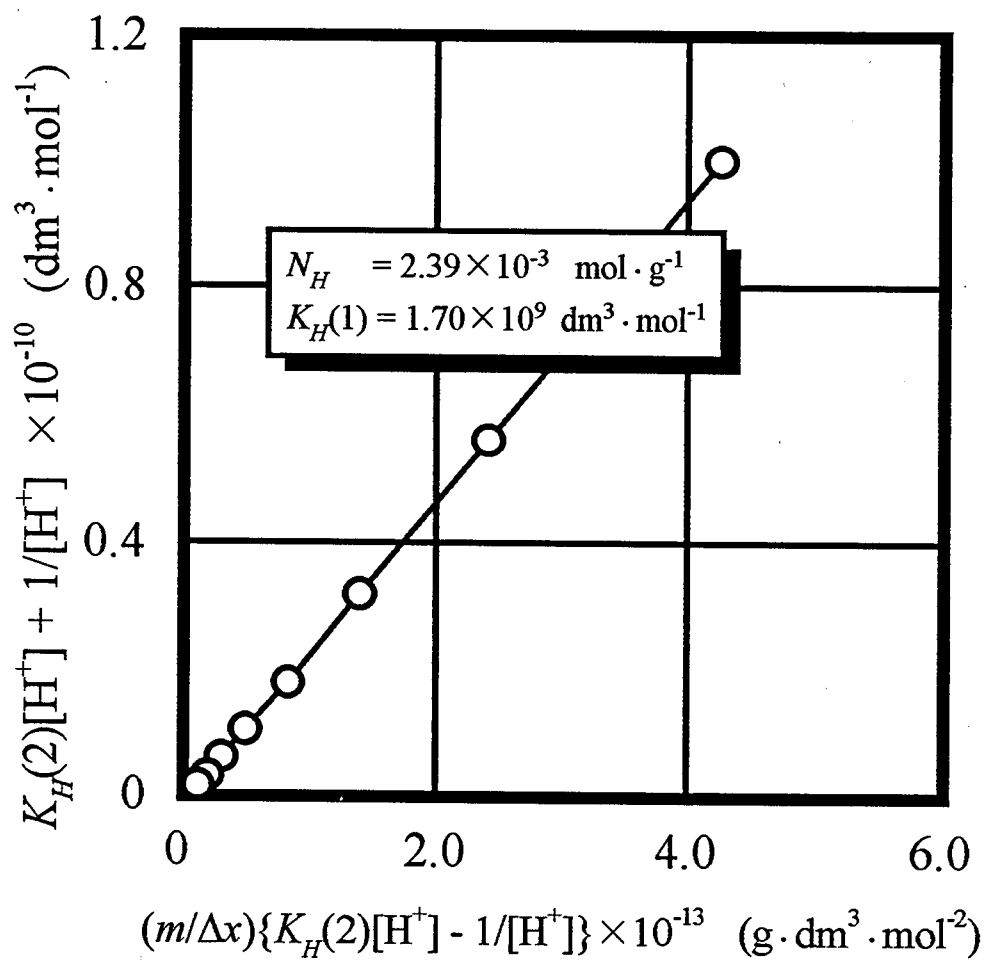


Fig.2-2. Replot of Fig.2-1 data by Eq.[2-13].

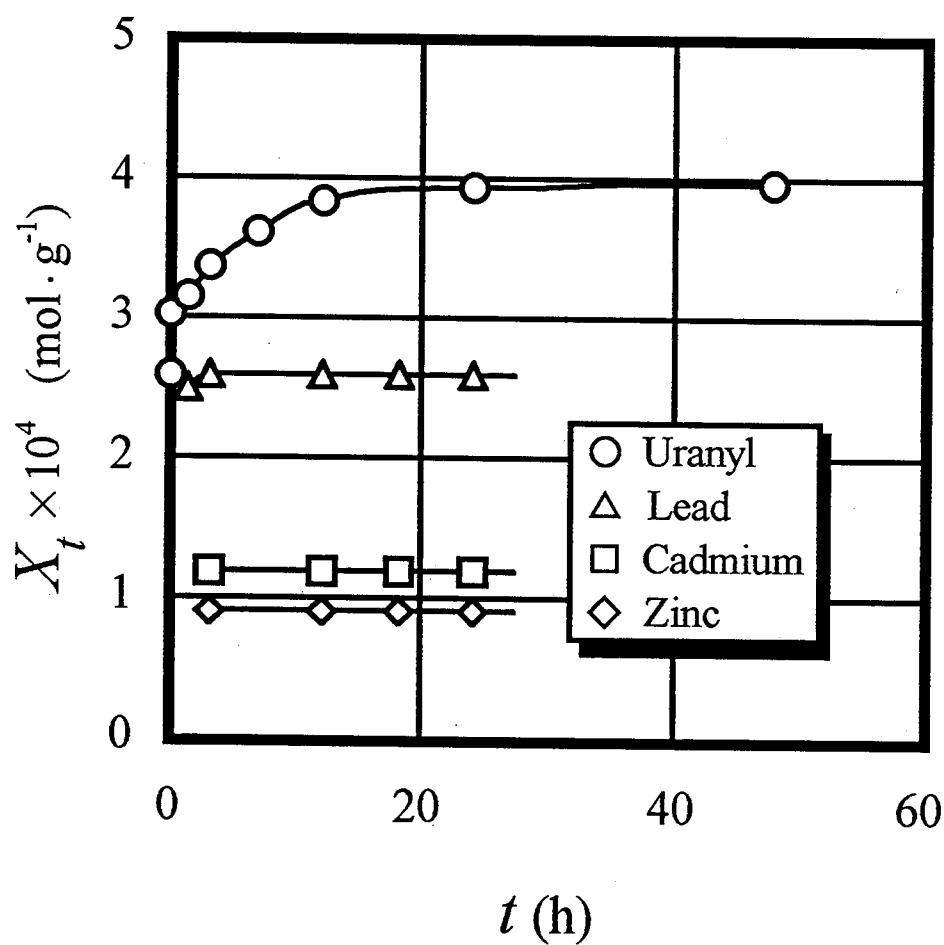


Fig.2-3. Uptake of divalent metal ions in acidic solutions as a function of adsorption time at 25°C. Hydrous titanium(IV) oxide (ca. 0.05g) was used as the adsorbent. Initial concentrations of the metal ions are $1.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ for all the runs.

shown in **Fig.2-3**. $X_t(\text{mol}\cdot\text{g}^{-1})$ denotes the adsorption amount of metal ions on 1g of HTO at adsorption time, t (h). As 24 h were enough to attain the equilibria for all the metal ions, the contact time of 48 h was adopted for the equilibrium experiments.

The variation of equilibrium amounts of adsorbed uranium with solution pH is shown in **Fig.2-4**. The figure depicts that the increase of solution pH resulted in more uranium adsorption.

In solutions which are basic or not so strongly acidic, it may be reasonable to consider that the surface sites are in either form of $-\text{SO}^-$, $-\text{SOH}$, $-\text{SOH}_2^+$, $-\text{SOM}^+$ or $-\text{SOM}(\text{OH})$. Then, Eq.[9] is rewritten as

$$X_M = N_M \frac{[\text{M}^{2+}](K_M(0) + K_M(1)/[\text{H}^+])}{(1 + K_H(1)[\text{H}^+] + K_H(2)[\text{H}^+]^2) + [\text{M}^{2+}](K_M(0) + K_M(1)/[\text{H}^+])} \quad [2-14]$$

Using the approximation that $K_M(0) \gg K_M(1)/[\text{H}^+]$ for acidic and $K_M(0) \ll K_M(1)/[\text{H}^+]$ for basic conditions, Eq.[2-14] yields the following relations:

(Under acidic conditions)

$$\frac{1 + K_H(1)[\text{H}^+] + K_H(2)[\text{H}^+]^2}{[\text{M}^{2+}]} = -K_M(0) + \frac{K_M(0)N_M}{X_M} \quad [2-15]$$

(Under basic conditions)

$$(1 + K_H(1)[\text{H}^+] + K_H(2)[\text{H}^+]^2) \frac{[\text{H}^+]}{[\text{M}^{2+}]} = -K_M(1) + \frac{K_M(1)N_M}{X_M} \quad [2-16]$$

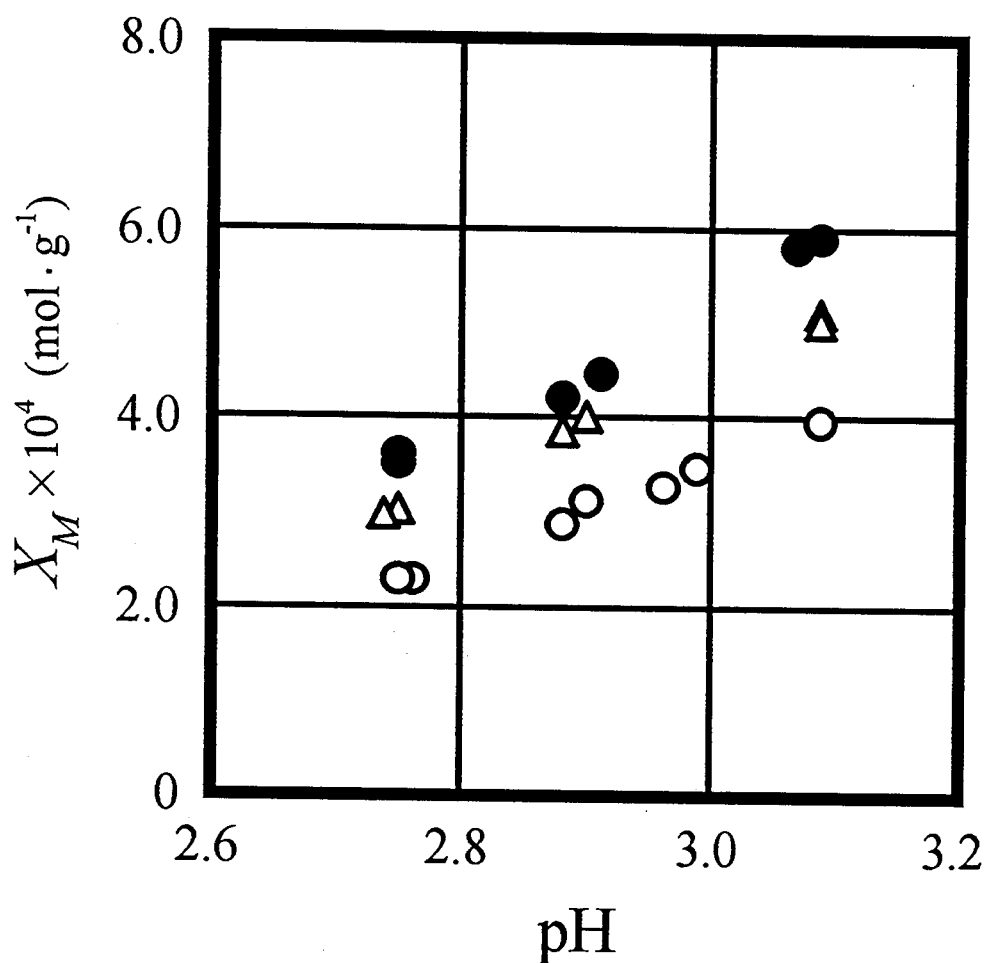


Fig.2-4. Effect of equilibrium pH on uranium adsorption in acidic solutions at 25°C. Hydrous titanium(IV) oxide (ca. 0.05g) was used as the adsorbent. Initial concentrations of uranyl nitrate for symbols ○, △ and ● are 1.0 , 1.5 and 2.0×10^{-4} mol · g⁻¹, respectively.

Figure 2-5 shows the replotted result of Fig.2-4 data by Eq.[2-15]. **Figures 2-6, 2-7 and 2-8** also exhibit the similar plots for lead, cadmium and zinc ions to uranium. The proposed model well explains the adsorption behavior of all the divalent metal ions onto HTO (probably onto the other metal oxides). The obtained values of N_M and $K_M(0)$, which can be evaluated from the intercepts and the slopes of straight lines in these figures, are listed in **Table 2-1**. As is seen in the table, there is no significant difference among the amounts of available sites, N_M , for all the metal ions, including uranium in basic (carbonate) solution, which will be dealt with in the next section. This fact strongly suggests that the model is applicable to most systems of divalent metal ions and hydrous metal oxides. The average of N_M is equal to 7.13×10^{-4} and it corresponds to about 1/3 of that for proton ($N_H = 2.39 \times 10^{-3}$).

Another adsorption parameter, $K_M(0)$, is considered to be a measure of "adsorptive force" or "adsorption strength" between a metal ion (M^{2+}) and an adsorption site ($-SO^-$) on the oxide. The data in Table 2-1 suggest that the "adsorptive force" is in the order of $Zn^{2+} < Cd^{2+} < Pb^{2+} < UO_2^{2+}$.

2.4.3 Adsorption of Uranium in Basic (Carbonate) Solutions

The results of equilibrium adsorption experiments in various carbonate concentrations are shown in **Fig.2-9**. The equilibrium pH was in the range of 8.0 to 9.5. $X_M(\text{mol} \cdot \text{g}^{-1})$ and $R(-)$ denote the equilibrium amount of uranium adsorbed on HTO and the mole ratio of sodium hydrogencarbonate to uranium nitrate initially added, respectively. The initial concentration of uranium was kept at $1.0 \times 10^{-4} (\text{mol} \cdot \text{dm}^{-3})$ throughout the experiments. The figure shows that

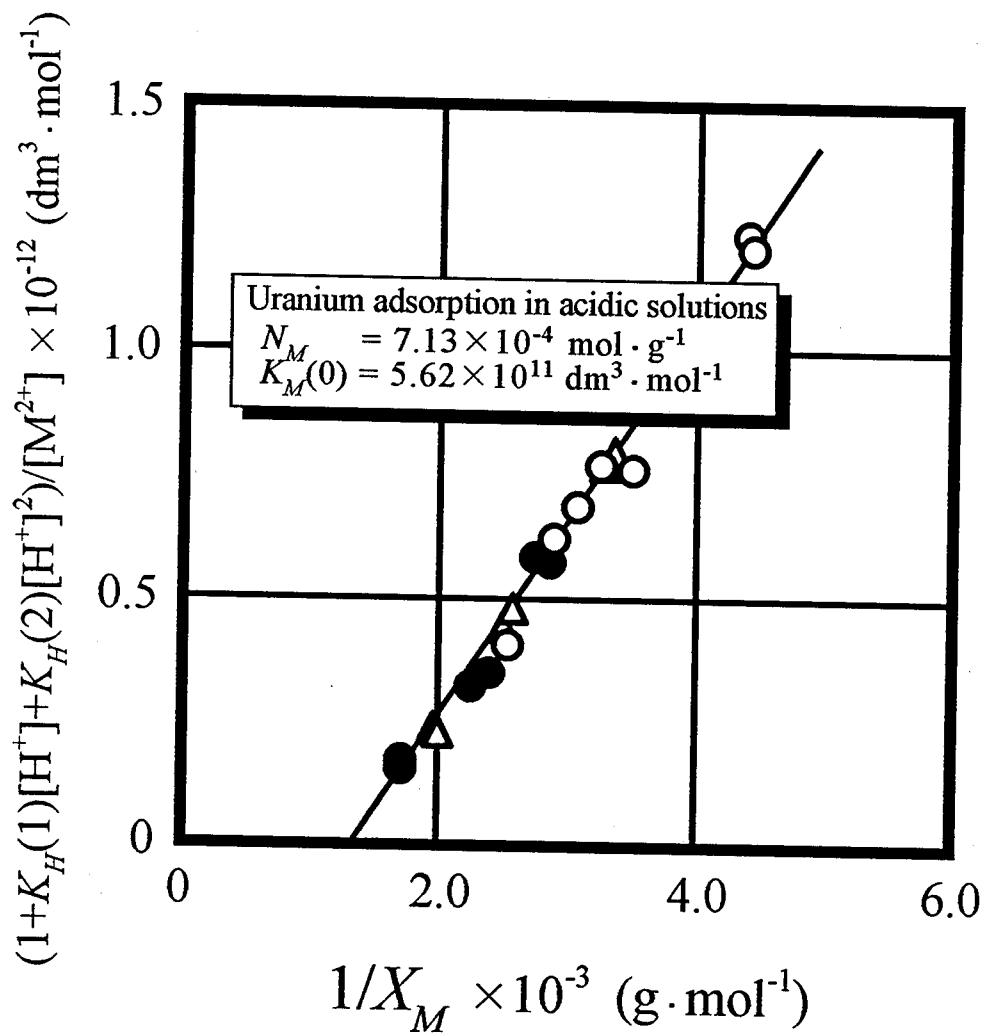


Fig.2-5. Fitting of uranium adsorption in acidic solutions to the theoretical isotherm (Eq.[2-15]).

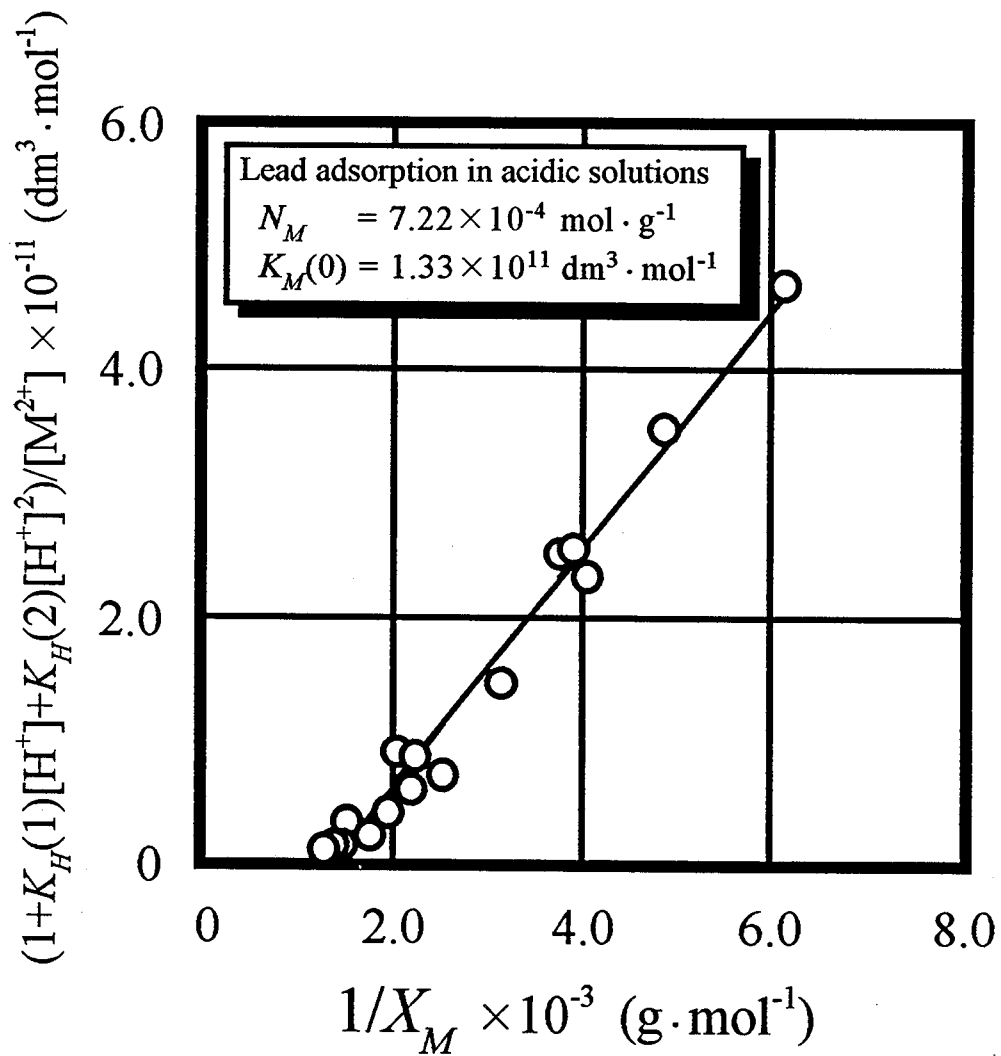


Fig.2-6. Fitting of lead adsorption in acidic solutions to the theoretical isotherm (Eq.[2-15]).

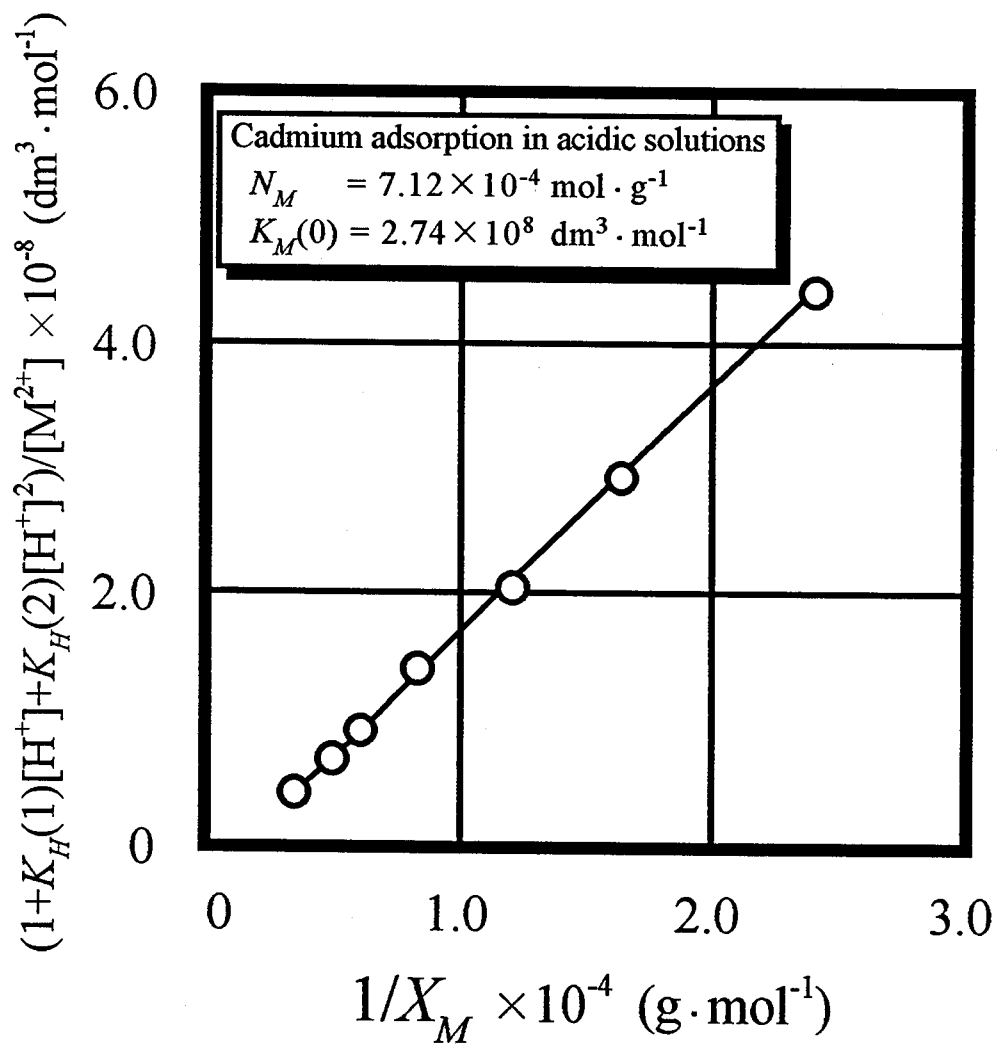


Fig.2-7. Fitting of cadmium adsorption in acidic solutions to the theoretical isotherm (Eq.[2-15]).

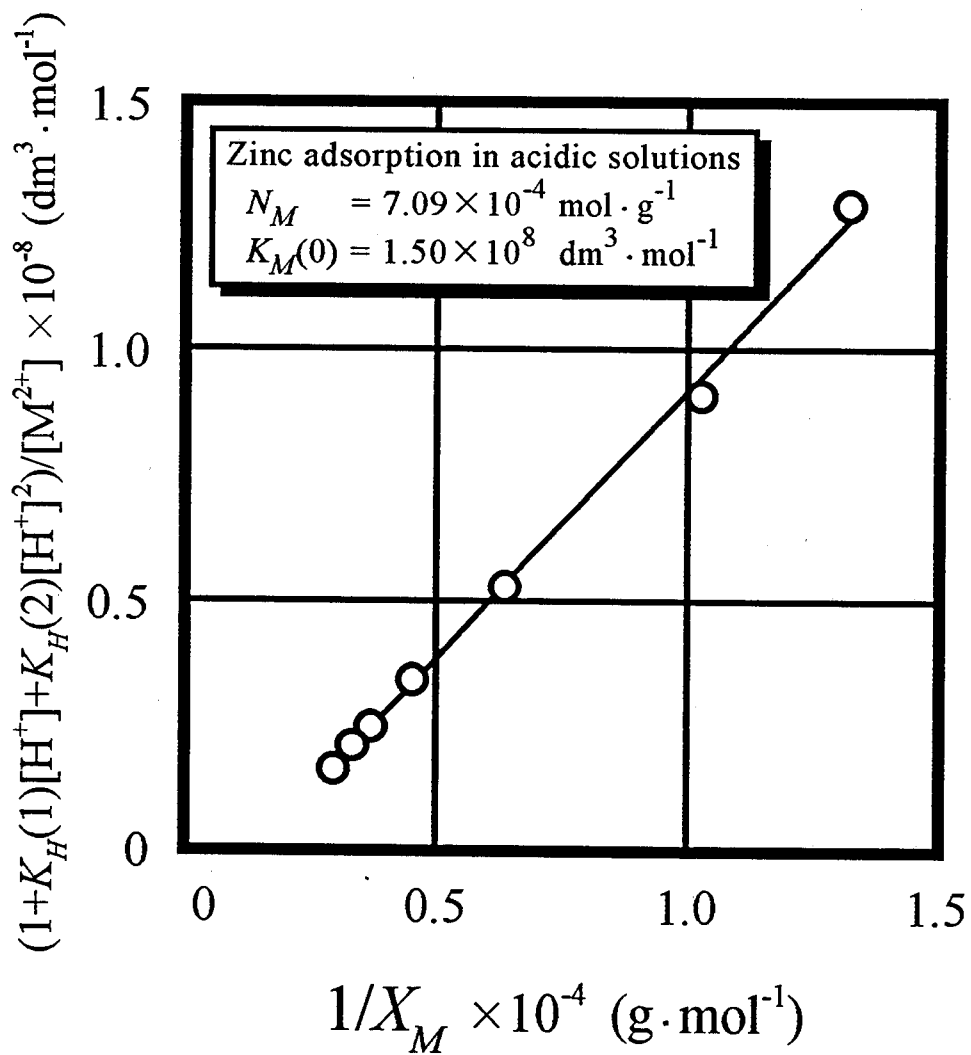


Fig.2-8. Fitting of zinc adsorption in acidic solutions to the theoretical isotherm (Eq.[2-15]).

Table 2-1 Adsorption constants of UO_2^{2+} , Pb^{2+} , Cd^{2+} and Zn^{2+}
to hydrous titanium(IV) oxide

adsorbate ion	solution condition	number of available sites, $N_M[\text{mole} \cdot \text{g}^{-1}]$	equilibrium constants $K_M(n)$
UO_2^{2+}	acidic	7.13×10^{-4}	$K_M(0) = 5.62 \times 10^{11}$
UO_2^{2+}	basic	7.10×10^{-4}	$K_M(1) = 7.23 \times 10^7$
Pb^{2+}	acidic	7.22×10^{-4}	$K_M(0) = 1.33 \times 10^{11}$
Cd^{2+}	acidic	7.12×10^{-4}	$K_M(0) = 2.74 \times 10^8$
Zn^{2+}	acidic	7.09×10^{-4}	$K_M(0) = 1.50 \times 10^8$

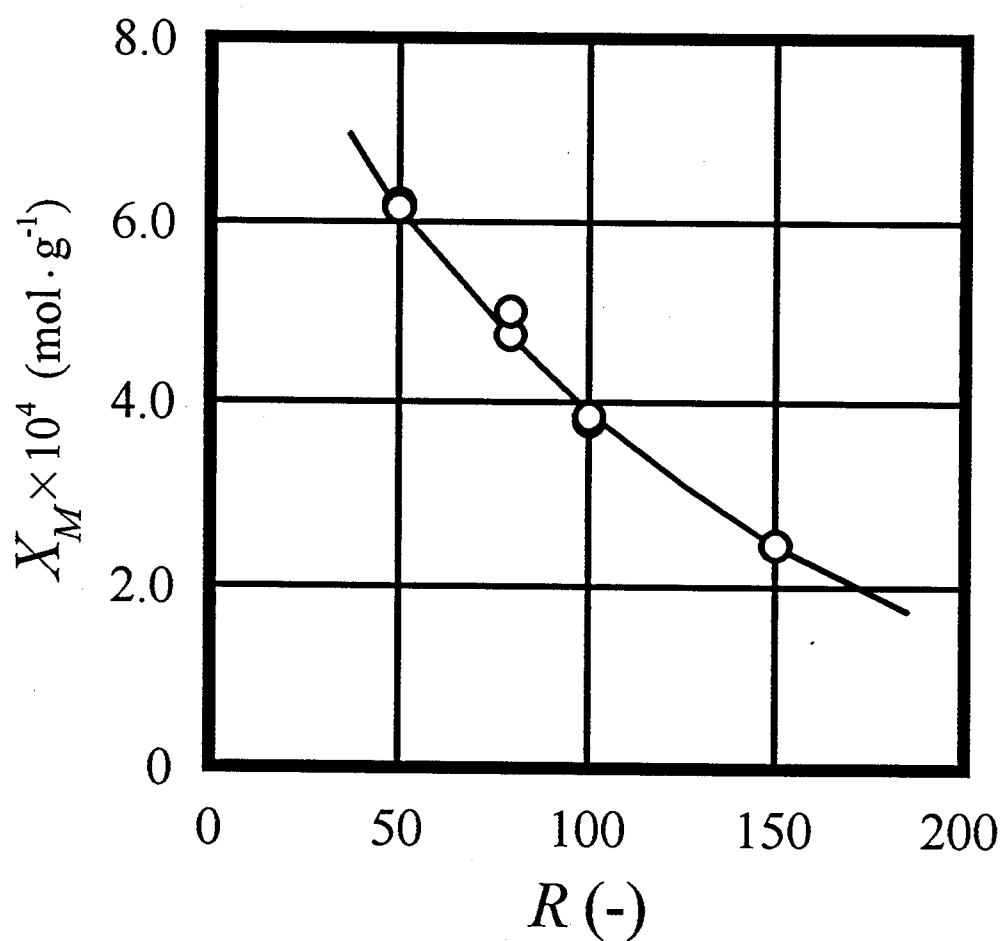


Fig.2-9. Effect of initial concentration of sodium hydrogencarbonate on uranium adsorption at 25°C. R denotes the mole ratio of sodium hydrogencarbonate to uranium nitrate initially added. Hydrous titanium(IV) oxide (ca. 0.04g) was used as the adsorbent. Initial concentration of uranium nitrate is $1.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$.

the R increase resulted in less uranium adsorption. The present model can explain this behavior as follows; In carbonate and alkaline solutions most of uranyl ions may be converted to the complexes with carbonate or hydroxide ions, while in acidic solutions they should remain free UO_2^{2+} cations which play a role of active adsorbate species in this system. In other words, the increase of R should make the decrease of uranyl concentration, i.e., the decrease of uranium uptake.

For a quantitative comparison of Fig.2-9 data with the model expressed by Eq.[2-14], it is necessary to exactly calculate the equilibrium UO_2^{2+} concentrations for the experimental runs. **Table 2-2** shows the possible complex forming reactions and the corresponding stability constants. In this table, the stability constants for HCO_3^- and H_2CO_3 forming reactions were given by Sillen and Martel(32), and those for the other reactions were given by Lemire and Tremaine(26). Prior to the use, the listed values were corrected for actual experimental conditions using the well-known Debye-Huckel's limiting law, since they are the extrapolated values to zero ionic strength. The calculated results corresponding to the data of Fig.2-9 are plotted in **Fig.2-10** together with the concentrations of uranyl tricarbonate which is the most dominant species in these conditions. It is seen that in these carbonate solutions the concentrations of free uranyl ions were extremely low and the increase of R from 50 to 150 resulted in the decrease of $[\text{UO}_2^{2+}]$ from about 10^{-15} to 10^{-17} ($\text{mol}\cdot\text{dm}^{-3}$). **Figure 2-11** demonstrates the comparison of the data of Fig.2-9 with the theoretical isotherm expressed by Eq.[2-14]. It is found that the experimental was in good accordance with the model (solid line). In other

Table 2-2 Stability constants of uranyl complexes.

Equilibrium formula	logarithm of stability constant
$\text{H}^+ + \text{CO}_3^{2-} \leftrightarrow \text{HCO}_3^-$	10.25
$\text{H}^+ + \text{HCO}_3^- \leftrightarrow \text{H}_2\text{CO}_3$	6.34
$\text{UO}_2^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{UO}_2\text{CO}_3(\text{aq})$	10.1
$\text{UO}_2^{2+} + 2\text{CO}_3^{2-} \leftrightarrow \text{UO}_2(\text{CO}_3)_2^{2-}$	17.1
$\text{UO}_2^{2+} + 3\text{CO}_3^{2-} \leftrightarrow \text{UO}_2(\text{CO}_3)_3^{4-}$	21.4
$\text{UO}_2^{2+} + \text{H}_2\text{O} \leftrightarrow \text{UO}_2(\text{OH})^+ + \text{H}^+$	-5.8
$2\text{UO}_2^{2+} + 2\text{H}_2\text{O} \leftrightarrow (\text{UO}_2)_2(\text{OH})_2^{2+} + 2\text{H}^+$	-5.6
$3\text{UO}_2^{2+} + 5\text{H}_2\text{O} \leftrightarrow (\text{UO}_2)_3(\text{OH})_5^+ + 5\text{H}^+$	-15.6
$3\text{UO}_2^{2+} + 7\text{H}_2\text{O} \leftrightarrow (\text{UO}_2)_3(\text{OH})_7^- + 7\text{H}^+$	-31
$\text{UO}_2^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{UO}_2(\text{OH})_2(\text{aq}) + 2\text{H}^+$	-12

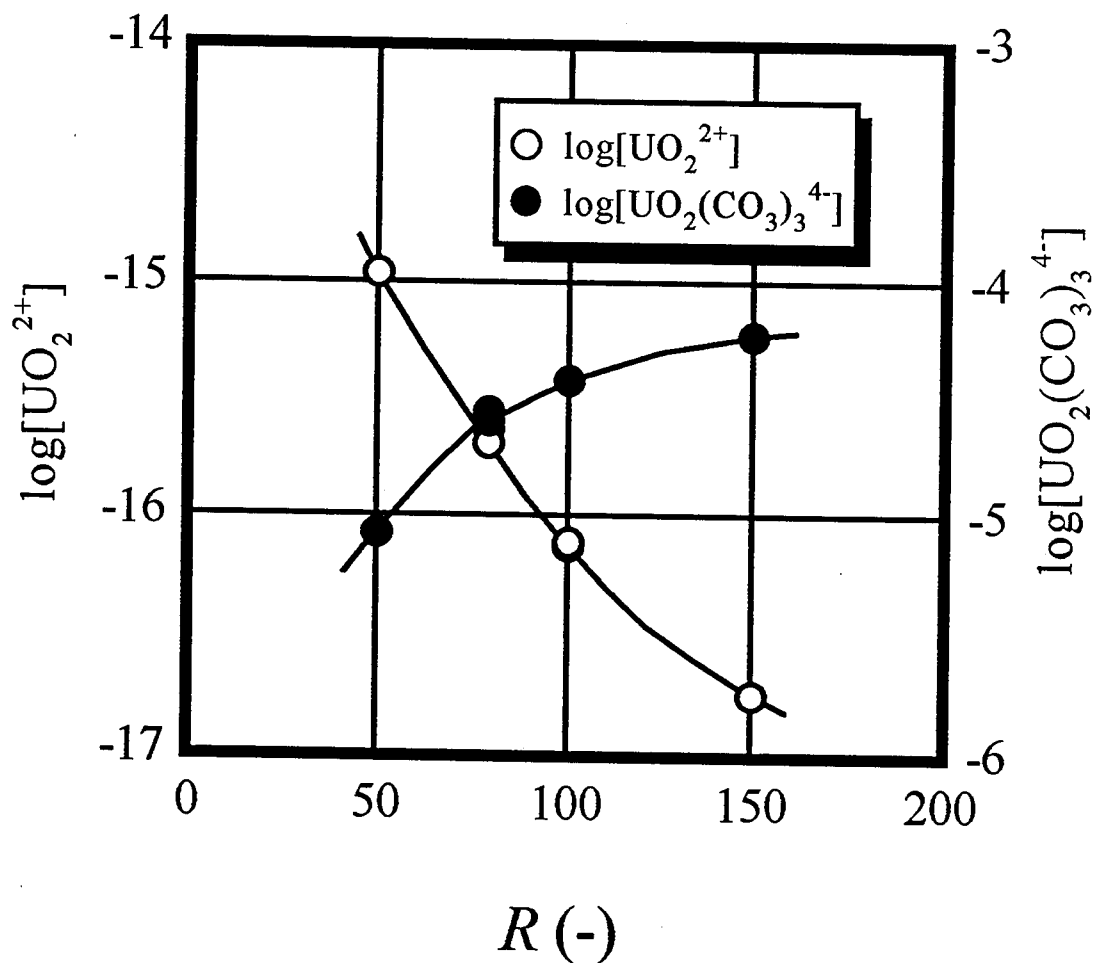


Fig.2-10. Calculated concentrations of uranyl and uranyl tricarbonate ions in carbonate solutions. The stability constants listed in Table 2-2 were used for the calculation after they were corrected for actual conditions by Debye-Huckel's limiting law.

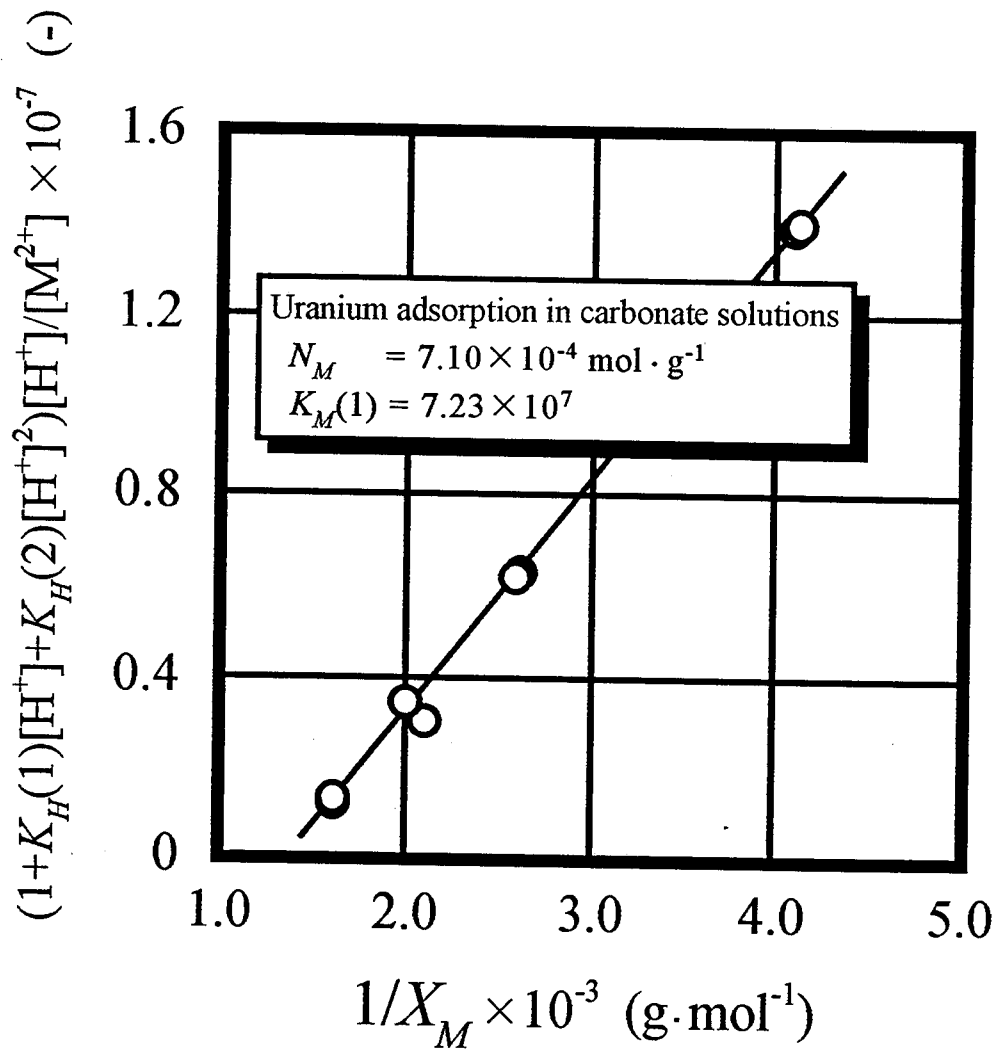


Fig.2-11. Fitting of uranium adsorption in basic (carbonate) solutions to the theoretical isotherm (Eq.[2-16]).

words, even in the presence of carbonate ions, the active species in uranium adsorption was not uranyl carbonates (such as $\text{UO}_2(\text{CO}_3)_3^{4-}$) but free uranyl cations. The obtained values of N_M and $K_M(1)$ are also included in Table 2-1.

Since $K_M(0)$ and $K_M(1)$ for uranium were already determined, now the change in the surface composition of uranium species ($-\text{SO}\cdot\text{UO}_2^+$ or $-\text{SO}\cdot\text{UO}_2\cdot\text{OH}$) on HTO with solution pH can be estimated. Rearranging Eq.[2-14] the following equation is obtained

$$X_M = N_M \frac{[\text{M}^{2+}]K_M(0)}{(1 + K_H(1)[\text{H}^+] + K_H(2)[\text{H}^+]^2) + [\text{M}^{2+}](K_M(0) + K_M(1)/[\text{H}^+])} + N_M \frac{[\text{M}^{2+}]K_M(1)/[\text{H}^+]}{(1 + K_H(1)[\text{H}^+] + K_H(2)[\text{H}^+]^2) + [\text{M}^{2+}](K_M(0) + K_M(1)/[\text{H}^+])} \quad [2-17]$$

As the first and second terms of the right hand side of Eq.[2-17] means the adsorbed amounts of $-\text{SO}\cdot\text{UO}_2^+$ and $-\text{SO}\cdot\text{UO}_2\cdot\text{OH}$ types, respectively, the fraction of $-\text{SO}\cdot\text{UO}_2^+$ species to the total adsorbed uranium can be expressed as

$$\frac{\{-\text{SOM}^+\}}{\{-\text{SOM}^+\} + \{-\text{SOM}(\text{OH})\}} = \frac{K_M(0)}{K_M(0) + K_M(1)/[\text{H}^+]} \quad [2-18]$$

Figure 2-12 shows the curve calculated from Eq.[2-18] as a function of pH. The figure reveals that in acidic region ($\text{pH} < 4$) deprotonated surface hydroxyl groups combine mainly with free uranyls (UO_2^{2+}) and in neutral or basic region ($\text{pH} > 4$) they complexate with uranyl hydroxides ($\text{UO}_2(\text{OH})^+$).

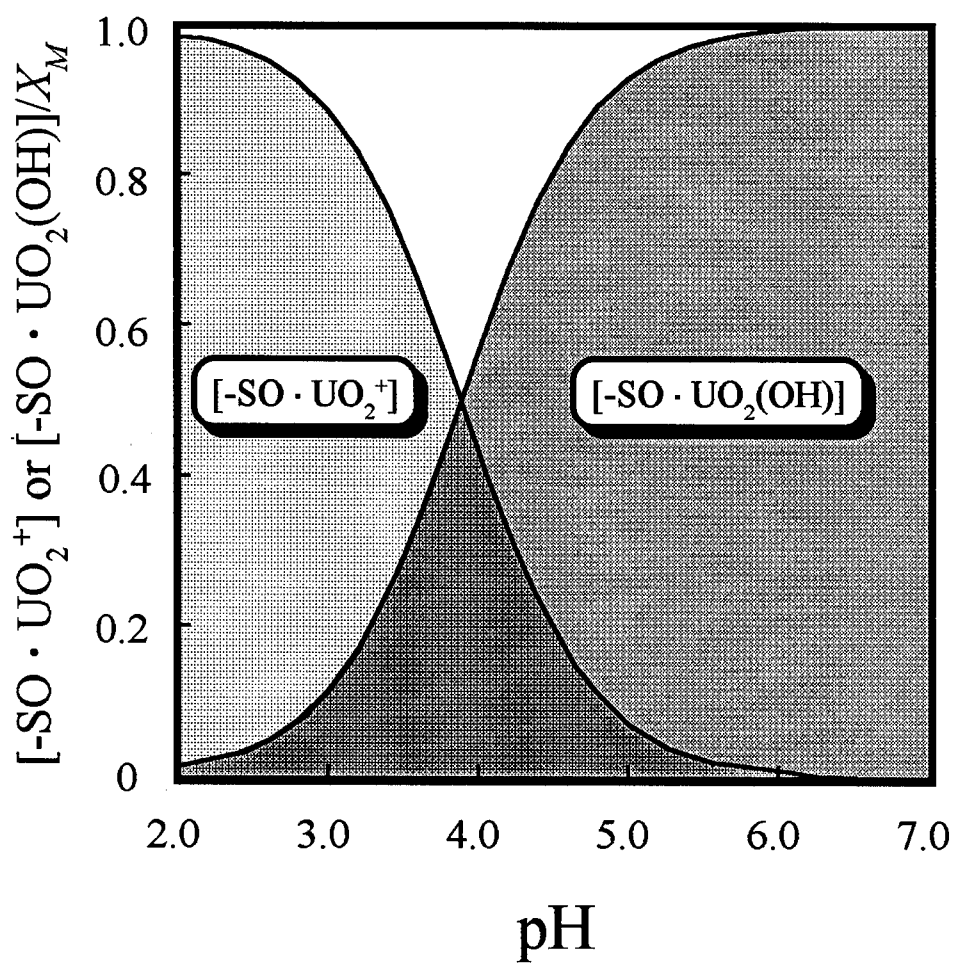


Fig.2-12. Change in surface uranium species ($-SO \cdot UO_2^+$ or $-SO \cdot UO_2 \cdot OH$) on hydrous titanium(IV) oxide with the solution pH.

2.5 Conclusions

A general adsorption model for divalent metal ions and hydrous metal oxides system was proposed. All the adsorption experiments, which were conducted in acidic or basic (carbonate) solutions using uranium, lead, cadmium and zinc as the adsorbates, confirmed the model. From the obtained model parameters, the following remarks were concluded; (1) A metal ion complexed with a single surface hydroxyl group, even though it was divalent. (2) The adsorbent had the same available sites of $7.13 \times 10^{-4} (\text{mol} \cdot \text{g}^{-1})$ for all the metal ions dealt with in this work. (3) A model parameter, $K_M(0)$, which may be a measure of "adsorptive force" between the metal ions and the surface site on HTO, was in the order of $\text{Zn}^{2+} < \text{Cd}^{2+} < \text{Pb}^{2+} < \text{UO}_2^{2+}$. (4) Even in carbonate solutions, the active species in uranium adsorption on HTO was not uranyl carbonates but free uranyl ion. (5) In acidic region ($\text{pH} < 4$) deprotonated surface hydroxyl groups combined mainly with free uranyles (UO_2^{2+}) and in neutral or basic region ($\text{pH} > 4$) they complexed with uranyl hydroxides ($\text{UO}_2(\text{OH})^+$).

2.6 Nomenclature

γ = surface density of hydroxyl groups on adsorbent ($\text{mol} \cdot \text{m}^{-2}$)

$K_H(n)$ = equilibrium constant for proton adsorption defined by Eq.[2-5]
($(\text{dm} \cdot \text{mol}^{-1})^n$)

$K_M(n)$ = equilibrium constant for metal ion adsorption defined by Eq.[2-6]

	$((\text{mol}\cdot\text{dm}^{-1})^{n-1})$
m = mass of adsorbent	(g)
N_H = amount of adsorption sites available for protons	$(\text{mol}\cdot\text{g}^{-1})$
N_M = amount of adsorption sites available for metal ions	$(\text{mol}\cdot\text{g}^{-1})$
X_M = amount of adsorbed metal ions	$(\text{mol}\cdot\text{g}^{-1})$
X_t = amount of adsorbed metal ions at time t	$(\text{mol}\cdot\text{g}^{-1})$
θ_M = fraction of adsorption sites complexated with metal ions	(-)

3. INFLUENCE OF DEHYDRATION PROCESS OF HYDROUS TITANIUM(IV) OXIDE ON ITS URANIUM ADSORPTION CHARACTERISTICS

3.1 Introduction

In the preceding chapter, a general adsorption model for the adsorption of divalent metal ions onto hydrous metal oxide was presented. The adsorption model explains the adsorption mechanism of uranium, lead, cadmium and zinc ions onto hydrous titanium(IV) oxide (HTO). The model enabled the determination of the equilibrium constant and the amount of adsorption sites available for metal ions.

Inorganic adsorbents such as hydrous metal oxides are normally prepared through several steps and finally dehydrated to the well-dried state. The dehydration process should give a distinctive influence on the adsorbents' characteristics (adsorption capacity and kinetics). However, most previous studies have mainly dealt with the pore structure of well-dried sorbents (6,7,8,25) or its effect on gas-solid reaction (1,2,3,5,10,11,31). In this chapter, the influence of the dehydration process on static and kinetic characteristics of uranium adsorption onto HTO was investigated. Seven kinds of HTO with different moisture contents were used in this work. From the results of conductometric titration of HTO, the influence of the dehydration on the amount of proton binding sites will be discussed. Furthermore, the influence of the dehydration process on the pore-size distribution of HTO will be

quantitatively discussed, based on two models, i.e., an equilibrium adsorption model presented in the preceding chapter and a simple mathematical model for adsorption kinetics presented in this chapter.

3.2 Experimental

3.2.1 Adsorbent

Titanium(IV) oxide sol was prepared by the same manner as the preceding chapter. The well-washed precipitate was centrifuged and vacuum-dried at room temperature to reach a desired moisture content. **Figure 3-1** shows a time-course of dehydration process of the precipitate. In this work seven kinds of HTO with different moisture contents of 400, 233, 184, 140, 100, 59 and 19% were prepared. In this text, these adsorbents will be abbreviated to T-400, T-233, T-184, T-140, T-100, T-59 and T-19, respectively. The adsorbent's moisture content(*MC*) was on the dry-weight (the weight of its ignition residue) basis, and the amount of adsorbent was also expressed by the dry weight.

3.2.2 Conductometric Titration of HTO

The total amount of adsorption sites (surface hydroxyl groups) on the adsorbent was determined by conductometric titration method(20). 0.4g of HTO powder was suspended in 1.0 dm³ of a solution containing 0.003 mol HNO₃ at 25°C, and the suspension was titrated with a 0.1M NaOH solution; 2 cm³ aliquots of the alkali were added to the suspension and the system was allowed to stand until there was no change in the conductivity. To eliminate the influence

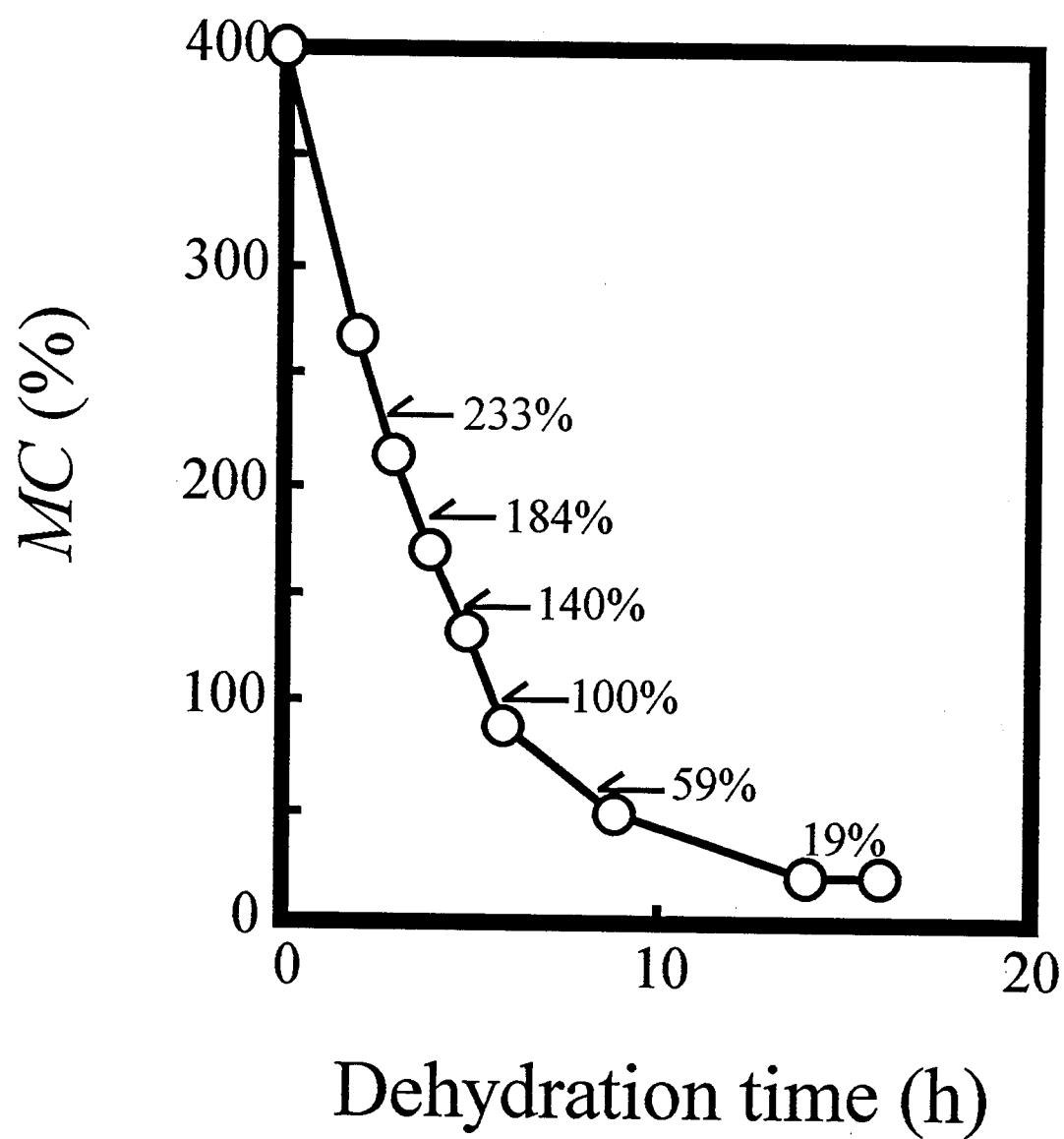


Fig.3-1. Time-course of vacuum-dehydration process of hydrous titanium(IV) oxide at room temperature.

of CO₂, N₂ gas was continuously bubbled through the system.

3.2.3 Adsorption Experiment of Uranium on HTO

Uranium adsorption experiments were conducted in nitric acid solutions. The detailed procedure is given in the preceding chapter. The amount of uranium adsorbed was calculated on the basis of 1 g adsorbent of its ignition residue. The initial uranium concentration was kept constant to be 1.0×10^{-4} mol·dm⁻³ for all adsorption experiments.

3.3 Results and discussion

3.3.1 Influence of Dehydration of HTO on the Amount of Available Sites for Uranium

In a preceding chapter, the author showed that possible reactions in an adsorption system of divalent metal ions onto hydrous metal oxides are summarized in two competitive reactions as

(Protonation of hydroxyl group)

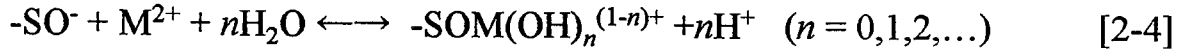


with

$$K_H(n) = \frac{\{-\text{SOH}_n^{(n-1)+}\}}{\{-\text{SO}^-\}[\text{H}^+]^n} \quad [2-5]$$

and

(Adsorption of divalent metal ion with water molecules)



with

$$K_M(n) = \frac{\{-\text{SOM}(\text{OH})_n^{(1-n)+}\}[\text{H}^+]^n}{\{-\text{SO}^-\}[\text{M}^{2+}]} \quad [2-6]$$

where [] and { } denote the concentrations of species in liquid phase and the concentrations of surface species, respectively, and $-\text{SO}^-$ and M^{2+} denote the deprotonated surface hydroxyl group (adsorption site) and the divalent metal ion in liquid phase, respectively. From Eqs.[2-5] and [2-6] a theoretical adsorption isotherm was derived as

$$X_M = N_M \frac{[\text{M}^{2+}] \sum K_M(n) / [\text{H}^+]^n}{\sum K_H(n) [\text{H}^+]^n + [\text{M}^{2+}] \sum K_M(n) / [\text{H}^+]^n} \quad [2-9]$$

where X_M ($\text{mol} \cdot \text{g}^{-1}$) and N_M ($\text{mol} \cdot \text{g}^{-1}$) represent the amount of adsorbed metal ions and the amount of adsorption sites available for the target metal ions, respectively and Σ denotes the summation for $n = 0$ to ∞ . For normal solutions, a practical adsorption isotherm was finally obtained as

$$X_M = N_M \frac{[\text{M}^{2+}] (K_M(0) + K_M(1) / [\text{H}^+])}{(1 + K_H(1) [\text{H}^+] + K_H(2) [\text{H}^+]^2) + [\text{M}^{2+}] (K_M(0) + K_M(1) / [\text{H}^+])} \quad [2-14]$$

Under acidic condition, where the relation of $K_M(0) \gg K_M(1)/[H^+]$ can be assumed, Eq.[6] is modified to the following simple equation.

$$\frac{1 + K_H(1)[H^+] + K_H(2)[H^+]^2}{[M^{2+}]} = -K_M(0) + \frac{K_M(0)N_M}{X_M} \quad [2-15]$$

As $K_H(1)$ and $K_H(2)$ is already determined as $1.70 \times 10^9 \text{ mol}^{-1} \cdot \text{dm}^3$ and $2.51 \times 10^{13} \text{ mol}^{-2} \cdot \text{dm}^6$ (in the preceding chapter), the two adsorption parameters of N_M and $K_M(0)$ can be obtained from the plot of the left-hand side of Eq.[2-15] vs. $1/X_M$. Thus obtained values of N_M and $K_M(0)$ is listed in **Table 3-1**.

Figure 3-2 shows the effect of pH on the equilibrium amount of uranium adsorbed, X_M ($\text{mol} \cdot \text{g}^{-1}$). Both of the increases of the solution's pH and the adsorbent's moisture content resulted in more uranium adsorption. The comparison of the theoretical expressed by Eq.[2-15] with the experimental data in Fig.3-2 (for T-400 adsorbent, as an example) is shown in **Fig.3-3**. Similar results were obtained for the other adsorbents, and all the data were in satisfactory accordance with the model (solid straight line). Two adsorption parameters of N_M and $K_M(0)$ were evaluated from the slope and the intercept of the line for each of the adsorbents. The variations of $N_M(0)$ and $K_M(0)$ with the moisture content of adsorbent are summarized in **Figs.3-4** and **3-5**, respectively. It should be noted that N_M decreased from 7.13×10^{-4} to $3.07 \times 10^{-4} \text{ mol} \cdot \text{g}^{-1}$ with the decrease of moisture content from 230 to 19%, while $K_M(0)$ remained almost constant independent of the moisture content.

An adsorbent, in general, contains a number of small pores which have various sizes and shapes, and adsorption sites are distributed on the pores'

Table 3-1 Summary of adsorption characteristics of adsorbents used in this work.

MC [%]	N_H [mol·g ⁻¹]	N_M [mol·g ⁻¹]	N_{mac} [mol·g ⁻¹]	N_{mes} [mol·g ⁻¹]	f [-]	k [h ⁻¹]	$\log K_M(0)$ [dm ³ ·mol ⁻¹]
400	2.39×10 ⁻³	7.13×10 ⁻⁴	7.13×10 ⁻⁴	-	-	-	11.7
233	2.41×10 ⁻³	7.14×10 ⁻⁴	6.28×10 ⁻⁴	8.57×10 ⁻⁵	0.88	1.71	11.6
184	2.35×10 ⁻³	5.23×10 ⁻⁴	4.60×10 ⁻⁴	6.28×10 ⁻⁵	0.88	0.94	11.5
140	2.40×10 ⁻³	5.25×10 ⁻⁴	3.34×10 ⁻⁴	1.89×10 ⁻⁴	0.64	0.22	11.4
100	2.49×10 ⁻³	4.51×10 ⁻⁴	2.57×10 ⁻⁴	1.94×10 ⁻⁴	0.57	0.23	11.4
59	2.40×10 ⁻³	4.20×10 ⁻⁴	2.02×10 ⁻⁴	2.18×10 ⁻⁴	0.48	0.17	11.3
19	2.39×10 ⁻³	3.07×10 ⁻⁴	8.75×10 ⁻⁵	2.18×10 ⁻⁴	0.29	0.06	1 1.5

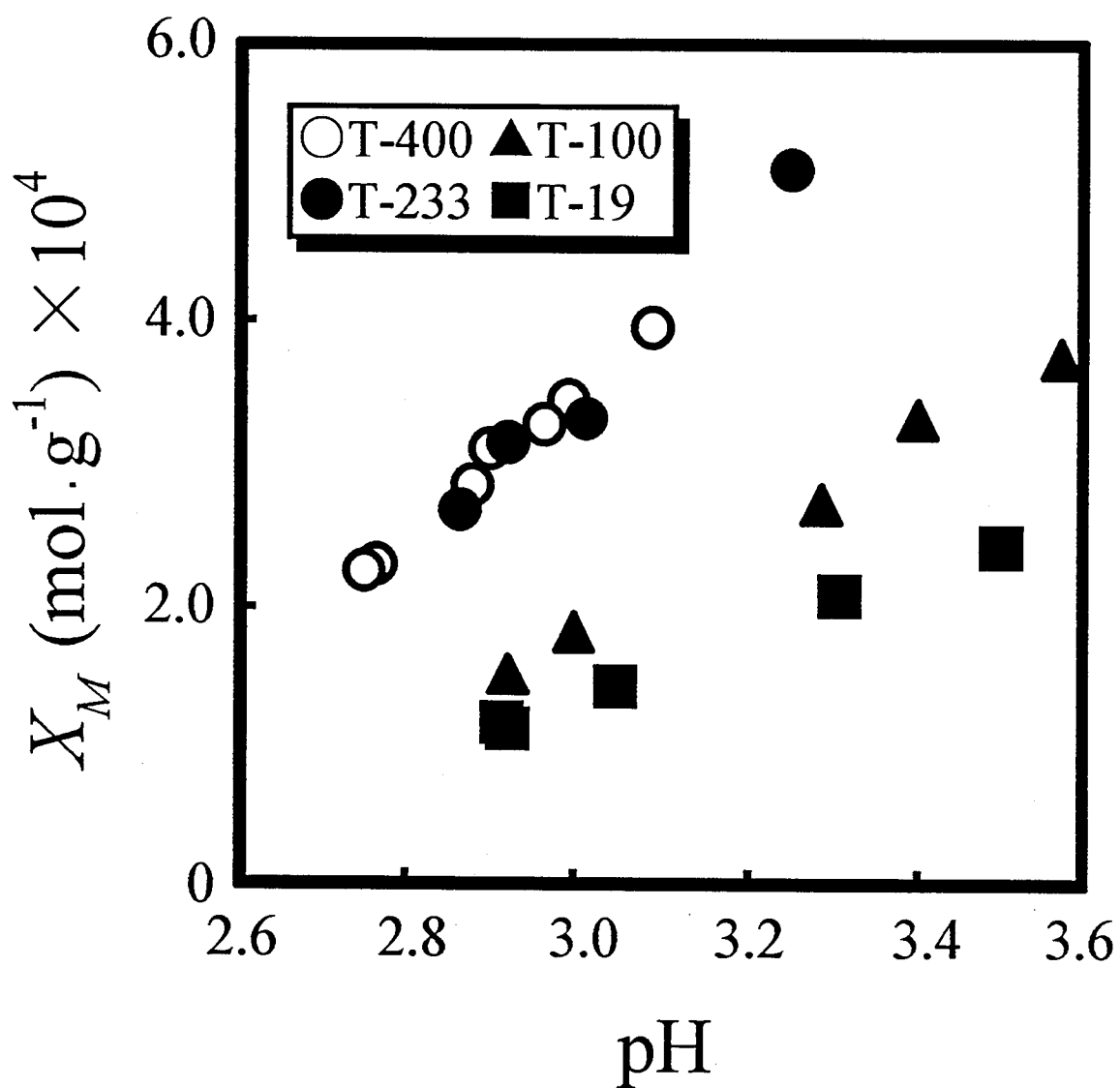


Fig.3-2. Effect of the equilibrium pH on uranium adsorption at 30°C. Initial concentration of uranium is $1 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$.

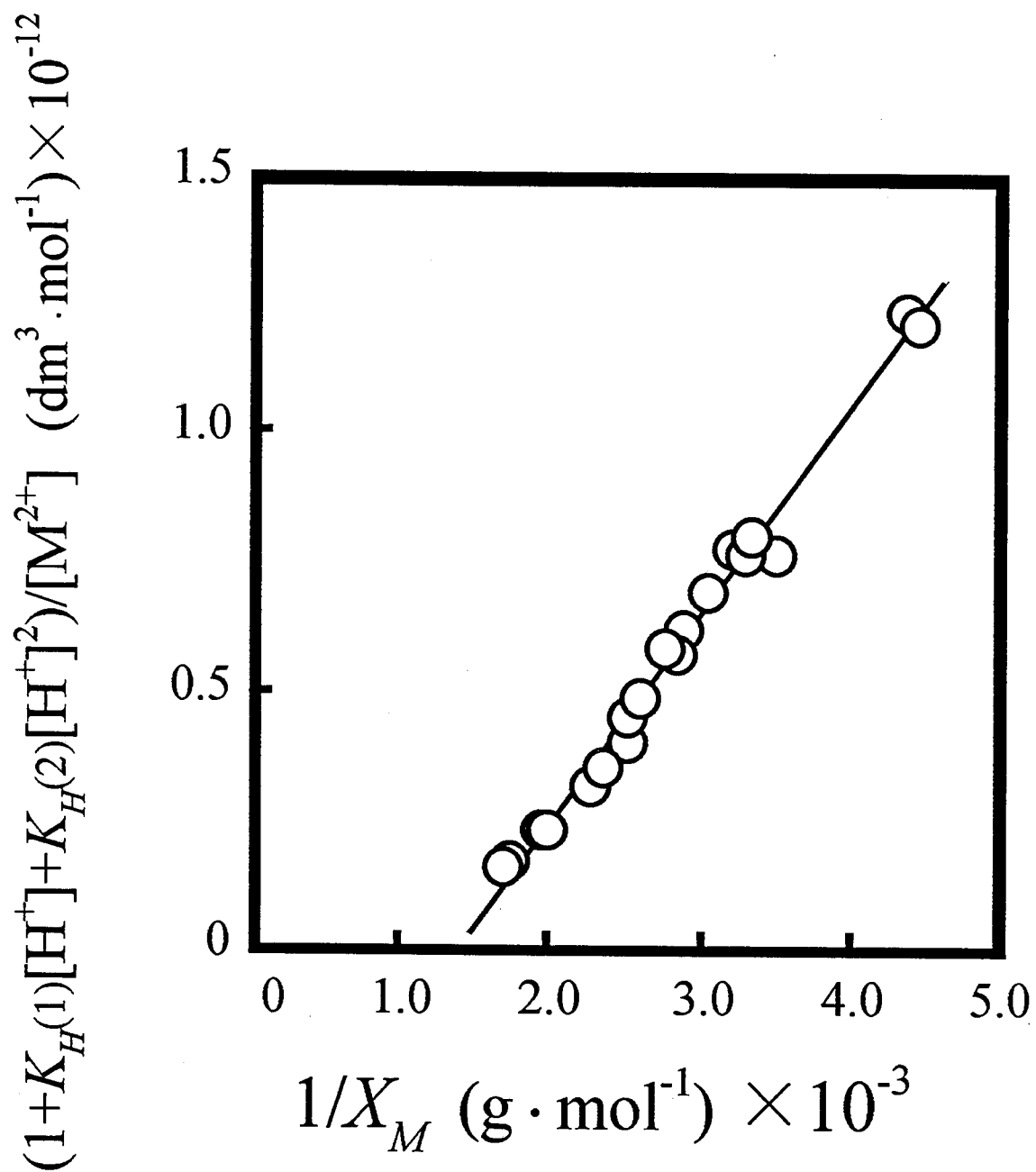


Fig.3-3. A typical fitting of the equilibrium adsorption data to Eq.[2-15] for T-400 adsorbent.

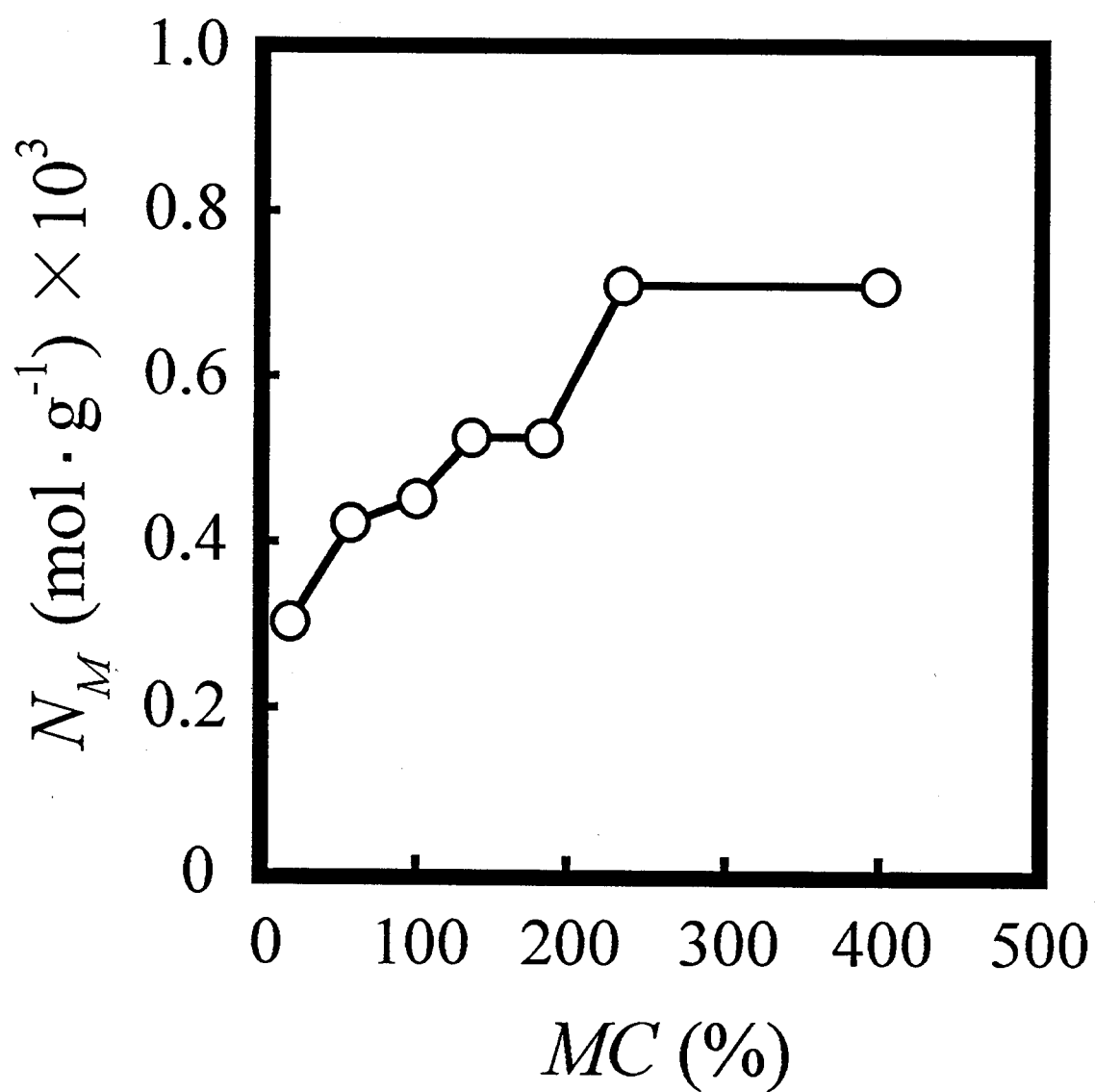


Fig.3-4. Relation between adsorbent's moisture content and the number of available sites for uranium, N_M , determined from the plot of Fig.3-3.

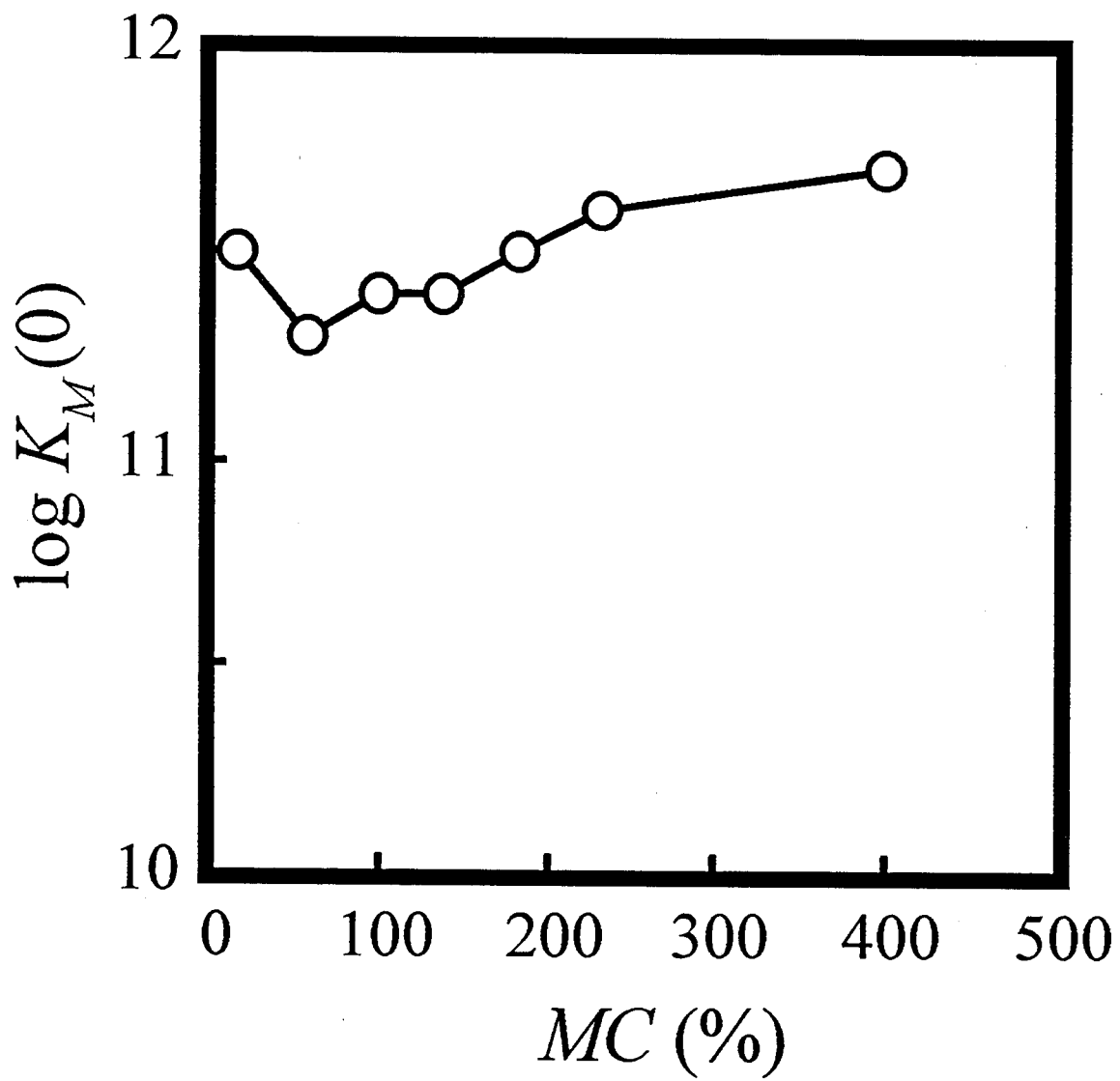


Fig.3-5 Relation between adsorbent's moisture content and the adsorption constant, $K_M(0)$, determined from the plot of Fig.3-3.

walls. An adsorbate ion can be adsorbed on the sites in relatively large pores, but it has no probability to access and to be adsorbed onto the surface sites inside smaller pores than itself. In other words, a site on an adsorbent is either active (available) or dead (non-available) for a target adsorbate ion. The experimental result demonstrates that dehydration process did not influence on the surface density of sites available for uranium and the equilibrium constant for site - uranyl surface reaction, but it greatly reduced the number of available sites.

In order to obtain more detailed information about the condition of adsorption sites, the number of active sites for proton, N_H was determined from the conductometric titration method for each of the adsorbents. A typical titration curve is presented in **Fig.3-6**, and the variation of N_H with the adsorbent's moisture content is depicted in **Fig.3-7**. The result showed that the number of active sites for proton was kept constant as about $2.4 \times 10^{-3} \text{ mol} \cdot \text{g}^{-1}$ for all the adsorbents.

The results shown in Figs.3-4, 3-5 and 3-7 are summarized as follows; (1)The proposed model by the author well explained the adsorption phenomena of uranium on HTO with various moisture contents. (2)The number of total sites (active sites for proton) in the adsorbents and the surface density of active sites for uranium were scarcely affected by dehydration process. (3)The fraction of active sites for uranium to the total sites, N_M/N_H decreased from 0.30 to 0.13 with the decrease of moisture content from 230 to 19%.

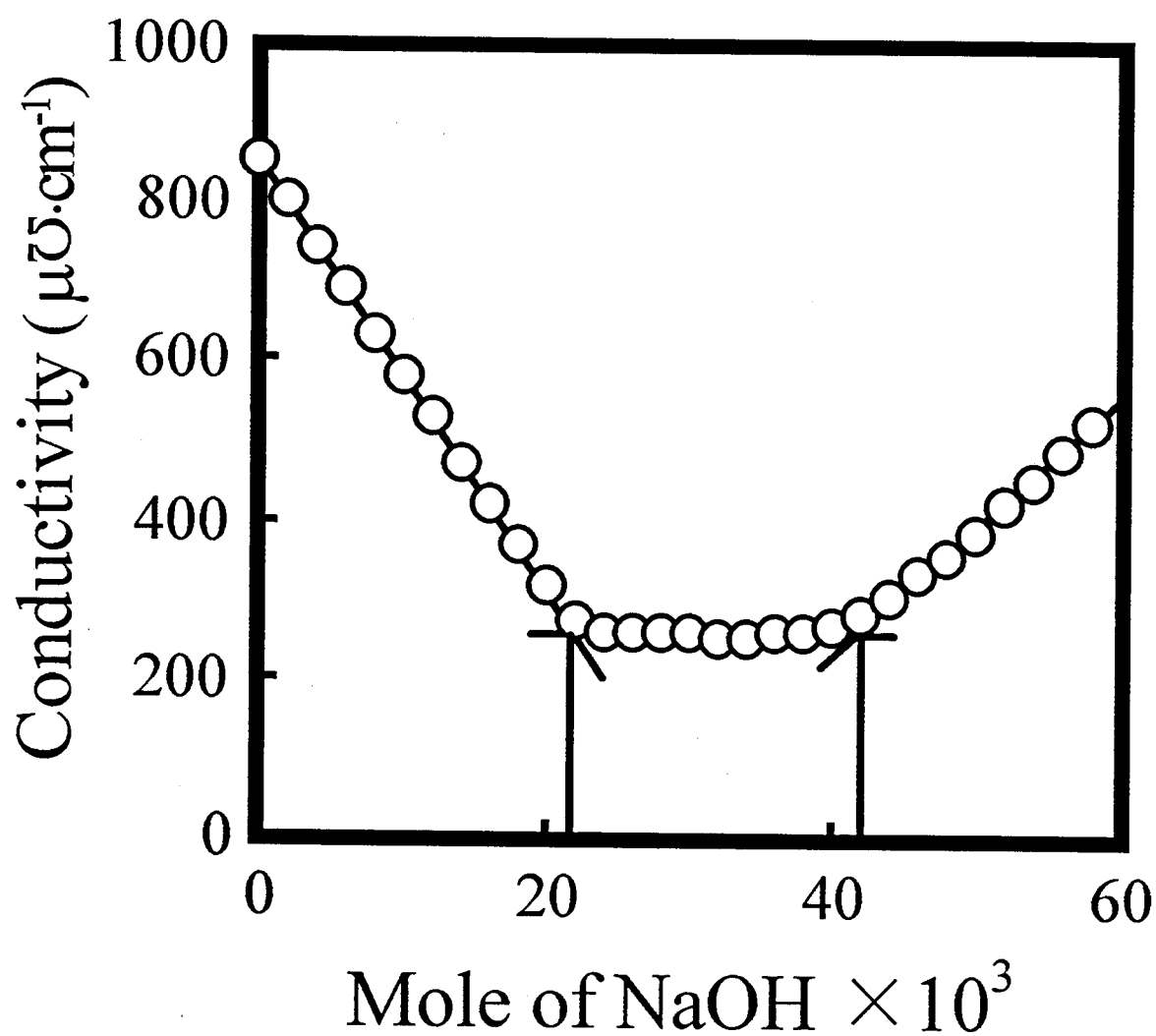


Fig.3-6 Conductometric titration curve of a 200-cm³ suspension by 0.02M HNO₃ solution. The suspension contained 0.1g of T-400 adsorbent.

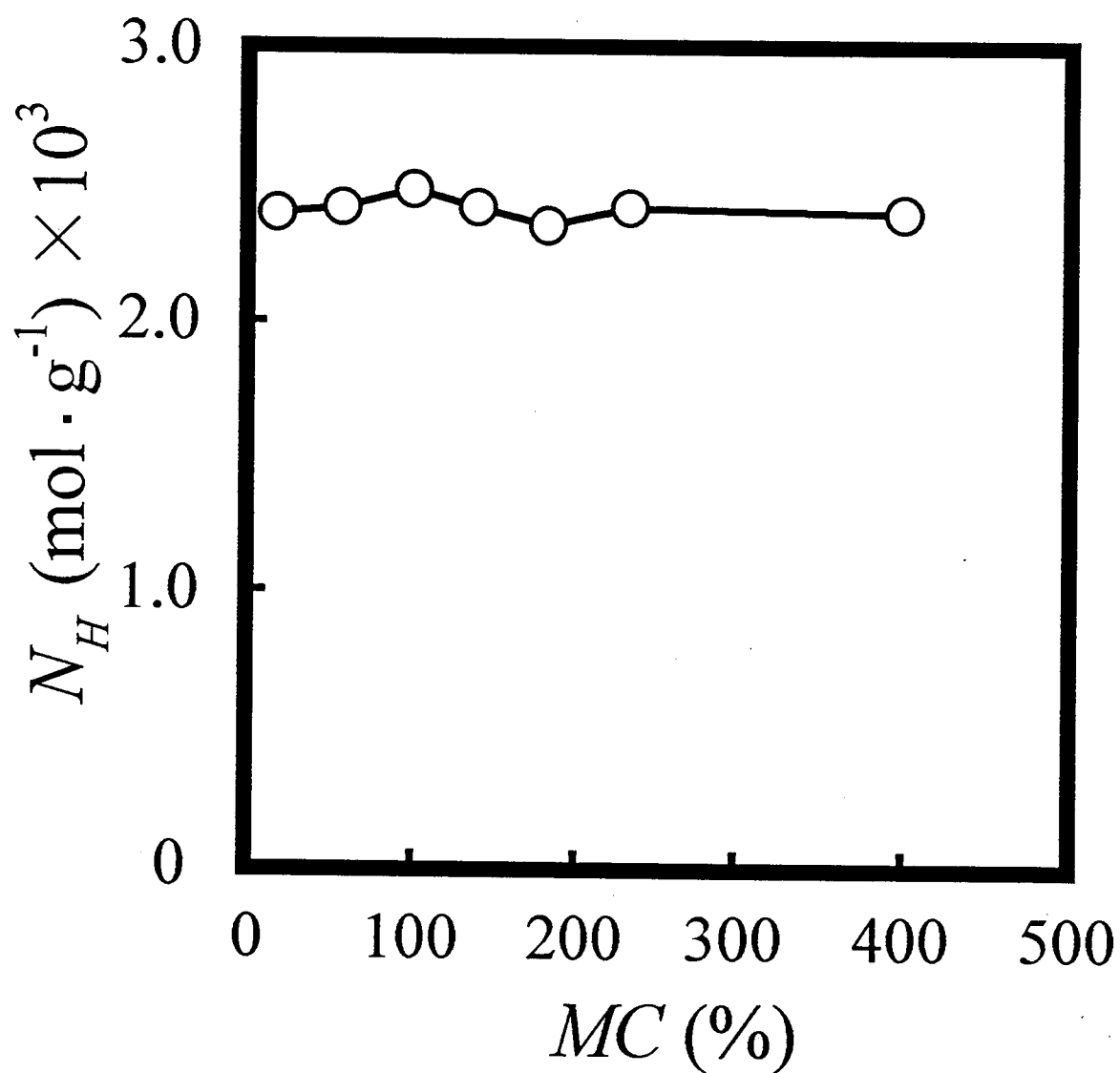


Fig.3-7 Relation between adsorbent's moisture content and the number of total adsorption sites (surface hydroxyl groups), N_H .

3.3.2 Adsorption Kinetics of HTO

Kinetic adsorption experiments for uranium were conducted under acidic conditions and the initial concentrations of uranium were kept constant to be $1.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$. The results are shown in **Fig.3-8**. X_t in the ordinate represents the amount of uranium adsorbed at time t (h). All the adsorption time-courses clearly show an interesting feature; It seems some amount of uranium had been adsorbed immediately after the adsorption started. This fact strongly suggests that the adsorption process of uranium onto the present adsorbents consists of two steps: one with a very rapid adsorption rate and another with a considerably slow rate. These two steps should correspond to the adsorption processes of uranyl cation onto the sites in easily accessible pores (macro-pore sites) and onto the sites in relatively small pores (meso-pore sites), respectively. In latter adsorption, the rate should be controlled by pore diffusion.

3.3.3 Pore Shrinkage of HTO by Dehydration

To confirm the above presumption and to discuss quantitatively about the influence of dehydration process on the kinetics of uranium adsorption, the numbers of macro-pore, meso-pore and micro-pore sites, (N_{mac} , N_{mes} and N_{mic} ($\text{mol} \cdot \text{g}^{-1}$), respectively), were estimated for each of the adsorbent. The micro-pore sites are not available for uranium but for proton. For obtaining these numbers from the kinetic data in Fig.3-8, the following assumptions were made. (1) The adsorption rate of uranium onto macro-pore sites is enough rapid and the adsorption equilibrium is reached almost instantaneously. (2) The

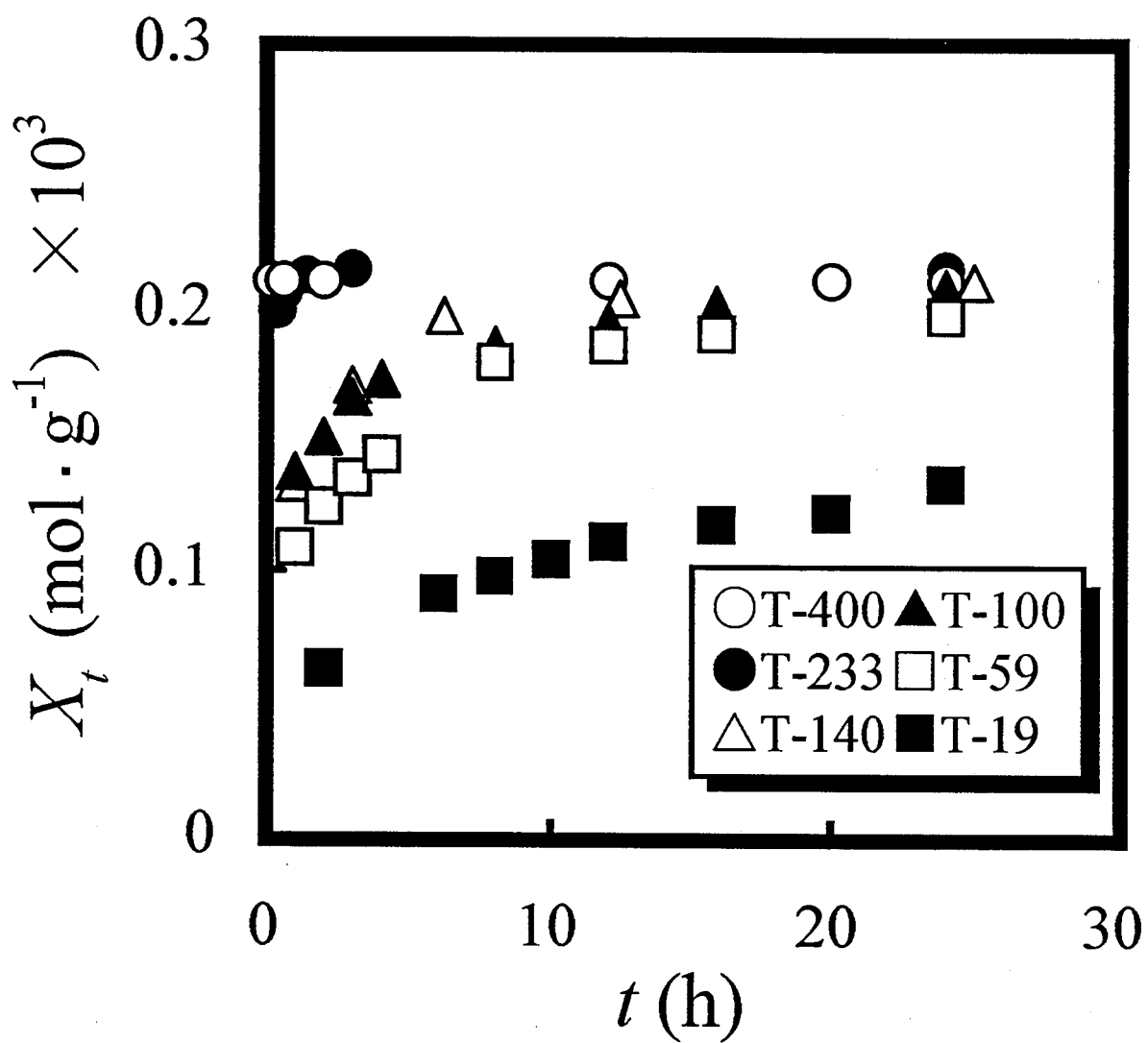


Fig.3-8 Time dependence of uranium adsorption at 30°C. Initial concentration of uranium is $1.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$.

kinetics of meso-pore adsorption can be approximated to a first-order reaction with the rate constant k (h^{-1}) as

$$X_t - X_{mac} = (X_M - X_{mac})(1 - e^{-kt}) \quad [3-1]$$

or

$$\ln \frac{1 - X_t / X_M}{1 - f} = -kt \quad [3-2]$$

where

$$f \equiv X_{mac} / X_M = N_{mac} / N_M \quad [3-3]$$

A nonlinear least-square method was applied to find two constants, f and k , in Eq.[3-2]. At the calculation the last data of X_t were adopted as X_M (the equilibrium value). The obtained constants for each of the adsorbents gave an excellent fit with the experimental data as is seen in **Fig.3-9**. As N_M is already known from the static experiment, N_{mac} , N_{mes} and N_{mic} were obtained as

$$N_{mac} = f \cdot N_M \quad [3-4]$$

$$N_{mes} = N_M - N_{mac} \quad [3-5]$$

and

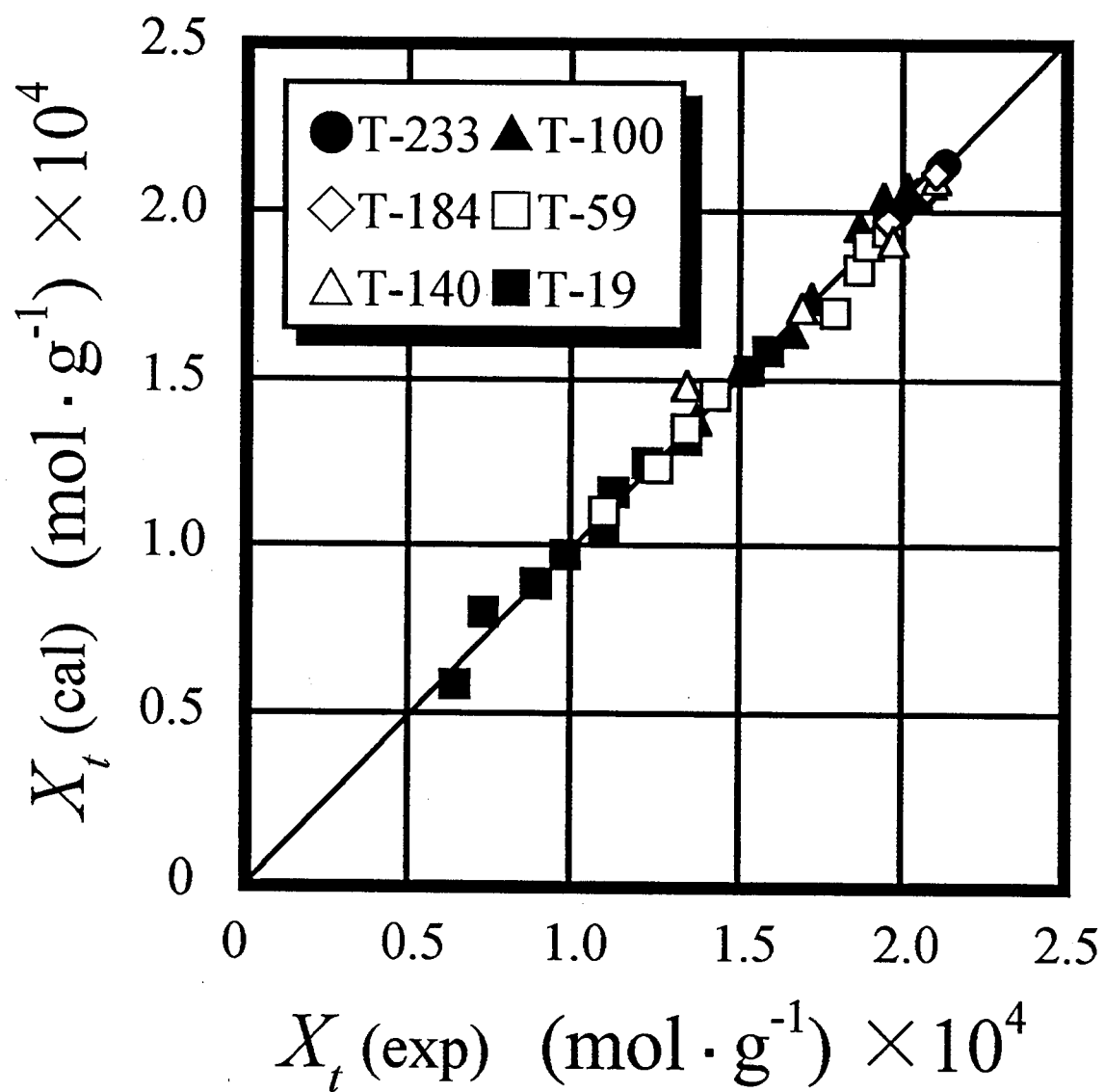


Fig.3-9 Comparison of the data of Fig.3-8 with a first-order kinetic model (Eq. [3-2]).

$$N_{mic} = N_H - N_M$$

[3-6]

The calculated values of f , k , N_{mac} , N_{mes} and N_{mic} for each of the adsorbents are summarized in Table 3-1 with N_M and $K_M(0)$ obtained from Fig.3-3. **Figure 3-10** shows the variation of pore composition with moisture content, and **Fig.3-11** shows the influence of moisture content on the rate constant of meso-pore adsorption process. It should be noted from these figures that by dehydration the macro- and meso-pores were converted to the meso- and micro-pores, respectively. The figures (particularly, Fig.3-11) also demonstrate a very interesting fact that the present adsorbent took either dry-type or wet-type pore structure by moisture content, and the structure conversion occurred at the moisture content of about 150%. The adsorbents with wet-type structure had a weak mechanical strength, but they had a lot of available sites in which the macro-pore sites were predominant. On the other hand, in the adsorbents with dry-type structure the number of macro-pore sites decreased with the decrease of moisture content, while that of meso-pore sites slightly increased. The critical condition (150% moisture content) will give a useful reference to determine an optimum degree of dehydration in adsorbent preparation.

Based on the results obtained in this work, it should be concluded that HTO (probably the other hydrous metal oxides) with more moisture content is more excellent in both of static and kinetic adsorption characteristics. Therefore, it is undesirable to prepare overdried adsorbents. Most of practical adsorbents had lost the majority of macro-pore sites, since they were commonly prepared in a well-dried state (1 - 5% of moisture content). Moreover, their number of total

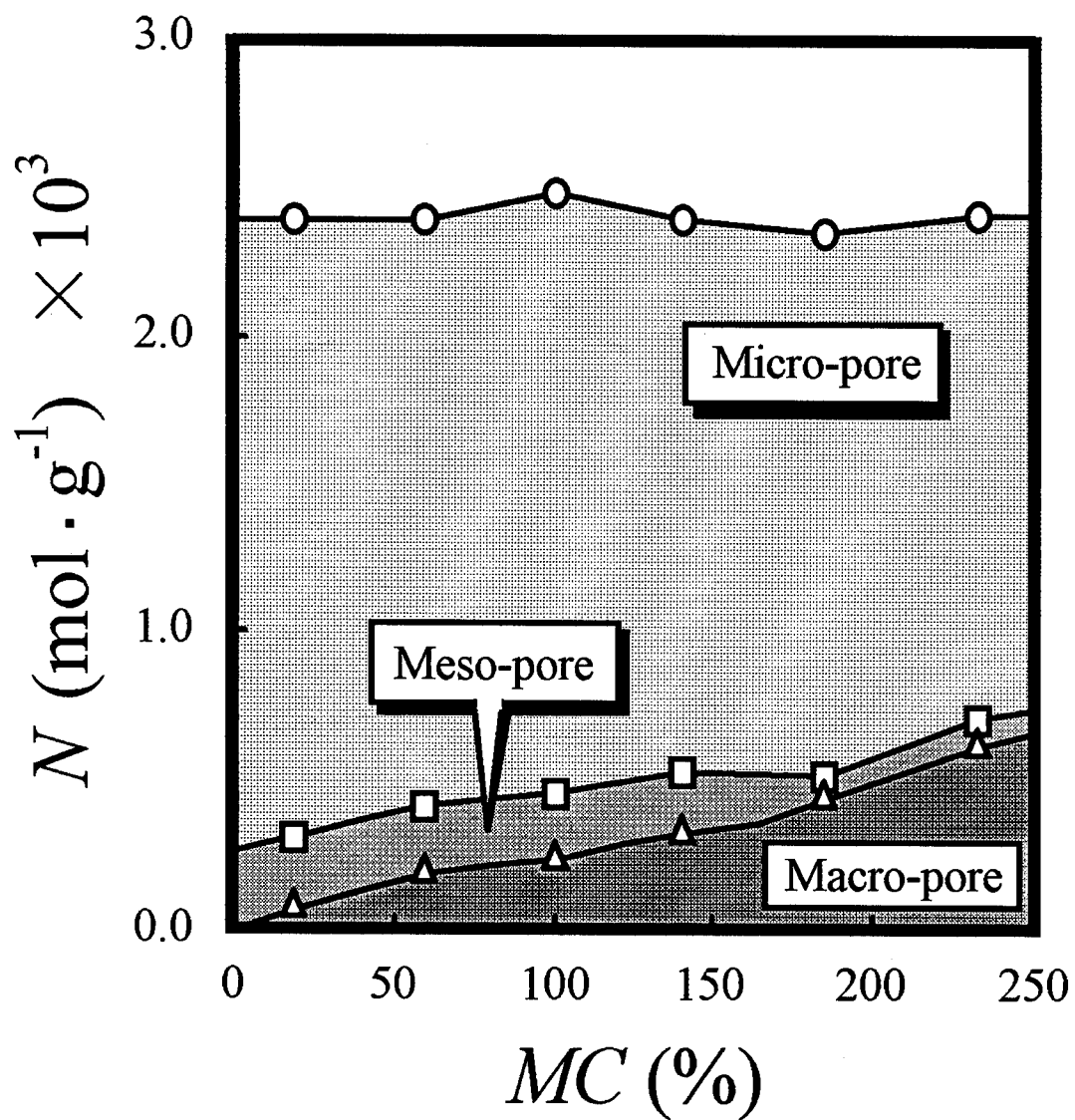


Fig.3-10 Variation of the amounts of macro-, meso- and micro-pore sites in hydrous titanium(IV) oxide with moisture content.

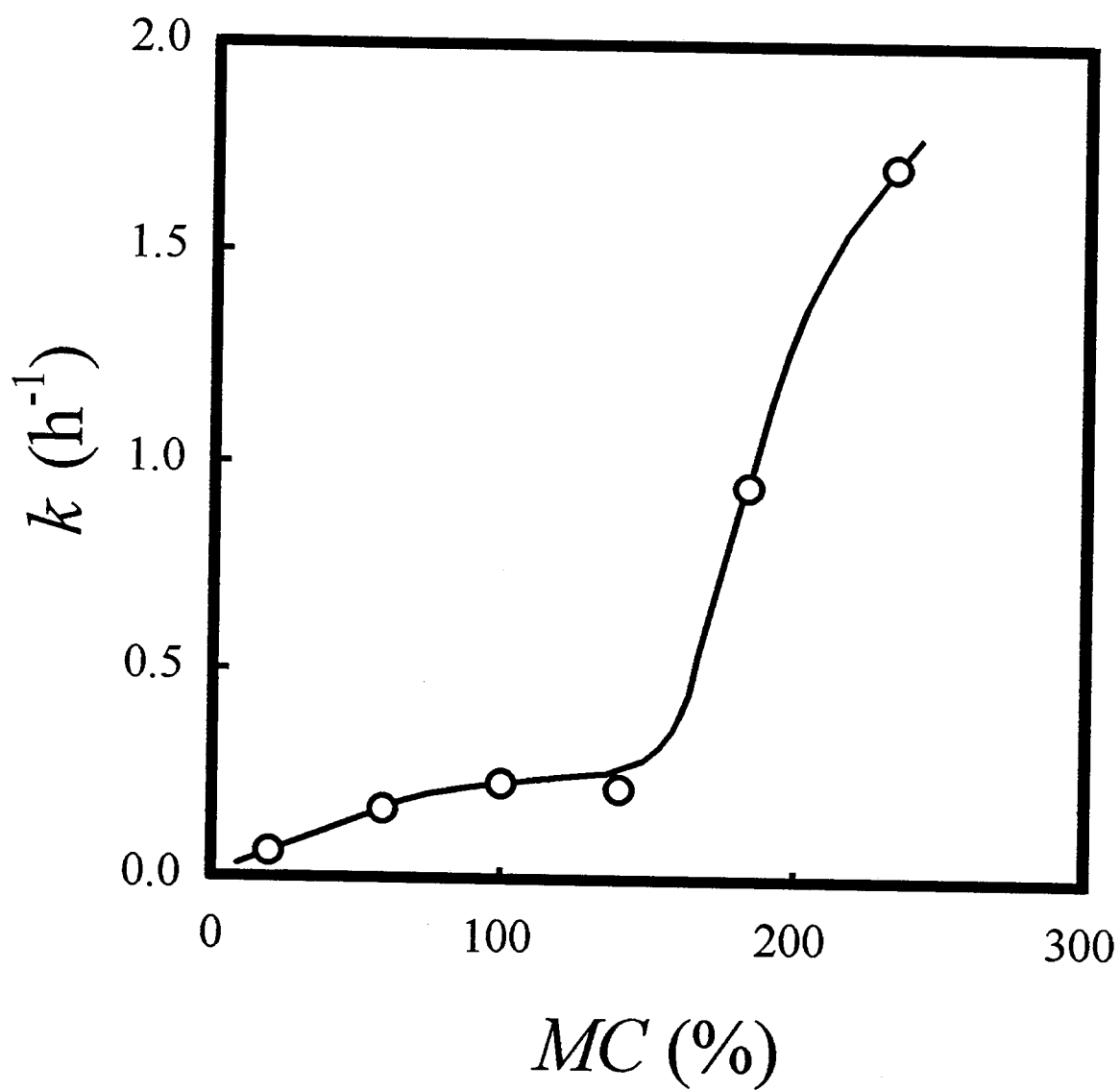


Fig.3-11 Adsorption rate constants of uranium onto meso-pore sites in hydrous titanium(IV) oxide with various moisture contents.

available sites should be reduced to about 1/3 as compared with them in wet state.

3.4 Conclusions

The equilibrium and kinetic data of uranium adsorption experiments onto hydrous titanium(IV) oxides with various moisture contents were compared with a model proposed in the preceding chapter and with a mathematical expression for adsorption kinetics given in the present work, respectively. On the basis of these results, the followings were concluded.

(1) The equilibrium data agreed well with the adsorption model, independent of moisture content. The number of available adsorption sites for uranium decreased abruptly with the decrease of moisture content in the range of moisture content < 230%, while the number of total adsorption sites was kept constant through dehydration process.

(2) The kinetic adsorption data revealed that the adsorption process of uranium onto the present adsorbents composed of the two steps, that is, macro-pore and meso-pore adsorption processes. The adsorption rate in the meso-pore process was apparently controlled by the pore diffusion of uranyl cation, while the macro-pore process proceeded very rapidly.

(3) As the moisture content decreased by dehydration, the pore contraction took place in the adsorbent as macro-pore meso-pore micro-pore. According to the moisture content, the adsorbent took either pore structure of dry-type or wet-type, and the structure conversion occurred at the moisture content of about 150%.

3.5 Nomenclature

γ	= surface density of hydroxyl groups on adsorbent	(mol·m ⁻²)
$K_H(n)$	= equilibrium constant for proton adsorption defined by Eq.[2-9]	((dm·mol ⁻¹) ⁿ)
$K_M(n)$	= equilibrium constant for metal ion adsorption defined by Eq.[2-14]	((mol·dm ⁻¹) ⁿ⁻¹)
m	= mass of adsorbent	(g)
N_H	= amount of adsorption sites available for protons	(mol·g ⁻¹)
N_M	= amount of adsorption sites available for metal ions	(mol·g ⁻¹)
θ_M	= fraction of adsorption sites complexated with metal ions	(-)
X_M	= amount of adsorbed metal ions	(mol·g ⁻¹)
X_t	= amount of adsorbed metal ions at time t	(mol·g ⁻¹)

4. GENERAL CONCLUSIONS

A general adsorption model for divalent metal ions and hydrous metal oxides system proposed in Chapter 1. The theoretical adsorption isotherm was confirmed by several experiments using uranium, lead, cadmium and zinc ions as adsorbates. In Chapter 2, the influence of dehydration process on the pore structure of HTO was quantitatively discussed based on the adsorption model and a mathematical model for adsorption kinetics. The general conclusions are:

(1) A metal ion complexed with a single surface hydroxyl group, even though it was divalent.

(2) Even in carbonate solutions, the active species in uranium adsorption on HTO was not uranyl carbonates but free uranyl ion.

(3) In acidic region ($\text{pH} < 4$) deprotonated surface hydroxyl groups combined mainly with free uranils (UO_2^{2+}) and in neutral or basic region ($\text{pH} > 4$) they complexed with uranyl hydroxides ($\text{UO}_2(\text{OH})^+$).

(4) The number of available adsorption sites for uranium decreased abruptly with the decrease of moisture content in the range of moisture content $< 230\%$, while the number of total adsorption sites was kept constant through dehydration process.

(5) As the moisture content decreased by dehydration, the pore contraction took place in the adsorbent as macro-pore meso-pore micro-pore. According to the moisture content, the adsorbent took either pore structure of dry-type or wet-type, and the structure conversion occurred at the moisture content of about 150%.

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PART II

APPLICATIONS OF HUMIC ACID TO AQUEOUS-PHASE SEPARATION OF METAL IONS

1 GENERAL INTRODUCTION

For the recovery of valuable elements or the removal of harmful heavy metals from aqueous environments, adsorption is one of the most promising technique. Many biopolymers derived from microbes and plants are known to bind metals strongly. The use of biopolymers as adsorbents has been a topic of intense research in recent years (7,13,14,15,19). Jang et al.(14) developed a loop fluidized bed reactor for the separation of dissolved copper and cobalt ions, in which alginic acid was used as an adsorbent. However, the percentage of metal complexing agent(alginic acid) in the whole adsorbent was only about 3% on a wet weight basis.

Humic substances are widely present in natural waters and soils. They are formed by random condensation of breakdown products of terrestrial and aquatic plants and extracellular metabolites of phytoplankton. Humic substances are usually divided into two fractions, humic acid (HA) and fulvic acid (FA). HA is defined in operational terms as the fraction of humic substance soluble in alkaline solutions and insoluble in acidic solutions, while FA is the fraction soluble in both alkaline and acidic solutions. Both of them have a high complexing ability with various heavy metal ions. Moreover, they are ecologically acceptable matter. Most previous studies dealt with the structure and the nature of humic substances or their complexes (4,5,6,8,9,20,22,26,31,33,34). As a few examples of their practical applications, Heitkamp and Wagener (10) and Ho and Miller (11) tried to use HA for the recovery of uranium. However, it is difficult to use HA as the sole

adsorbent because of their high solubility in water. To immobilize it, Heitkamp and Wagener, and Ho and Miller employed anion exchange resins and hematite particles as the carriers, respectively. Since the carriers are almost inert materials in adsorption, the ratio of HA to the carrier is very important. In the studies mentioned above, the percentage of HA in the whole adsorbent was only 25% (10) or 3.5% (11) on a dry-weight basis.

The purpose of this study is to develop new HA adsorbents for the aqueous-phase separation of metal ions, and investigate the adsorption mechanism and the ability of the newly developed adsorbents. In the field of biotechnology, the techniques of immobilizing various enzymes have been investigated for their practical application (1,16,18,28,29). The formation of calcium alginate gels allows of immobilization of biological materials under mild conditions (17). This technology, which has been used extensively for the immobilization of living cells and of enzymes, was applied to the immobilization of HA. By the immobilizing method, a spherical adsorbent (HA-gel) in which HA was immobilized by a combination of calcium alginate gel and activated carbon powder(ACP) was obtained.

In the following chapter, The conditions for preparing HA-gel such as alginate concentration, ACP concentration, gelation time and calcium concentration will be discussed.

In Chapter 3, the metal adsorption ability of HA-gel was examined using lead ion as an adsorbate. Based on a simple model for the complexation between divalent metal ions and organic polymers in acidic media ($\text{pH} < 4.5$), the metal complexation strength and capacity of HA, alginic acid(AA) and HA-

gel will be quantitatively discussed.

In Chapter 4, a membranous HA-gel (HA-M) was developed in order to increase the adsorption rate. Based on the complexation model presented in Chapter 3 and a simple mathematical model for complexation kinetics, influence of the immobilization on the lead complexation capacity and kinetics of HA will be quantitatively discussed. For the regeneration of HA-M, the desorption of lead from HA-gel will also be discussed.

In Chapter 5, another HA insolubilized by heating treatment (IHA) was prepared. A general complexation model for the complexation of divalent metal ions on organic polymers with acidic groups will be derived, based on two equilibrium reactions, that is, deprotonation of acidic groups (adsorption sites) on the organic polymer and complexation of metal ions with the deprotonated sites. The theoretical adsorption isotherm will be confirmed by experiments carried out in the range of about pH3 to pH6.5 using lead and cadmium ions as adsorbates. From the model, the numbers of proton binding and metal binding acidic groups, and the acid-dissociation and metal-complexation constants of HA and IHA will be determined. Based on these parameters, the effect of insolubilization on the metal-complexation ability of HA will also be discussed.

2 IMMOBILIZATION OF HUMIC ACID IN CALCIUM ALGINATE GEL

2.1 Introduction

For the aqueous-phase separation of metal ions, a new adsorbent of immobilized humic acid, HA-gel, was developed. Humic acid(HA) has an excellent complexing ability with heavy metals, while it easily dissolves in water.

In this chapter, the conditions for preparing HA-gel was dealt with. The formation of calcium alginate gels allows of immobilization of biological materials under mild conditions (17). This technology, which has been used extensively for the immobilization of living cells and of enzymes, was applied to the immobilization of HA. Since the calcium alginate gel allows the migration of molecular relatively easily, the technique has limited application for immobilizing macromolecules. HA has a wide molecular weight distribution, and the lower molecular weight component of HA may discharge from calcium alginate gels. Then, another immobilizing agent, activated carbon powder (ACP), was used in combination with calcium alginate gel to entrap the lower molecular weight component of HA. For the development of a new adsorbent, the conditions for preparing HA-gel such as alginate concentration, ACP concentration, gelation time and calcium concentration will be discussed.

2.2 Experimental

2.2.1 Materials

Sodium salt of alginic acid (AA) and humic acid (HA) were obtained from Wako Pure Chemical Industries and Aldrich Chemical Co., respectively. They were used without further purification. Activated carbon powder (ACP) was purchased from Wako Pure Chemical Industries. It was screened by a 100-mesh (0.149-mm) sieve and the undersize fraction was used.

2.2.2 Immobilization of HA

Aqueous solutions of AA and HA containing ACP were well mixed. It was extruded, dropwise, into an excess of CaCl_2 solution in a stirred vessel. The particles of HA-entrapped calcium alginate (HA-gel) were left to harden in the CaCl_2 solution. The formed HA-gel was removed from the solution and it was washed repeatedly with distilled water.

2.2.3 Conductometric Titration

The number of acidic groups of AA and HA was determined by conductometric titrations (12). For this purpose AA or HA sodium salt was added to 0.3 dm^3 of distilled water and mechanically stirred at 30°C . To eliminate CO_2 , N_2 gas was continuously bubbled through the system. After reaching the thermal equilibrium, the solution containing AA or HA was titrated with a volumetric standard solution of HNO_3 or NaOH ($0.1 \text{ mol}\cdot\text{dm}^{-3}$). The conductivity of the solution was measured by a conductometer (TOA

Digital Conductometer CM-15A).

2.2.4 Effectiveness of Immobilization

HA-gel was prepared varying AA, HA, ACP and CaCl_2 concentrations. The HA-gel was mechanically stirred in distilled water or 0.1 M CaCl_2 solution at 30 °C . The concentration of HA in bulk phase was measured in order to determine the discharge of HA from HA-gel. The concentration of HA was measured by a spectrophotometric method at 300 nm.

2.3 Results and Discussion

2.3.1 Number of Acidic Groups

The structure and the properties of HA, in general, greatly depend on the HA's origin. AA, used here as the immobilizing agent, also has a complexing ability with divalent metal ions. The number of titrable acidic groups of AA and HA was determined as an indication of their metal complexing capacity. **Figure 2-1** shows the conductometric titration curves for 300 cm³ of a solution containing 0.2 g of AA (○) or HA (□) with 0.1M HNO_3 at 30°C. The titration curve gives the end point by the intersection of two straight lines. No end point was obtained from the titration with 0.1M NaOH. The endpoint or endpoints can be used to estimate the analytical number or concentration of acidic groups present (9). The total number of acidic groups on AA and HA were determined from these titration curves as 4.01×10^{-3} and 3.40×10^{-3} mol·g⁻¹, respectively. In Part I (Chapter 2), the total number of acidic groups on well-

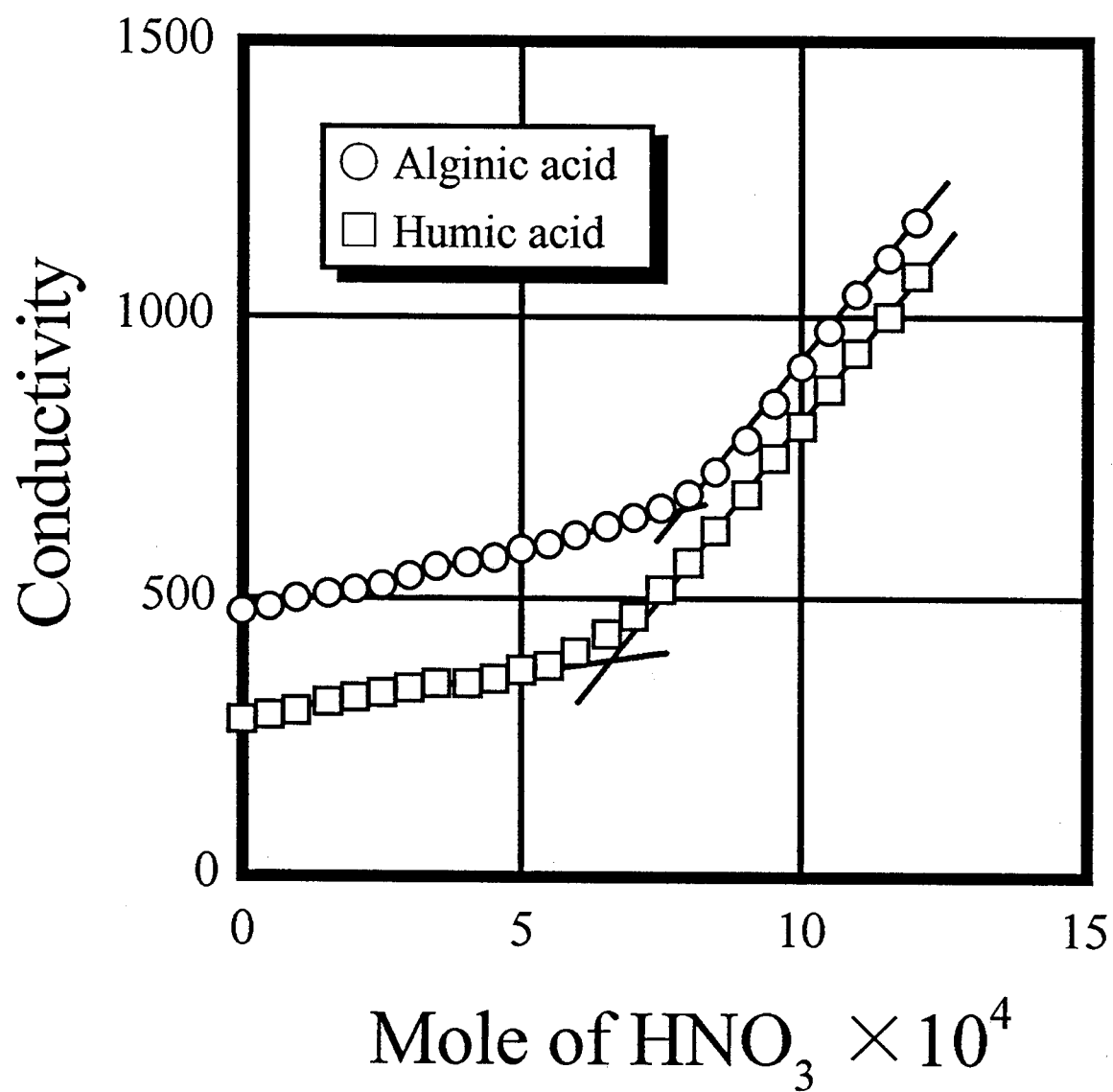


Fig.2-1. Conductometric titration curves for 300 cm³ of a solution containing 0.2g of AA or HA with 0.1 mol·dm⁻³ HNO₃ at 30°C.

known inorganic adsorbent, hydrous titanium (IV) oxide (HTO), was determined as $2.4 \times 10^{-3} \text{ mol} \cdot \text{g}^{-1}$. Comparing the proton binding capacity of AA, HA and HTO, the biopolymers used in this study are obviously superior to HTO.

2.3.2 Entrapping Effect of Calcium Alginate

Figure 2-2 shows the time dependence of the percentage of HA discharged from two kinds of calcium alginate gels. H and A represent the weight percentages of HA and AA initially contained in the wet gel, respectively. Calcium alginate gel particles containing HA were formed in 0.1 M CaCl_2 solution and left the particles in the CaCl_2 solution for 1 h. The gels were mechanically stirred in distilled water at 30°C . The discharge of HA was stopped within 24 h. The gel containing only 1% of AA could entrap 75% of HA. Furthermore, the higher content of AA (2%) resulted in the lower discharge of HA (20%). Since calcium alginate gel has a molecular weight cut-off ability (35) and HA has a wide molecular weight distribution, the percentage of HA discharged from the gel can be regarded as the percentage of the undersize fraction of HA sieved by the gel matrix.

Figure 2-3 shows the effect of AA concentration on the percentage of HA discharged from calcium alginate gel. The gels containing 5% of HA were prepared in the same manner as mentioned above. The gels were stirred in distilled water at 30°C for 24 h. The discharge of HA decreased with the increase of AA concentration, however, it was not so effective. In addition,

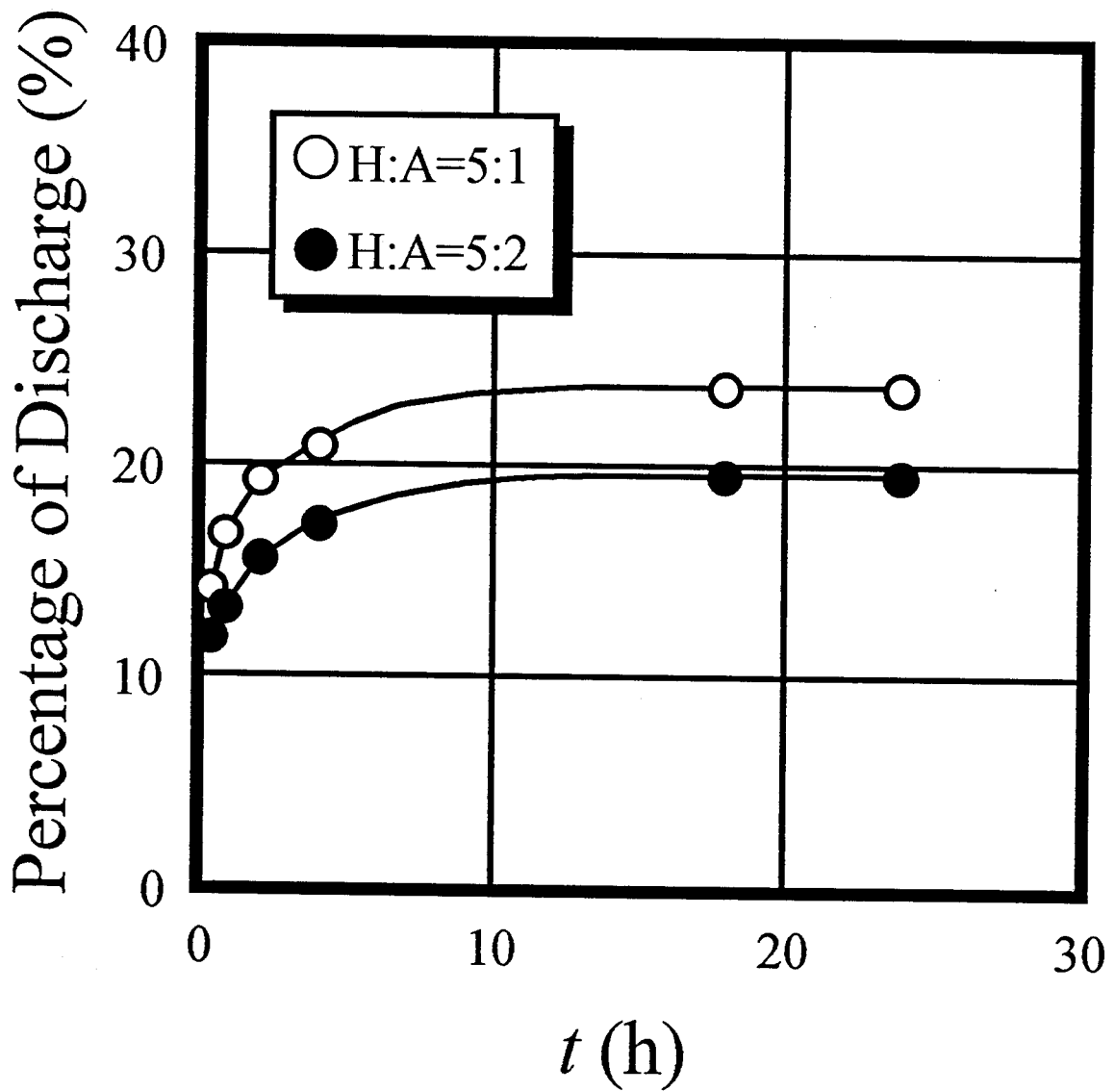


Fig.2-2. Time dependence of the percentage of HA discharged from calcium alginate gel (in the absence of ACP) in distilled water at 30°C. H and A represent the weight percentages of HA and AA initially contained in the wet gel, respectively.

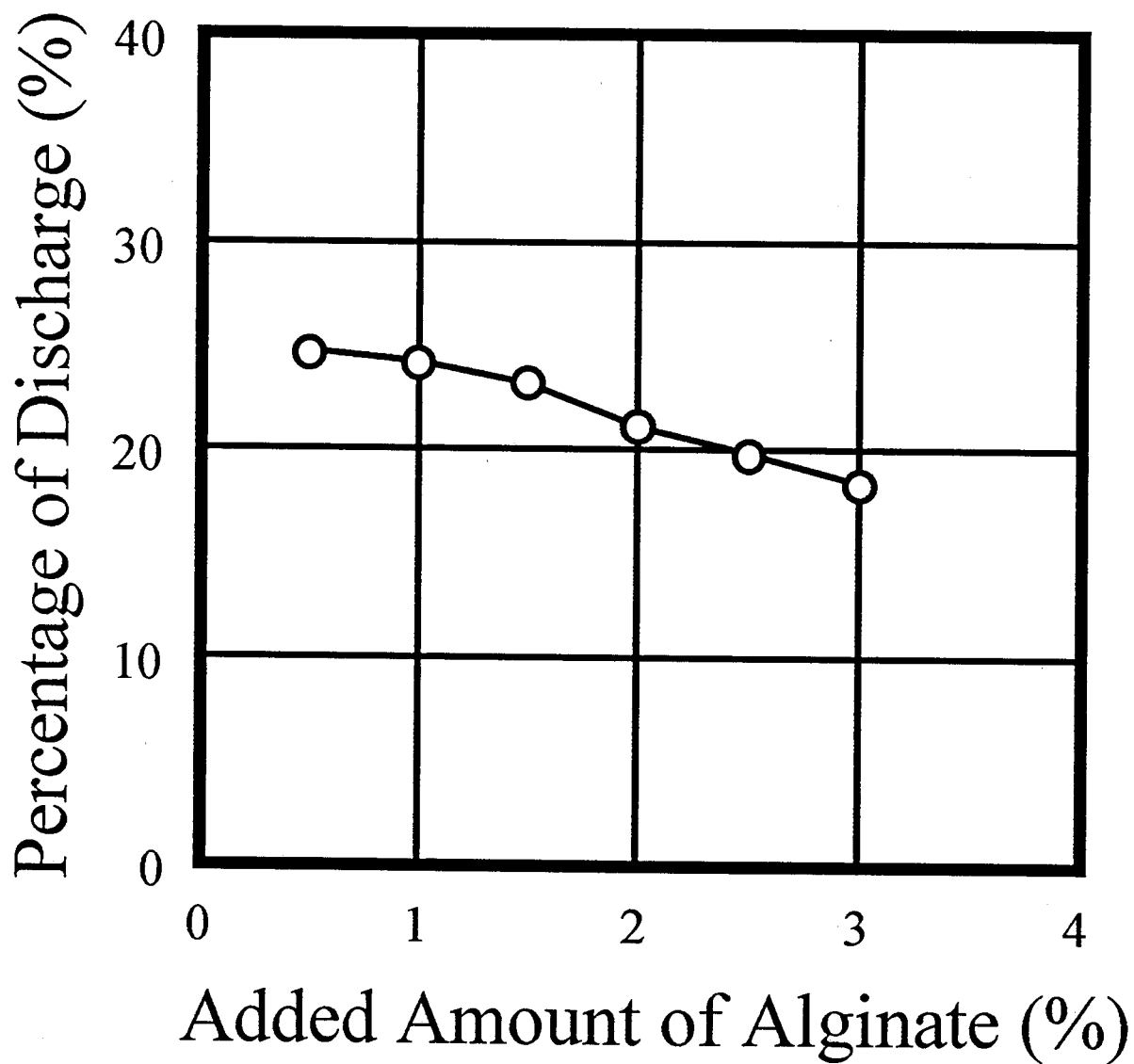


Fig.2-3. Effect of AA concentration on the percentage of HA discharged from calcium alginate gel containing 5 wt-% HA (in the absence of ACP) in distilled water at 30°C.

because of the poor solubility of AA in water and the high viscosity of its solution, the optimum AA concentration for the preparation of HA-gel was determined as 1%.

2.3.3 Entrapping Effect of Activated Carbon Powder

The matrix of calcium alginate gel could not entrap lower molecular weight HA and about 25% of HA was discharged from the gel's interior to the water phase. As the metal complexation capacity of lower molecular weight HA is 2-6 times larger than that of higher molecular weight HA (27), it is important to entrap the lower molecular weight HA in the adsorbent. Activated carbon is an effective adsorbent for the removal of humic substance dissolved in water. Humic substance divided into lower (apparent molecular weight 100-1000 as polyethylene glycol) and higher (apparent molecular weight 1000-5000 as polyethylene glycol) molecular weight fractions are adsorbed well onto micro- and meso-pores of activated carbon, respectively (25). Taking into account these facts, it can be expected that the addition of ACP to calcium alginate gel is effective to prevent the escape of lower molecular weight HA. However, the excess addition of ACP may inhibit the formation of HA-gel. **Figure 2-4** shows the effect of ACP concentration on the percentage of HA discharged from HA-gels. The gels were prepared in 0.1 M CaCl_2 solution and stirred in the solution at 30°C for 24 h. *R* represents the weight ratio of ACP to HA initially contained in the HA-gels. The discharge of HA decreased with the increase of the ACP concentration, and the discharge was almost completely prevented by the addition of the HA's weight in ACP.

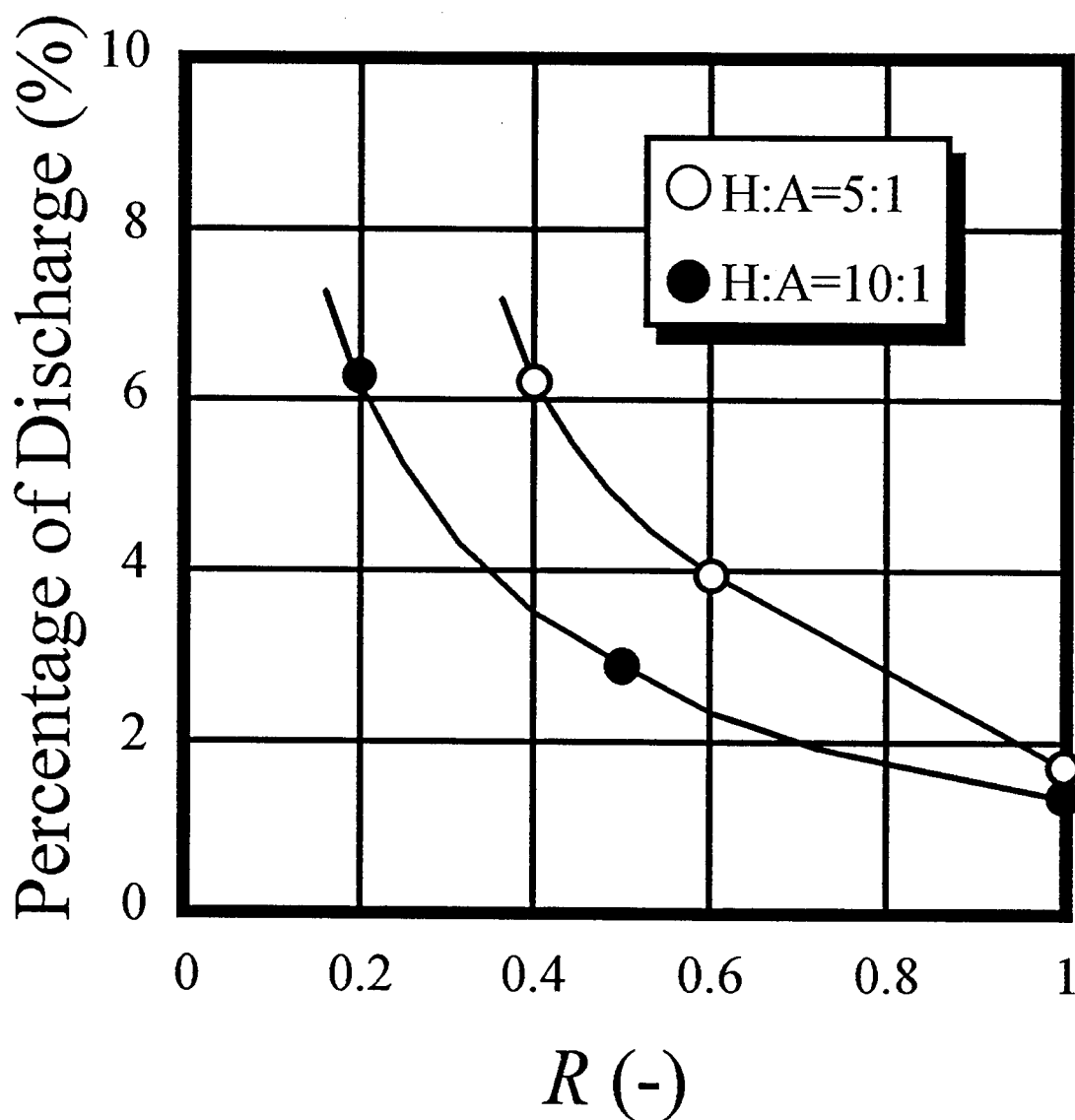


Fig.2-4.Effect of ACP concentration on the percentage of HA discharged from HA-gels in 0.1M CaCl_2 solution at 30 °C. R represents the weight ratio of ACP to HA initially contained in the HA-gels.

2.3.4 Effect of CaCl_2 Concentration and Gelation Time

The percentages of HA discharged from HA-gels in solutions of various CaCl_2 concentrations were shown in Fig.2-5. The gels were formed in solutions of various concentrations and stirred in the solutions at 30°C for 24 h. H, C and A represent the weight percentages of HA, ACP and AA initially contained in the wet gel, respectively. From the results shown in Fig.2-5, the addition of the same weight of ACP as HA almost completely prevented the discharge of HA. The formation of HA-gel was not possible at concentrations up to 0.03 M (grayed region in Fig.2-5). Rigid and spherical HA-gels could be formed at concentrations above 0.05 M, and the discharge of HA in 0.1 M CaCl_2 solution was negligible. Figure2-6 shows the percentage of HA discharged from HA-gels prepared with various gelation times, t . HA-gels prepared in 0.1 M CaCl_2 solution with various gelation times were stirred in distilled water at 30°C for 24 h. The gelation of HA-gel was completed within 30 min and the discharge of HA was essentially negligible. From the results shown in Figs.2-5 and 2-6, the optimum concentration of CaCl_2 and the gelation time for the preparation of HA-gel were determined as 0.1 M and 30 min.

2.4 Conclusions

For the aqueous-phase separation of metal ions, a new adsorbent of immobilized humic acid, HA-gel, was developed. HA, which has an excellent complexing ability with heavy metals, was immobilized by calcium alginate gel

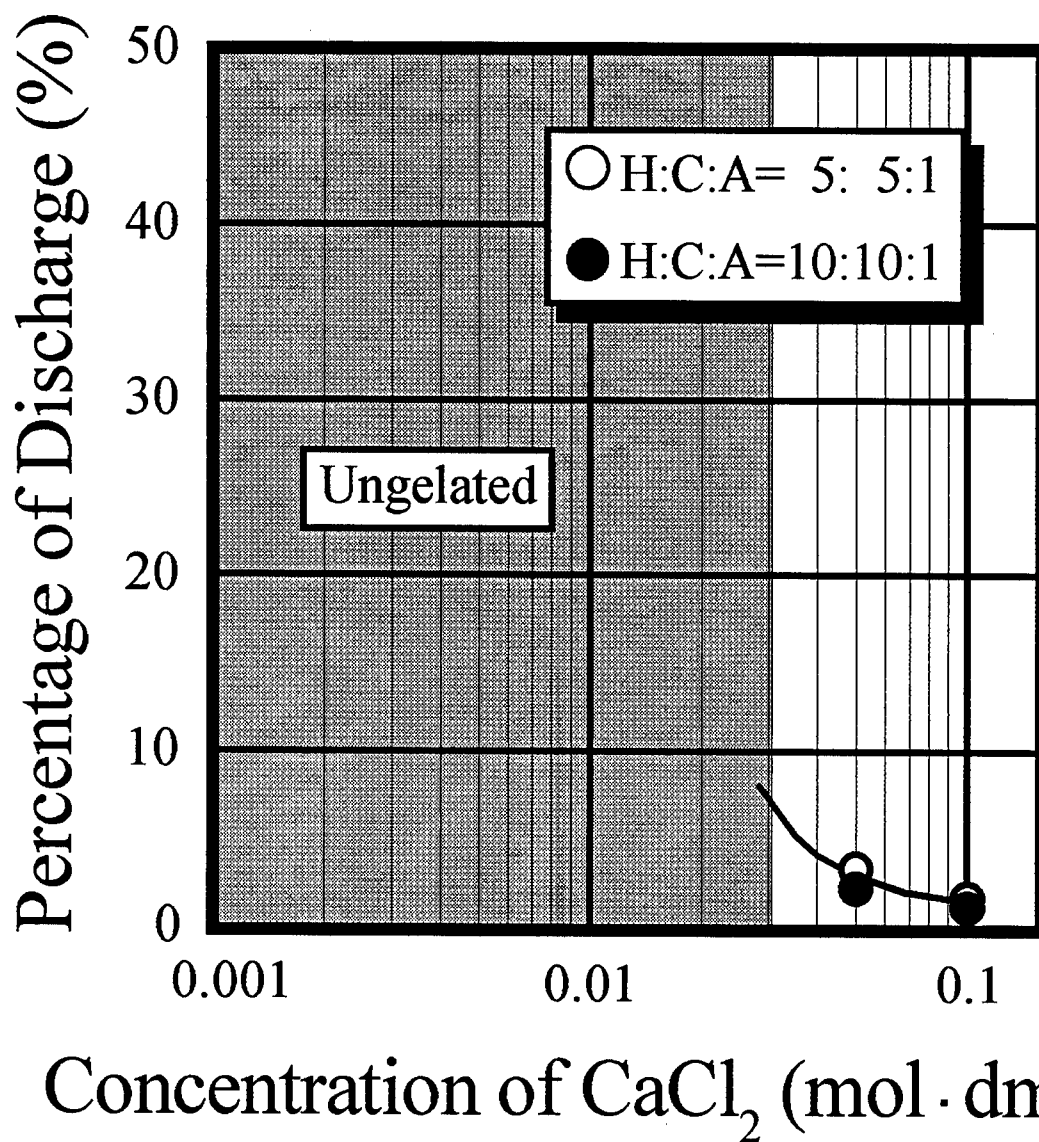


Fig.2-5. The percentages of HA discharged from HA-gels in solutions of various CaCl_2 concentrations at 30°C . H, C, and A represent the weight percentages of HA, ACP and AA initially contained in the wet gel, respectively.

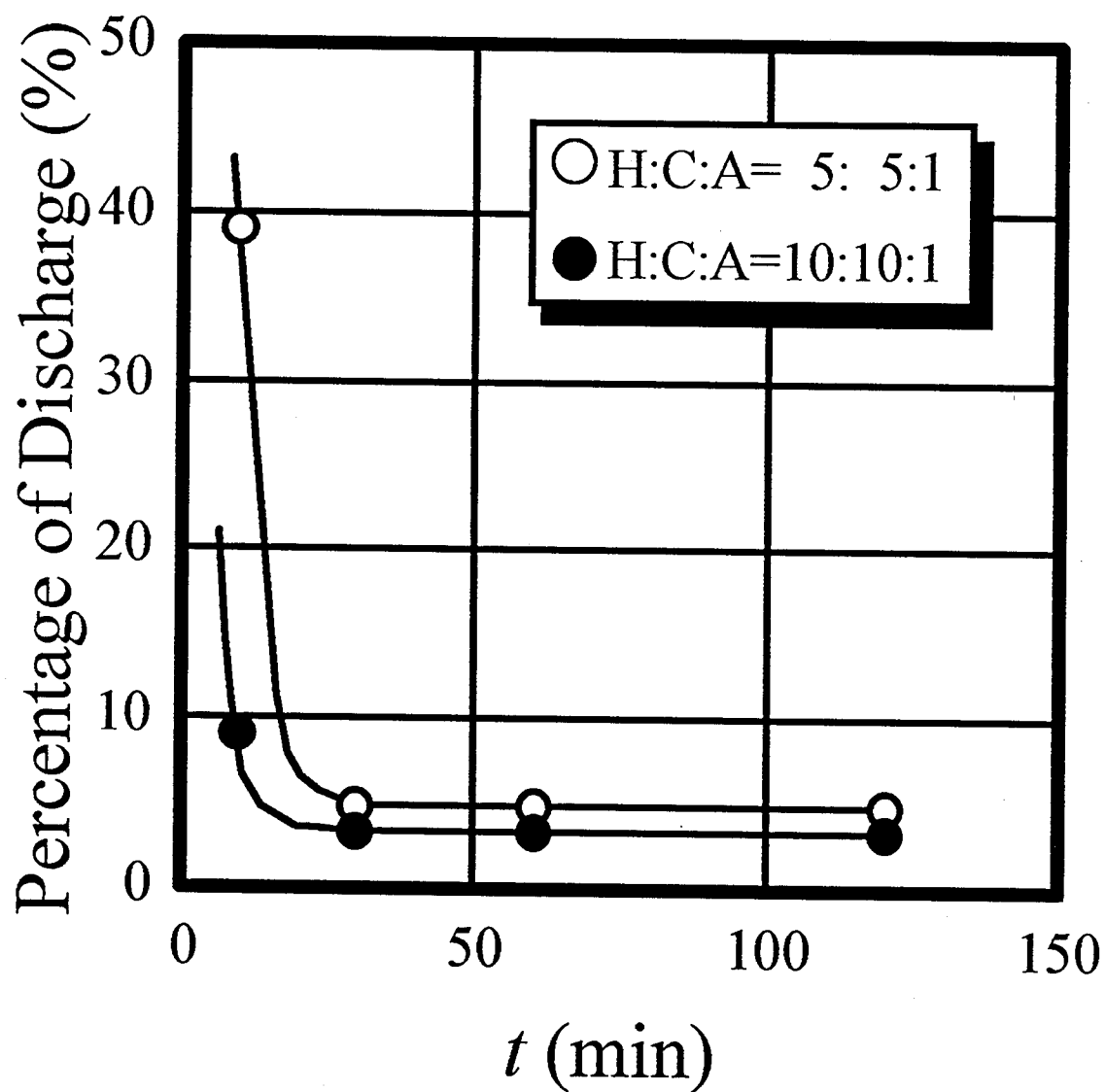


Fig.2-6. The percentages of HA discharged from HA-gels with various gelation times, t [min], in distilled water at 30°C. Prior to this experiments, the gels were immersed in 0.1M CaCl_2 solutions for various time periods.

in combination with activated carbon powder. The conditions for preparing HA-gel were experimentally examined. Proton binding capacity of HA and AA were determined as an indication of metal complexation capacity. On the basis of these results, the followings were concluded.

(1) The proton binding capacity of HA was determined by the conductometric titration as $3.40 \times 10^{-3} \text{ mol} \cdot \text{g}^{-1}$. AA, used as an immobilizing agent, also had the proton binding capacity of $4.01 \times 10^{-3} \text{ mol} \cdot \text{g}^{-1}$.

(2) Calcium alginate gel effectively entrapped higher molecular weight component of HA and ACP was effective for lower molecular weight component. HA was almost completely entrapped by a combination of these two immobilizing agents.

(3) Optimum conditions for preparing HA-gel were determined as follows. AA: 1 wt-%, ACP: HA's weight in ACP, CaCl_2 : 0.1 M, gelation time: 30 min.

(4) This immobilizing technique enabled the preparation of HA-gel comprising as much as about 50 wt-% HA on dry-weight basis or 15 wt-% on wet-weight basis.

3 ADSORPTION OF LEAD IONS ON HUMIC ACID IMMOBILIZED BY CALCIUM ALGINATE PARTICLE

3.1 Introduction

The preceding chapter have dealt with the immobilization technique of HA by the use of two carrier materials, that is, calcium alginate and activated carbon powder (ACP). By the immobilizing technique, a new adsorbent (HA-gel) comprising as much as about 50% of HA on a dry-weight basis was obtained. Heitkamp and Wagener (10) and Ho and Miller (11) tried to use HA immobilized by anion exchange resins (10) or hematite particles (11) for the recovery of uranium. In these studies, the percentage of HA in the whole adsorbents was only 25 % or 3.5 % on a dry-weight basis, respectively. Comparing the metal-complexing capacity of HA-gel and these HA-immobilizing adsorbents with HA contents, HA-gel is obviously superior to others.

In this chapter, the adsorption of lead ions on HA-gel was investigated. Based on a simple model for the complexation of divalent metal ions on organic polymers with acidic groups, the adsorption mechanism and the ability of this newly developed adsorbent will be discussed.

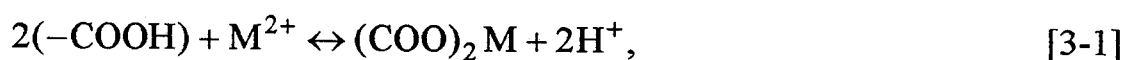
3.2 A Simple Organo-Metallic Complexation Model

Schnitzer and Khan (32) accounted for the acidic properties of humic compounds in terms of a range of aromatic carboxyl groups and to a lesser extent phenolic hydroxyl groups. Wilson and Kinney (36) showed that more than 90% of the COOH sites on HA were dissociated in seawater in pH 8, and virtually all the phenolic hydroxyl sites remained protonated. They also showed that only minor proportions (8-38%) of the acidic sites on dissolved organic matter (DOM) are available for metal ion binding, because most of the sites are not in close proximity and do not have the polydentate characteristic necessary for chelation of metal ions.

Taking into account these facts, a simple model for the complexation of divalent heavy metal ions and an organic polymer such as humic acid in an acidic media is built. The model is based on three assumptions:

- (a) A divalent heavy metal ion binds with two sites (carboxyl groups) on an organic polymer.
- (b) The polymer has a definite number of available sites for complexation. The unavailable sites are not taken into account.
- (c) In acidic media of pH < 4.3, the available sites are either protonated to -COOH or complexed with metal ions.

From the above assumptions, the complexation of metal ions and an organic polymer in acidic media can be expressed by the cation exchange reaction,



where M^{2+} represents the divalent heavy metal ion. The complexation constant

of Eq. [1], K [mol·dm⁻³], is defined as

$$K = \frac{\alpha_M C_H^2}{\alpha_H^2 C_M}$$

$$= \frac{\alpha_M C_H^2}{(1 - \alpha_M)^2 C_M}, \quad [3-2]$$

where α_H and α_M represent the fractions of the sites on the polymers covered by H^+ and M^{2+} at the equilibrium state, respectively, and C_H and C_M [mol·dm⁻³] are the equilibrium concentrations of H^+ and M^{2+} , respectively. Defining the amount of divalent metal ions complexed with (or adsorbed on) the polymer as X_M [mol·g⁻¹], and the number of available sites for complexation as N_M [mol·g⁻¹], Eq. [3-2] is modified to

$$K = \frac{(2X_M / N_M) C_H^2}{\{1 - (2X_M / N_M)\}^2 C_M} \quad [3-3]$$

or

$$2(X_M / C_H)(C_M / X_M)^{1/2} = N_M (C_M / X_M)^{1/2} / C_H - (2N_M / K)^{1/2}. \quad [3-4]$$

Equation [3-4] represents the adsorption isotherm of divalent metal ions on the organic polymer. The plot of $2(X_M / C_H)(C_M / X_M)^{1/2}$ vs $(C_M / X_M)^{1/2} / C_H$ gives a straight line, and the parameters of N_M and K can be obtained from the slope and the intercept of the line, respectively.

3.3 Experimental

3.3.1 Adsorbent

Calcium alginate gel containing HA and ACP was used as the adsorbent. An aqueous solution containing HA (0-15%), sodium alginate (1%), and the HA's weight in activated carbon powder (ACP) was well mixed. It was extruded, dropwise, into an excess of CaCl_2 solution (0.1 M) in a stirred vessel. The particles of HA-entrapped calcium alginate (HA-gel) were left to harden in the CaCl_2 solution for 30 min. The formed HA-gel was removed from the solution and it was washed repeatedly with distilled water. The detailed preparation method of HA-gel is given in preceding chapter. The shapes of the particles were nearly spherical and they had a diameter of 2-4 mm.

3.3.2 Complexation between Lead and Humic or Alginic Acid

Kinetic experiments for the Pb-HA system were conducted to determine the time for attaining equilibrium. The reaction was carried out in a 10-mm spectrofluorometer cell (JASCO FP-550A). The extent of complexation was determined from the measurement of the intensity of fluorescence (30). The maximum emission intensity for the HA present occurred at 450 nm upon excitation at 365 nm (shown in **Fig. 3-1**). Equilibrium experiments were carried out in the following manner. A 0.285 dm³ solution containing a certain amount of $\text{Pb}(\text{NO}_3)_2$ was prepared. The pH was adjusted to a desired value by HNO_3 . A 0.015 dm³ polymer solution containing 0.015 g of HA or AA was prepared. After reaching the thermal equilibrium at 30°C, both solutions were

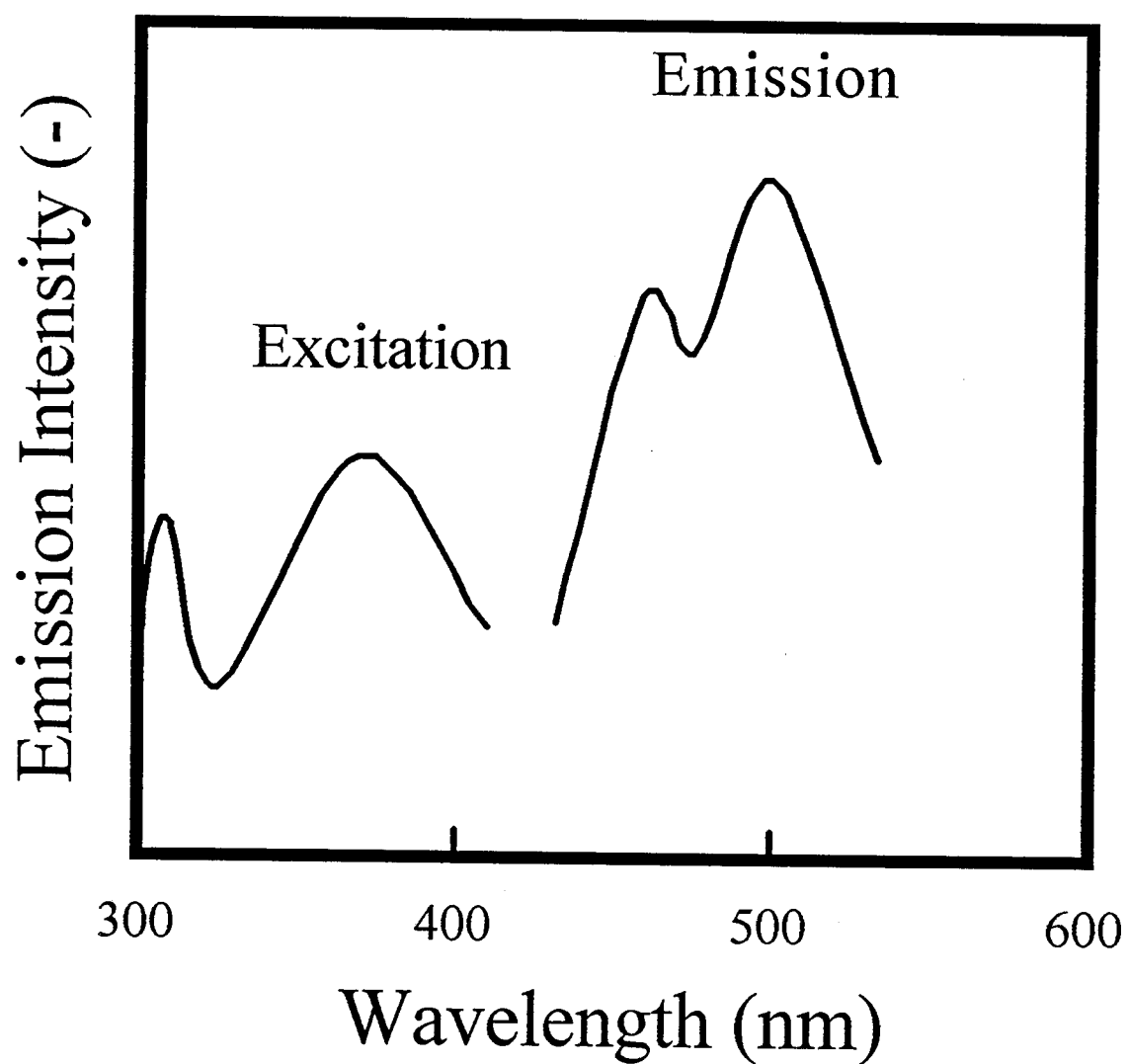


Fig.3-1. Typical excitation and emission spectra of HA. Excitation spectra are for an emission wavelength of 450 nm and emission spectra for an excitation wavelength of 370 nm.

mixed and the complexation reaction was initiated. The solution was stirred for a necessary time to attain the complexation equilibrium. Then, it was filtered through a membrane filter (pore size = 0.05 μm), and the pH and lead concentration of the filtrate were by a pH meter (Orion Research 501) and by atomic absorption spectrophotometer (Hitachi A-1800), respectively. The amount of lead complexed with the polymer was determined from the difference between the lead concentrations in the initial and the equilibrium states.

3.3.3 Adsorption of Lead on HA-gel

A 1 dm³ solution containing a necessary amount of $\text{Pb}(\text{NO}_3)_2$ was prepared and its pH was adjusted by HNO_3 . After reaching the thermal equilibrium at 30 °C, a certain amount of HA-gel (ca. 1g) was added to the solution. After reaching the adsorption equilibrium, the concentrations of lead and pH in the bulk phase were measured.

3.4 Results and Discussion

3.4.1 Organo-Metallic Complexation

The structure and the properties of humic acid, in general, greatly depend on the HA's origin. To examine the validity of the complexation model represented by Eq. [3-4] and to know the adsorption characteristics of the HA present, complexation experiments were carried out for the Pb-HA system. **Figure 3-2** shows a typical result of the kinetic experiments. The reaction

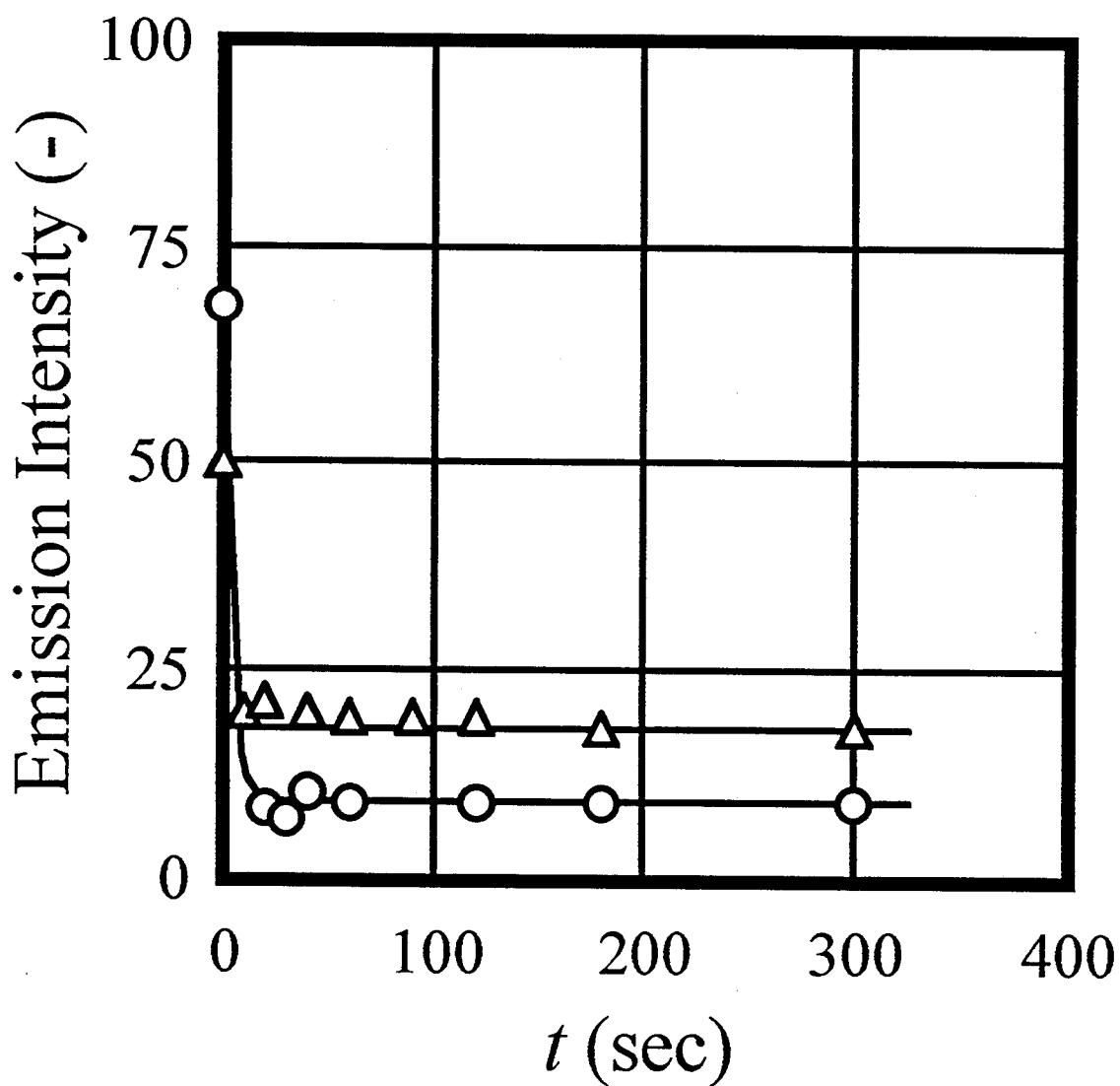


Fig.3-2. Time dependence of lead-HA complexation at 30°C. Initial concentrations of lead ion and HA are $5.0 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$ and $0.02 \text{ g} \cdot \text{dm}^{-3}$ (Δ), and $1.0 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ and $0.16 \text{ g} \cdot \text{dm}^{-3}$ ($\circ$), respectively.

proceeded very rapidly and a few seconds or so were enough to attain the equilibrium. From the results the contact time for the equilibrium experiments (shown in **Fig.3-3**) was determined as 30 min. The ordinate of Fig.3-3, X_{MHA} , represents the equilibrium amount of Pb complexed with 1 g of HA. The figure shows that the pH increase of the adsorption system resulted in more formation of Pb-HA complexes. The comparison of the data of Fig.3-3 with the complexation model expressed by Eq.[3-4] is shown in **Fig.3-4**. The data agreed well with the model (solid line), and the number of sites available for metal complexation on 1g of HA, N_{MHA} , and the complexation constant of the Pb-HA system, K_{HA} , were derived from the slope and intercept of the line as $N_{MHA} = 1.84 \times 10^{-3} \text{ mol} \cdot \text{g}^{-1}$ and $K_{HA} = 1.53 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$, respectively.

Alginate acid, used here as the immobilizing agent, also has a complexing ability with divalent metal ions. **Figure 3-5** shows that the experimental results of the Pb-AA system are similar to those in Fig.3-3. Since the complexation of metal ions with AA in a liquid state is very rapid (13,14), the same contact time as that in the previous Pb-HA system was adopted. The comparison of the data of Fig.3-5 with Eq.[3-4] is presented in **Fig.3-6**. Similarly to HA, the complexation of Pb with AA was also consistent with the model. The number of available sites on AA and the complexation constant were obtained as $N_{MAA} = 3.44 \times 10^{-3} \text{ mol} \cdot \text{g}^{-1}$ and $K_{AA} = 1.32 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$, respectively. Comparing the complexing abilities of AA and HA with Pb ions, the former is obviously superior to the latter in both terms of capacity and strength. However, AA is not suitable as an adsorbent material because it is poorly soluble in water and a solution containing more than 10% of AA cannot be prepared.

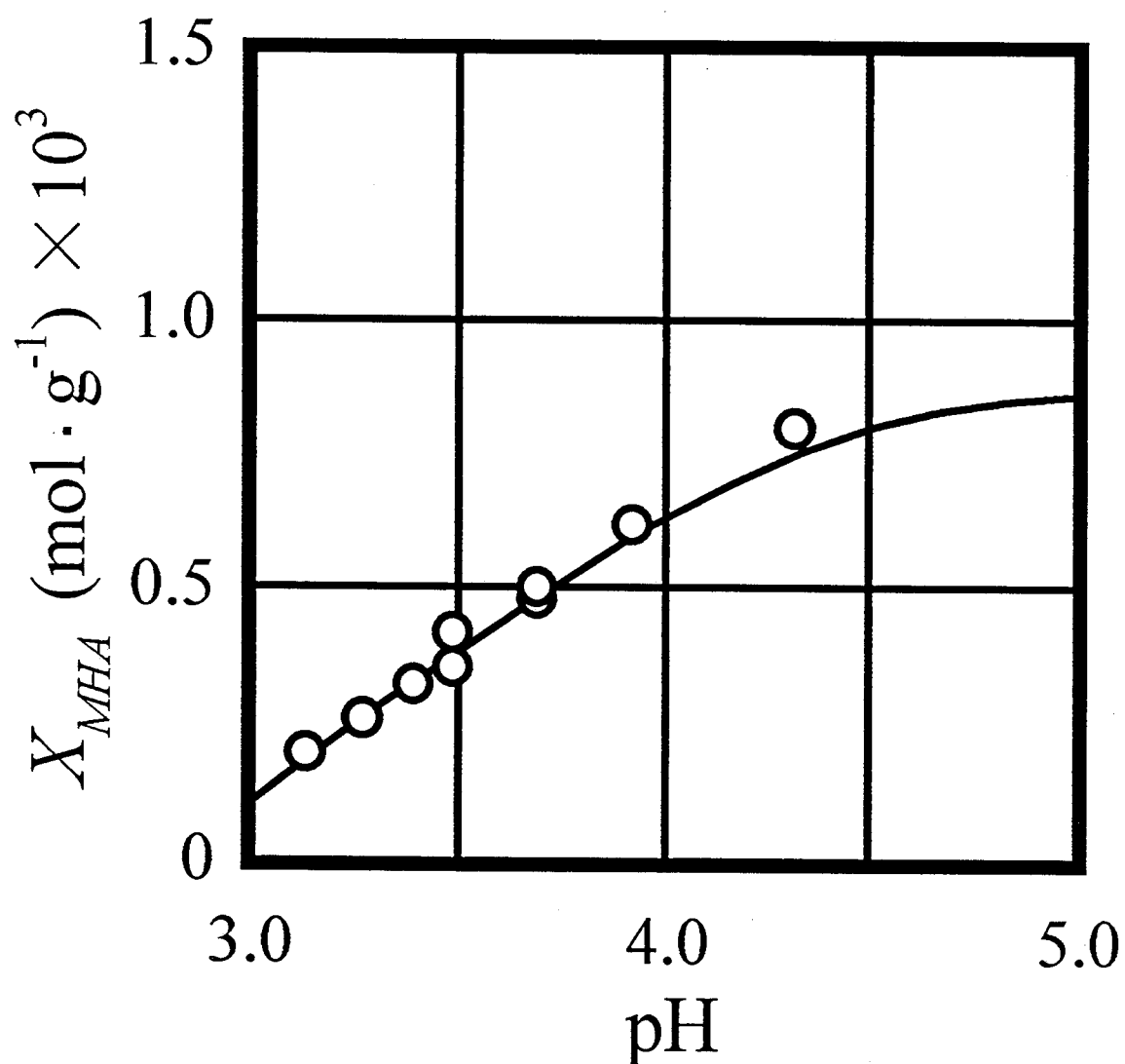


Fig.3-3. Effect of equilibrium pH on lead-HA complexation at 30°C. Initial concentrations of lead ion and HA are $1.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ and $0.05 \text{ g} \cdot \text{dm}^{-3}$, respectively. The solid line represents the theoretical curve calculated from Eq.[3-6].

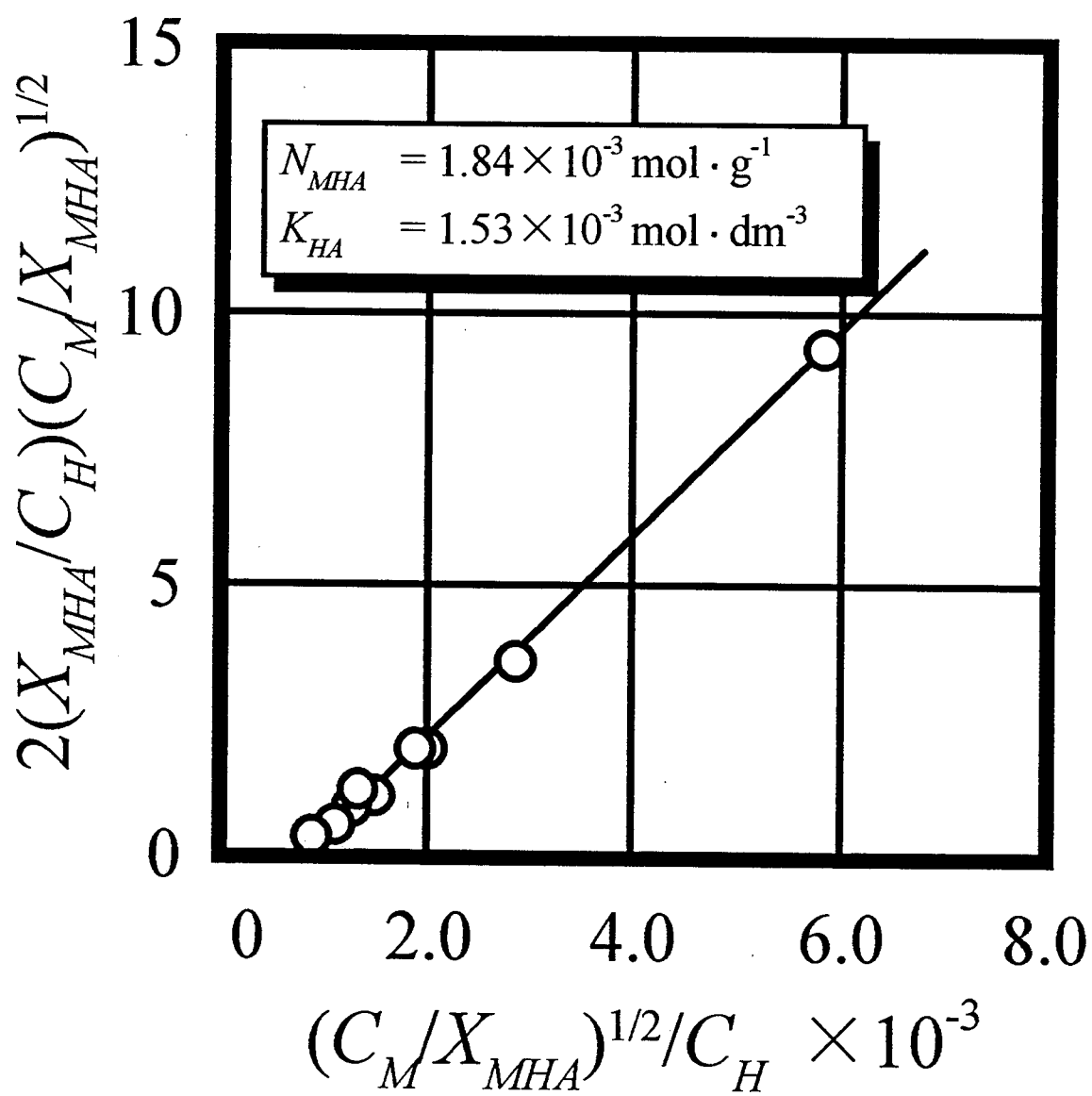


Fig.3-4. Fitting of the data of Fig.3-3 to Eq.[3-4].

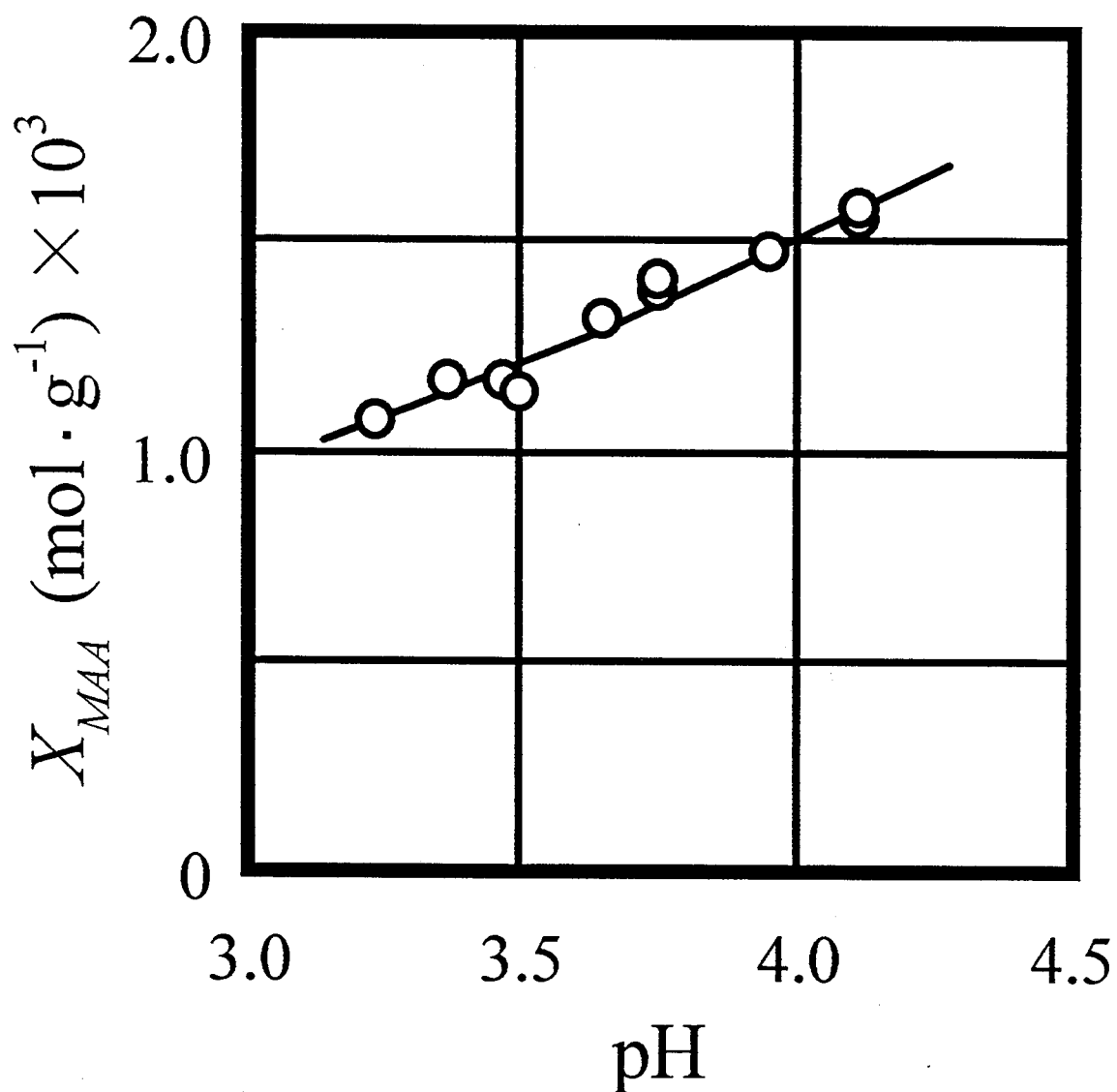


Fig.3-5. Effect of equilibrium pH on lead-AA complexation at 30°C. Initial concentrations of lead ion and HA are $1.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ and $0.033 \text{ g} \cdot \text{dm}^{-3}$, respectively. The solid line represents the theoretical curve calculated from Eq.[3-7].

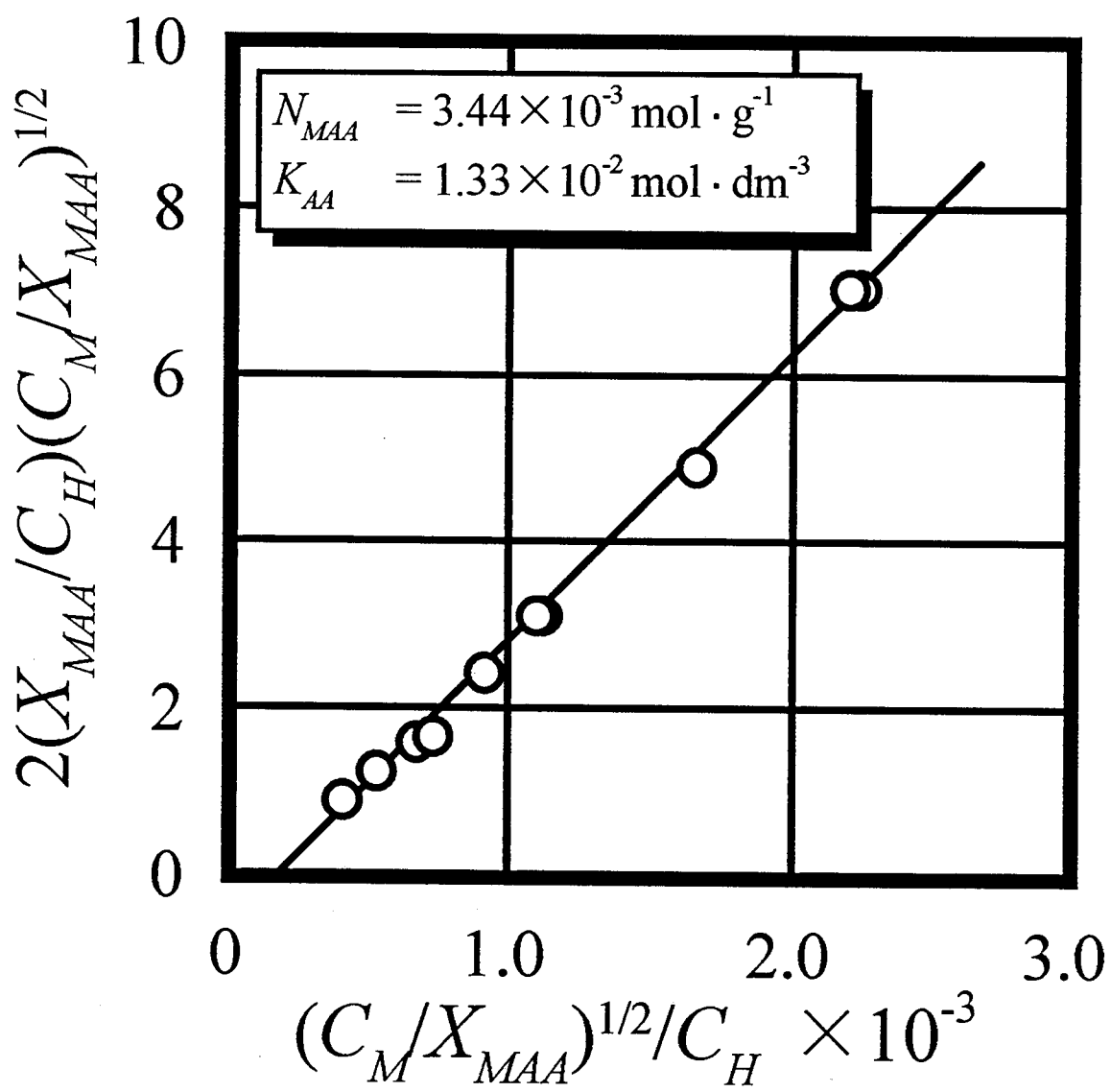


Fig.3-6. Fitting of the data of Fig.3-5 to Eq.[3-4].

Activated carbon powder (ACP), used as another immobilizing agent in HA-gel, is also a well-known adsorbent for various kinds of molecules, but it cannot be expected to have a complexing ability with ions. By the adsorption experiments for the Pb-ACP system, it was confirmed that ACP adsorbed a negligible amount of lead, compared with HA or AA.

3.4.2 Adsorption of Lead Ions on HA-gel

Prior to the equilibrium experiments, kinetic experiments for the lead-HA-gel system were conducted. The HA-gels containing 5, 10, and 15% of HA on a wet-weight basis (45.5, 47.6, and 48.4% on a dry-weight basis) were used for the experiments. Typical examples of the results are presented in Fig.3-7. X_t denotes the adsorption amount of lead on 1 g of HA-gel. As 50 h were enough to attain the equilibrium for all the gels, the contact time of 50 h was adopted for the equilibrium experiments. From Figs.3-2 and 3-7 it is seen that the present method of immobilization apparently had a serious effect on kinetic behavior of organo-metallic complexation. The remarkable decrease in the adsorption (or complexation) rate is caused by the increase in diffusion resistance of lead ions due to the gel network. Therefore, the preparation of a small or thinner HA-gel will be required for actual operation.

The influence of pH on the equilibrium amounts of lead adsorbed, X_M , on several HA-gels is shown in Fig.3-8. Triangle symbols refer to a particular HA-gel which contained no humic acid. The adsorbed amount increased with the increase of the HA content. The same data are fitted to Eq.[3-4] in Fig.3-9. The plotted symbols correspond to those in Fig.3-8. The adsorption

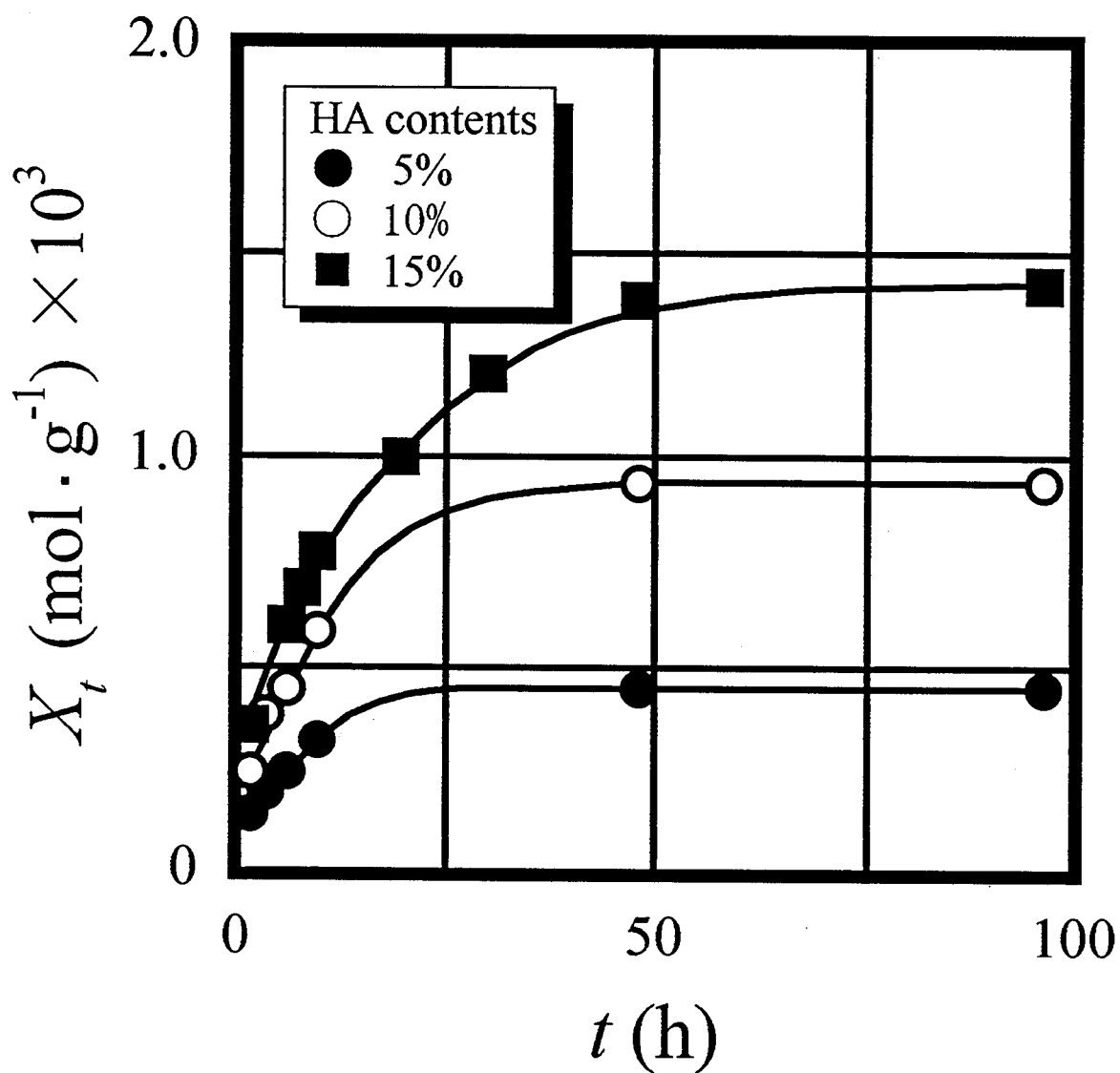


Fig.3-7. Time dependence of lead adsorption on HA gels containing 5%(●), 10%(○), and 15% (■) of HA at 30°C. All the HA-gels contain 1% AA and HA's weight in ACP. Initial concentration of lead ion is $1.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$.

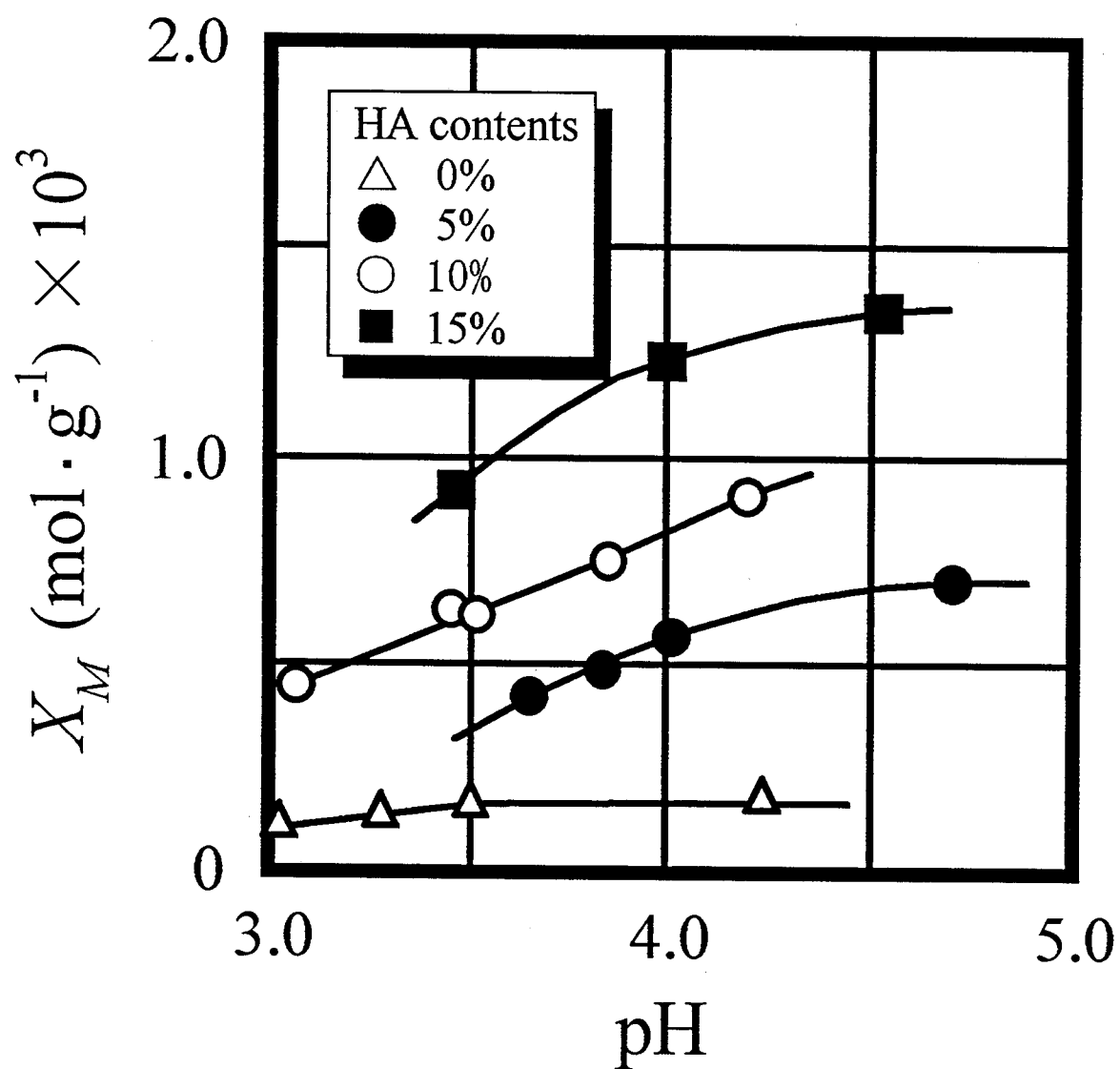


Fig.3-8. The pH dependence of lead adsorption on HA-gels containing 0%($\triangle$), 5%($\bullet$), 10%($\circ$), and 15% ($\blacksquare$) of HA at 30°C. Initial concentration of lead ion is $2.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$.

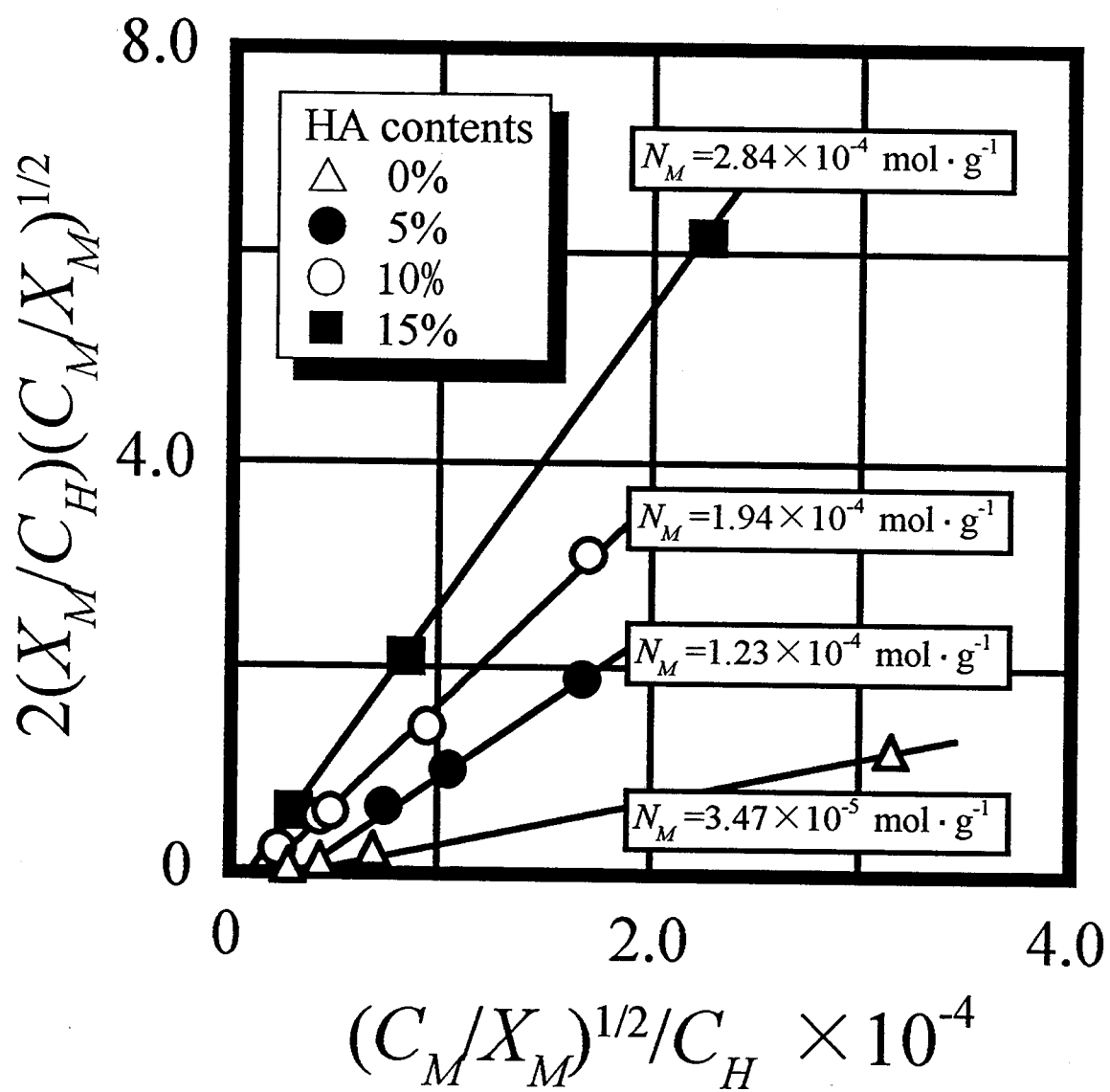


Fig.3-9. Fitting of the data of Fig.3-8 to Eq.[3-4].

mechanism of lead on HA-gel was also consistent with the foregoing organo-metallic complexation model. The slopes of the lines express the numbers of available sites on 1 g of HA-gel.

3.4.3 Estimation of the Amount of Lead Adsorbed on HA-gel

From the fact that the adsorption of lead on HA-gel (i.e., immobilized HA and AA) agreed with the complexation model, the adsorbed amount of lead on 1 g of HA-gel, X_M , can be expressed as

$$X_M = P_{HA} \cdot X_{MHA} + P_{AA} \cdot X_{MAA} \quad [3-5]$$

where X_{MHA} and P_{HA} represent the amount of lead adsorbed by the HA component and the weight fraction of HA in the gel, respectively. Similarly, X_{MAA} and P_{AA} denote the quantities with respect to AA. Applying the adsorption isotherm of Eq.[3-4] to the components in the gel, X_{MHA} and X_{MAA} can be evaluated as

$$X_{MHA} = (N_{MHA} / 4K_{HA})[(2K_{HA} + C) - \{C(4K_{HA} + C)\}^{1/2}] \quad [3-6]$$

$$X_{MAA} = (N_{MAA} / 4K_{AA})[(2K_{AA} + C) - \{C(4K_{AA} + C)\}^{1/2}] \quad [3-7]$$

where $C \equiv C_H^2/C_M$. The solid lines in Figs.3-3 and 3-5 represent the theoretical curves calculated from Eqs.[3-6] and [3-7], respectively. P_{HA} and P_{AA} are the values determined from the composition of HA-gel. Since N_{MHA} , N_{MAA} , K_{HA}

and K_{AA} were already obtained, X_M can be calculated by using Eqs.[3-5]-[3-7]. **Figure 3-10** demonstrates the agreement of the calculated adsorption amounts on HA-gels with the experimental.

3.5 Conclusion

Humic acid, which has an excellent complexing ability with heavy metal ions, was used as an adsorbent material for the recovery of lead. It was immobilized by a combination of alginate gel and activated carbon powder. By the present immobilizing method, the adsorbent (HA-gel) comprising as much as about 50% of HA on a dry-weight basis was obtained. A simple complexation model for divalent heavy metal ions and organic matter in acidic media was proposed. The model was confirmed by two kinds of experiments in which humic and alginic acids in liquid state were used as adsorbents. On the basis of these results, the followings were concluded.

- (1) The complexation constants and the number of available sites were given as $K_{HA} = 1.53 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ and $N_{HA} = 1.84 \times 10^{-3} \text{ mol} \cdot \text{g}^{-1}$ for humic acid, and $K_{AA} = 1.33 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ and $N_{AA} = 3.44 \times 10^{-3} \text{ mol} \cdot \text{g}^{-1}$ for alginic acid, respectively.
- (2) The comparison of the model with the experimental data showed that the model also explained the adsorption on HA-gels in acidic media.
- (3) The complexation constants of the lead-HA and lead-AA systems and number of available sites for complexation of HA and AA were not influenced by immobilization.

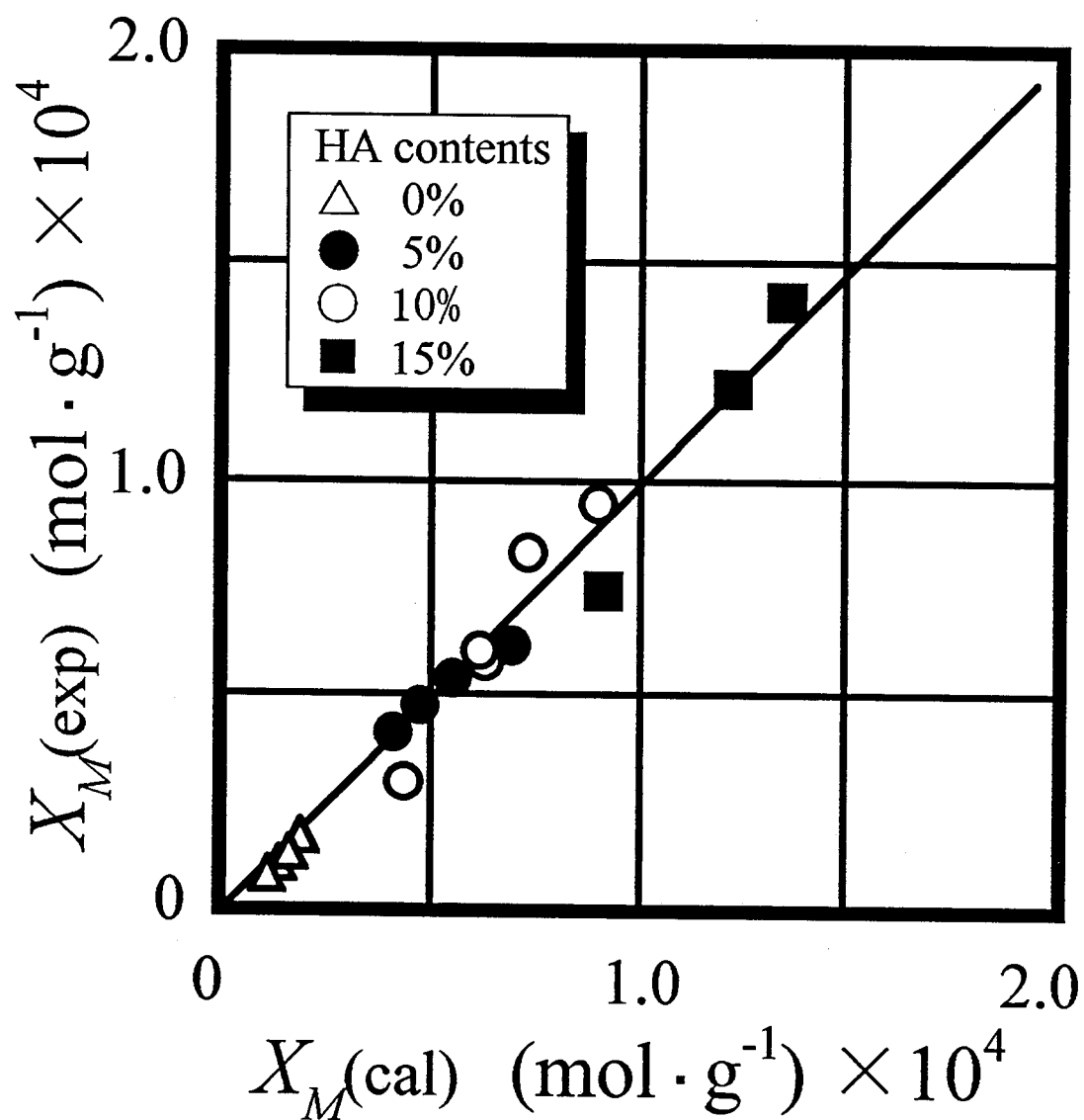


Fig.3-10. Comparison between the experimental amounts of lead adsorbed on several kinds of HA-gels and calculated from Eqs.[3-5]-[3-7]. The symbols are the same as those in Fig.3-8.

(4) The alginate gel used as an immobilizing agent affected the rate of adsorption to a remarkable extent.

3.6 Nomenclature

K = metal complexation constant of polymer (dm³·mol⁻¹)

N_M = number of acidic groups available for metal-complexation (mol·g⁻¹)

P = weight fraction of polymer in the gel (-)

X_M = amount of metal ions complexed with polymer (mol·g⁻¹)

α_M = fraction of acidic groups complexed with metal ions (-)

Subscripts

AA = Values for alginic acid

HA = Values for humic acid

4 ADSORPTION OF LEAD IONS ON HUMIC ACID IMMOBILIZED BY CALCIUM ALGINATE MEMBRANE

4.1 Introduction

The preceding chapter presented a simple model for divalent metal ions and organic matter. Based on the model, the adsorption mechanism and the ability of this newly developed adsorbent (HA-gel) have been investigated. The complexation constants and capacities of lead-HA and lead-AA systems were not influenced by immobilization. However, the alginate gel used as an immobilizing agent affected the rate of lead adsorption to a remarkable extent. The remarkable decrease in the adsorption rate is caused by the increase in diffusion resistance of lead ions due to the gel network (7,15,35,19). Therefore, the preparation of a small or thinner HA-gel will be required for actual operation.

In this chapter, a membranous HA-gel (HA-M) was developed in order to increase the adsorption rate and the HA content on a wet-weight basis. Based on the adsorption model presented in the preceding chapter and a simple mathematical model for adsorption kinetics, the lead adsorption ability of HA-M will be discussed. Furthermore, the lead desorption characteristics of HA-M will be experimentally examined for the regeneration of HA-M.

4.2 Experimental

4.2.1 Adsorbent

Calcium alginate membrane containing HA and ACP was used as the adsorbent. An aqueous solution containing HA, sodium alginate, and activated carbon powder (ACP) was well mixed. It was extruded, dropwise, on a glass plate and dried at 60°C. Then it was immersed in an excess of CaCl₂ solution (0.1 M). The membranes of HA-entrapped calcium alginate (HA-M) were left to harden in the CaCl₂ solution for 1 h. The formed HA-M was removed from the solution and it was washed repeatedly with distilled water. The membranes had a diameter and thickness of about 5 and 0.3 mm.

4.2.2 Adsorption of Lead on HA-M

A 1 dm³ solution containing a necessary amount of Pb(NO₃)₂ was prepared and its pH was adjusted by HNO₃. After reaching the thermal equilibrium at 30°C, a certain amount of HA-M was added to the solution. The time course of the lead adsorption on HA-M was measured from the change of lead concentration in the bulk phase. After reaching the adsorption equilibrium, the pH in the bulk phase was measured.

4.2.3 Desorption of Lead from HA-M

A 0.3 dm³ solution containing a necessary amount of HNO₃ was prepared. After reaching the thermal equilibrium at 30°C, a certain amount of HA-M, on which a certain amount of lead was adsorbed, was added to the solution. The

time course of the lead desorption from HA-M was measured from the change of lead concentration in the bulk phase. After reaching the desorption equilibrium, the pH in the bulk phase was measured.

4.3 Results and Discussion

4.3.1 Entrapping Effect of Calcium Alginate

Figure 4-1 shows the percentage of HA discharged from calcium alginate membrane prepared from mixture solutions containing 2 % of HA and 0.5-3.0 % of AA (in the absence of ACP). Calcium alginate membranes containing HA were formed in $0.1 \text{ mol} \cdot \text{dm}^{-3}$ CaCl_2 solution and left the membranes in the CaCl_2 solution for 1 h. The gels were mechanically stirred in distilled water at 30°C for 24 h. The calcium alginate membrane could entrap about 85% of HA. However, the increase of AA concentration was not so effective for the entrapment of lower molecular weight HA.

4.3.2 Entrapping Effect of Activated Carbon Powder

The matrix of calcium alginate membrane could not entrap lower molecular weight HA and about 15% of HA was discharged from the membrane. **Figure 4-2** shows the effect of ACP concentration on the percentage of HA discharged from HA-M. R represents the weight ratio of ACP to HA initially contained in the HA-M. H and A represent the weight percentage of HA and AA in mixture suspensions from which the HA-M were prepared, respectively. The discharge of HA decreased with the increase of the ACP concentration, and the discharge

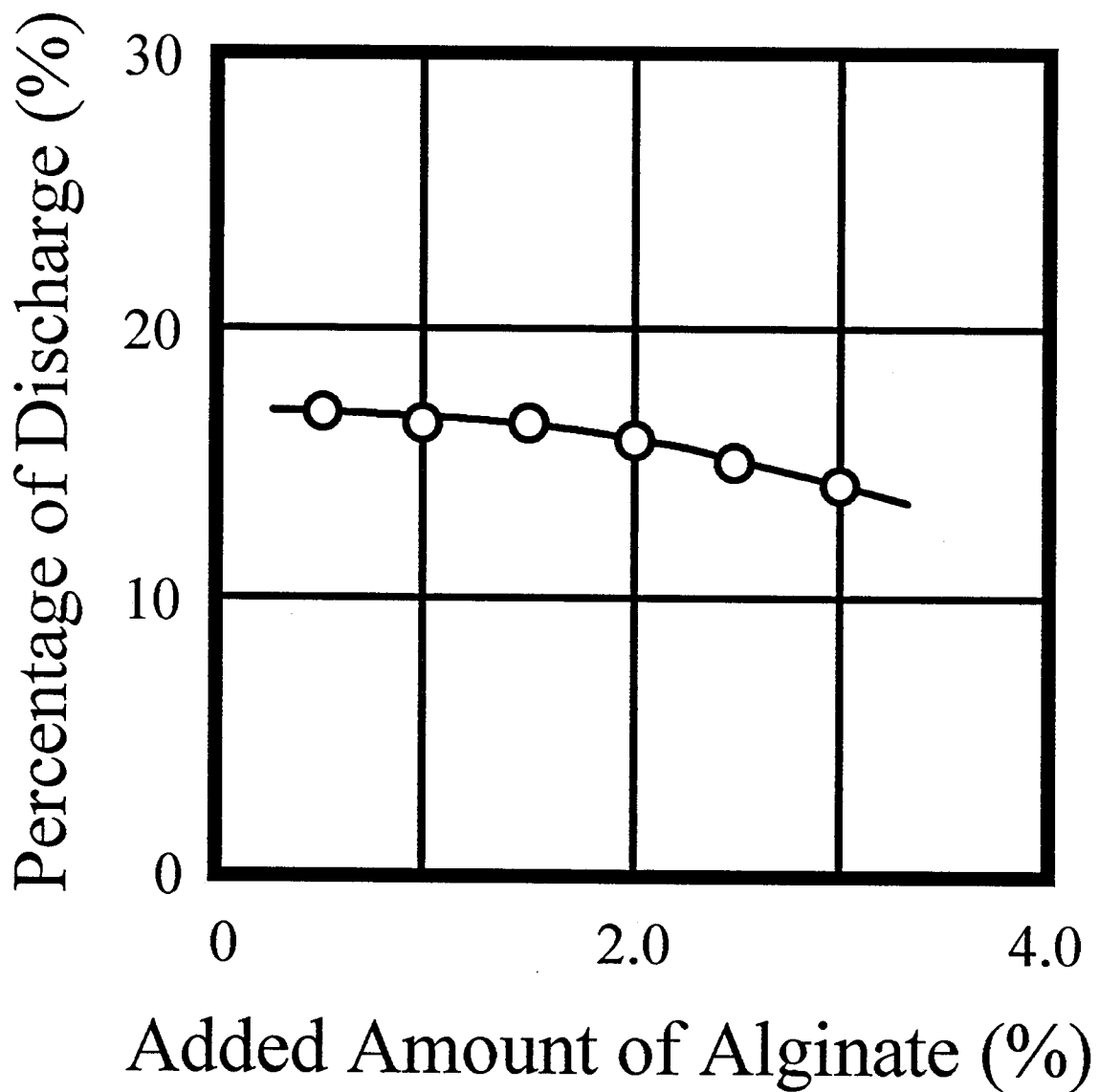


Fig.4-1. Effect of AA concentration on the percentage of HA discharged from calcium alginate gel membranes prepared from mixture solutions containing 2% of HA and 0.5-3.0% of AA (in the absence of ACP) in distilled water at 30°C.

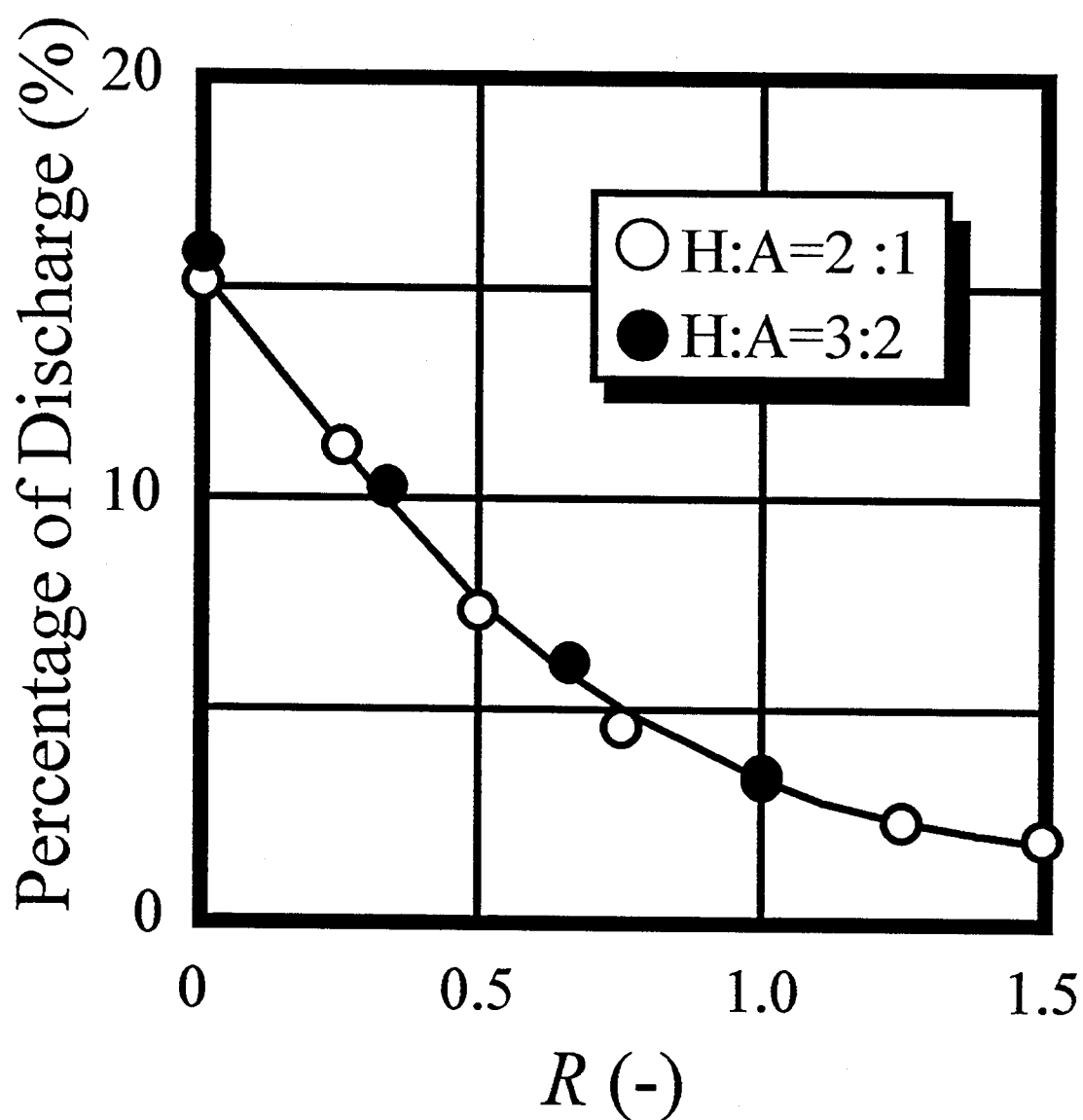
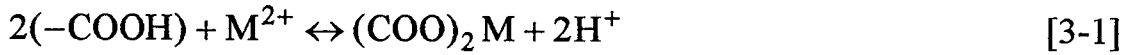


Fig.4-2. Effect of ACP concentration on the percentage of HA discharged from HA-M in 0.1M CaCl_2 solution at 30°C . R represents the weight ratio of ACP to HA initially contained in the HA-M. H and A represent the weight percentages of HA and AA in mixture suspensions from which the HA-M are prepared.

was almost completely prevented by the addition of the HA's weight in ACP. The HA-M containing excess ACP ($R > 1$) was easily destroyed by stirring.

4.3.3 Influence of Immobilization on Metal-HA Complexation

In the preceding chapter, a simple complexation model for the organic polymer and divalent metal ions in acidic media was presented as



with

$$K = \frac{(2X_M / N_M)C_H^2}{\{1 - (2X_M / N_M)\}^2 C_M} \quad [3-3]$$

where M^{2+} represents the divalent heavy metal ion. $C_H \text{ mol}\cdot\text{dm}^{-3}$ and $C_M \text{ mol}\cdot\text{dm}^{-3}$ denote the equilibrium concentrations of H^+ and M^{2+} , respectively. $X_M \text{ mol}\cdot\text{g}^{-1}$ and $N_M \text{ mol}\cdot\text{g}^{-1}$ are the amount of divalent metal ions complexed with (or adsorbed on) the polymer and the number of available sites for complexation, respectively. The adsorbed amount of lead on 1 g of HA-M, X_M , can be expressed as

$$X_M = P_{HA} \cdot X_{MHA} + P_{AA} \cdot X_{MAA} \quad [3-5]$$

where P_{AA} and P_{HA} represent the weight fraction of AA and HA in HA-M, respectively. Similarly, the subscripts *AA* and *HA* were used to designate the

quantities with respect to AA and HA, respectively. Applying the adsorption isotherm of Eq.[3-3] to the components in HA-M, X_{MHA} and X_{MAA} can be evaluated as

$$X_{MHA} = (N_{MHA} / 4K_{HA})[(2K_{HA} + C) - \{C(4K_{HA} + C)\}^{1/2}] \quad [3-6]$$

$$X_{MAA} = (N_{MAA} / 4K_{AA})[(2K_{AA} + C) - \{C(4K_{AA} + C)\}^{1/2}] \quad [3-7]$$

where $C \equiv C_H^2/C_M$. Since N_{HA} , N_{AA} , K_{HA} and K_{AA} were already obtained as $K_{HA} = 1.53 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ and $N_{HA} = 1.84 \times 10^{-3} \text{ mol} \cdot \text{g}^{-1}$ for HA, and $K_{AA} = 1.33 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ and $N_{AA} = 3.44 \times 10^{-3} \text{ mol} \cdot \text{g}^{-1}$ for AA, X_M can be calculated by using Eqs.[3-3] and [3-5]-[3-7]. **Figure 4-3** shows the comparison between the calculated adsorption amounts on HA-M with the experimental. H, C, and A represent the weight percentage of HA, ACP, and AA in mixture suspensions from which the HA-M were prepared, respectively. Figure 4-3 demonstrates a good agreement of the experimental data with the model. This means that the complexation constant and the number of available sites for complexation of HA and AA was not influenced by immobilization.

4.3.4 Influence of Alginate Concentration on Adsorption Rate

Alginic acid used here as the immobilizing agent, also has a complexing ability with divalent metal ions. Therefore, the increase of AA content in HA-M may result in the increase of mechanical strength and adsorption capacity of HA-M. On the contrary, it should be noted that the increase of AA content may

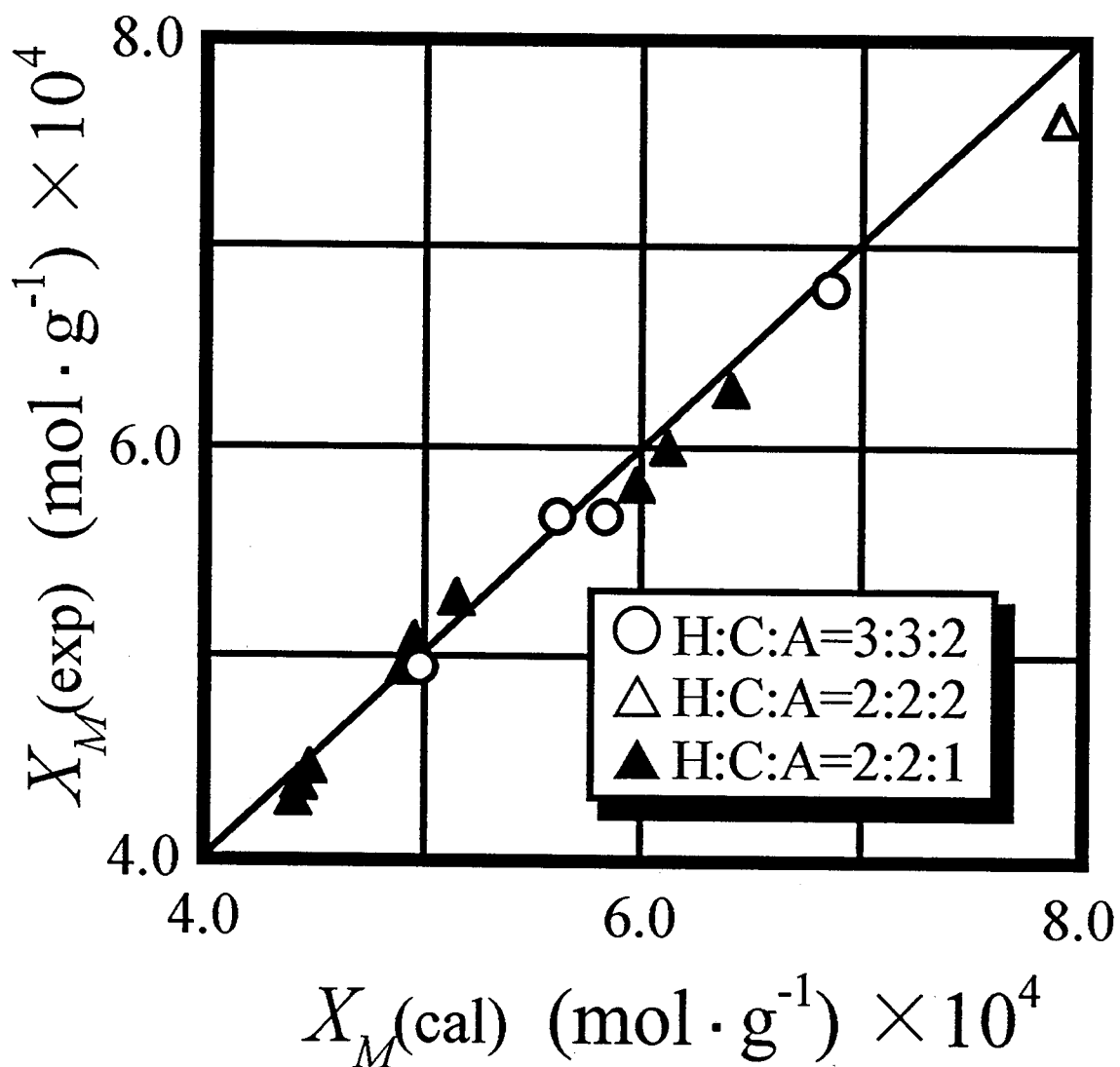


Fig.4-3. Comparison between the experimental amounts of lead adsorbed on several kinds of HA-M and calculated from Eqs.[3-5]-[3-7]. H, C, and A represent the weight percentages of HA, ACP, and AA in the mixture suspensions, respectively.

also increase the diffusion resistance of lead ions due to the gel network. Kinetic adsorption experiments for lead were conducted under acidic conditions. The results are shown in **Fig.4-4**. X_t in the ordinate represents the amount of lead adsorbed at time t [h]. The results suggest that the adsorption rate of lead onto HA-M is influenced by the AA content. To discuss quantitatively about the influence of immobilization on the lead adsorption rate, the rate constant was estimated for each of the adsorbent. For obtaining the rate constant from the kinetic data in Fig.4-4, the adsorption process of lead onto HA-M was approximated to a first-order reaction model with the rate constant k [h⁻¹] as

$$X_t / X_M = 1 - e^{-kt} \quad [4-1]$$

or

$$\ln(1 - X_t / X_M) = -kt \quad [4-2]$$

Figure 5 shows the fitting of the data in Fig.4-4 to Eq. [4-2]. The data agreed well with the model, and the rate constant, k , was derived from the slope of the line. The rate constant of the lead adsorption on HA-M increased from 0.83 to 1.89 h⁻¹ with the decrease of AA concentration in mixture suspension from 2 to 1 %. However, the HA-M prepared from the mixture suspension containing AA less than 1% had a weak mechanical strength and it was easily destroyed by stirring.

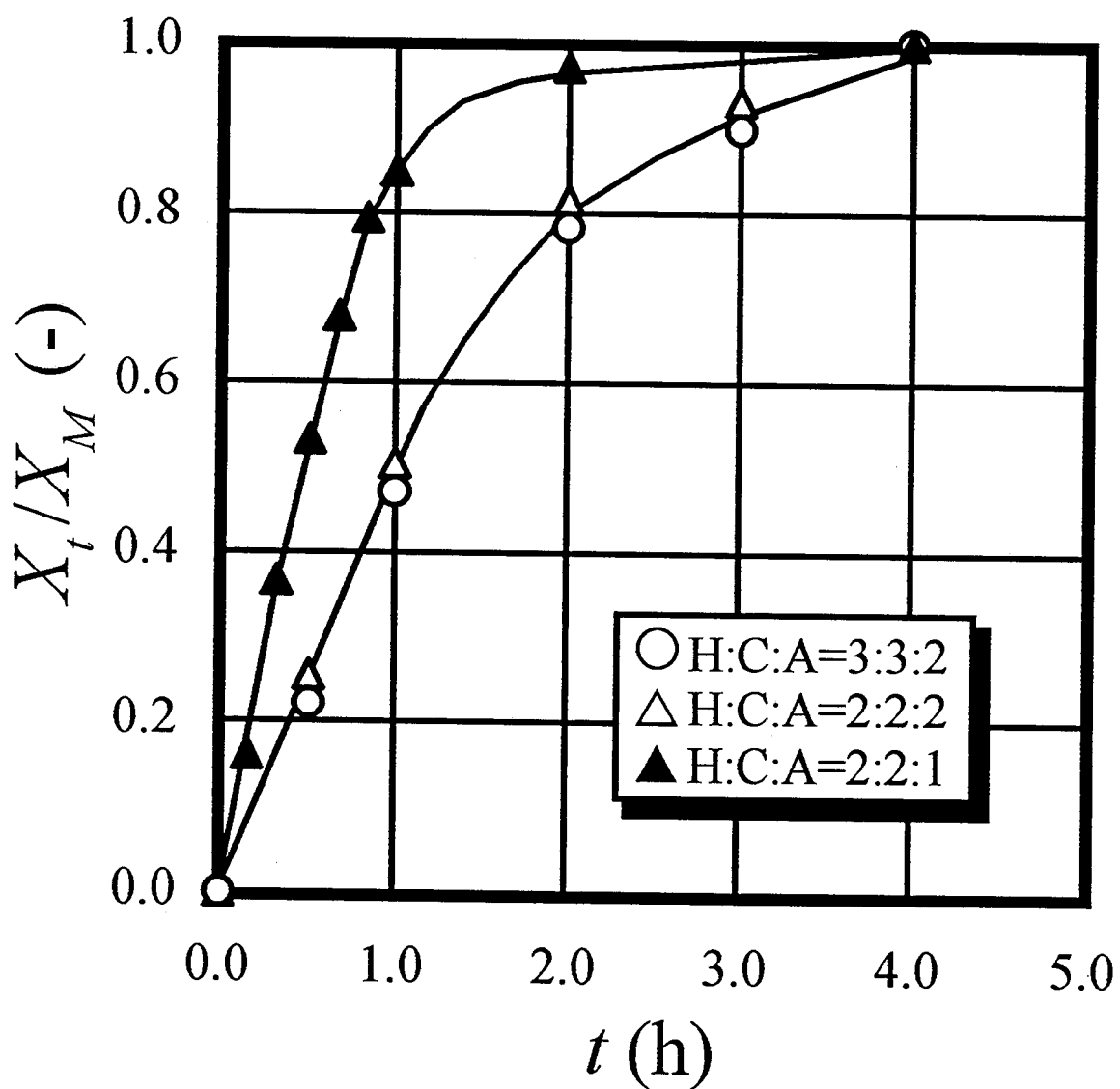


Fig.4-4. Time dependence of lead adsorption on HA-M at 30°C. Initial concentration of lead ion, volume of the system, and equilibrium pH are $2.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$, 1.0 dm^3 , and pH 3.8, respectively.

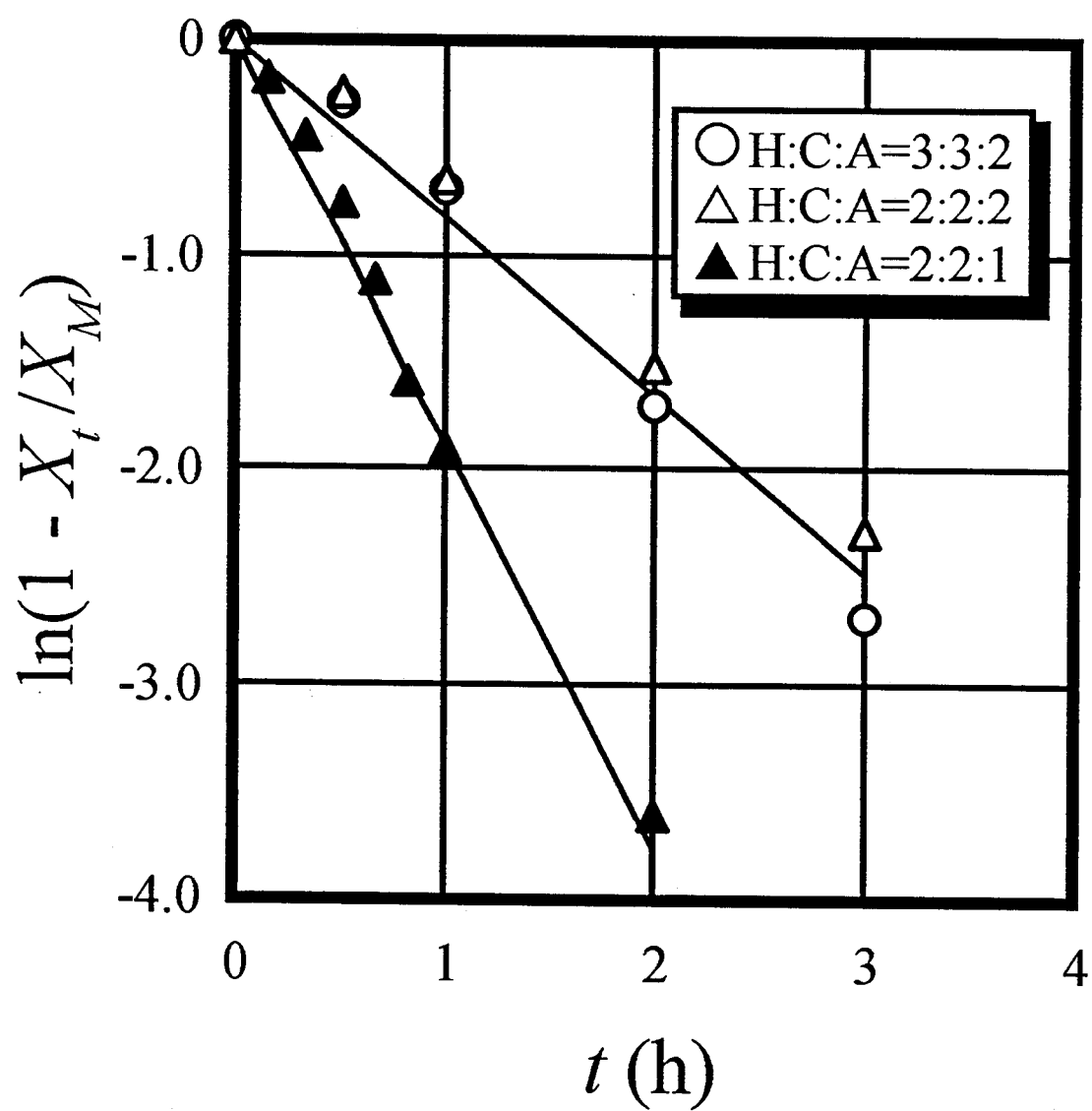


Fig.4-5. Fitting of the data of Fig.4-4 to Eq.[4-2].

Kinetic experiments of lead adsorption on HA-gel particles, which had diameters of 2.33, 3.03 and 3.62 mm, were conducted. The results are shown in **Fig.4-6**. Solid triangle symbols refer to HA-M (same as Fig.4-5). All the adsorbents were prepared from the same mixture suspension (H:C:A=2:2:1). The data in Fig.4-6 were also fitted to Eq. [4-2]. The results are shown in **Fig.4-7**. The rate constant of lead adsorption on HA-gel particles increased from 0.30 to 0.61 h⁻¹ with the decrease of diameter from 3.62 to 2.33 mm. Comparing the rate constants of HA-M and HA-gel particles, the former has three times or more larger rate constant than the latter. On the other hand, The number of available sites for metal complexation on 1 g of HA-M or HA-gel, N_M , can be expressed as

$$N_M = P_{HA} \cdot N_{MHA} + P_{AA} \cdot N_{MAA}. \quad [4-3]$$

P_{HA} and P_{AA} are the values determined from the composition of the adsorbent. Since N_{MHA} and N_{MAA} were already obtained, N_M can be calculated by using Eqs.[4-3]. The number of available metal complexation sites for HA-M (H:C:A = 2:2:1) was estimated as $N_M = 1.42 \times 10^{-3}$ mol·g⁻¹ on a dry-weight basis or 1.01×10^{-3} mol·g⁻¹ on a wet-weight basis. For HA-gel particle (H:C:A = 15:15:1), N_M was calculated as 1.00×10^{-3} mol·g⁻¹ on a dry-weight basis or 0.51×10^{-3} mol·g⁻¹ on a wet-weight basis. This adsorbent is a maximum HA containing HA-gel particle used in this study. From the results, HA-M is obviously superior to HA-gel particle in both terms of adsorption rate and capacity.

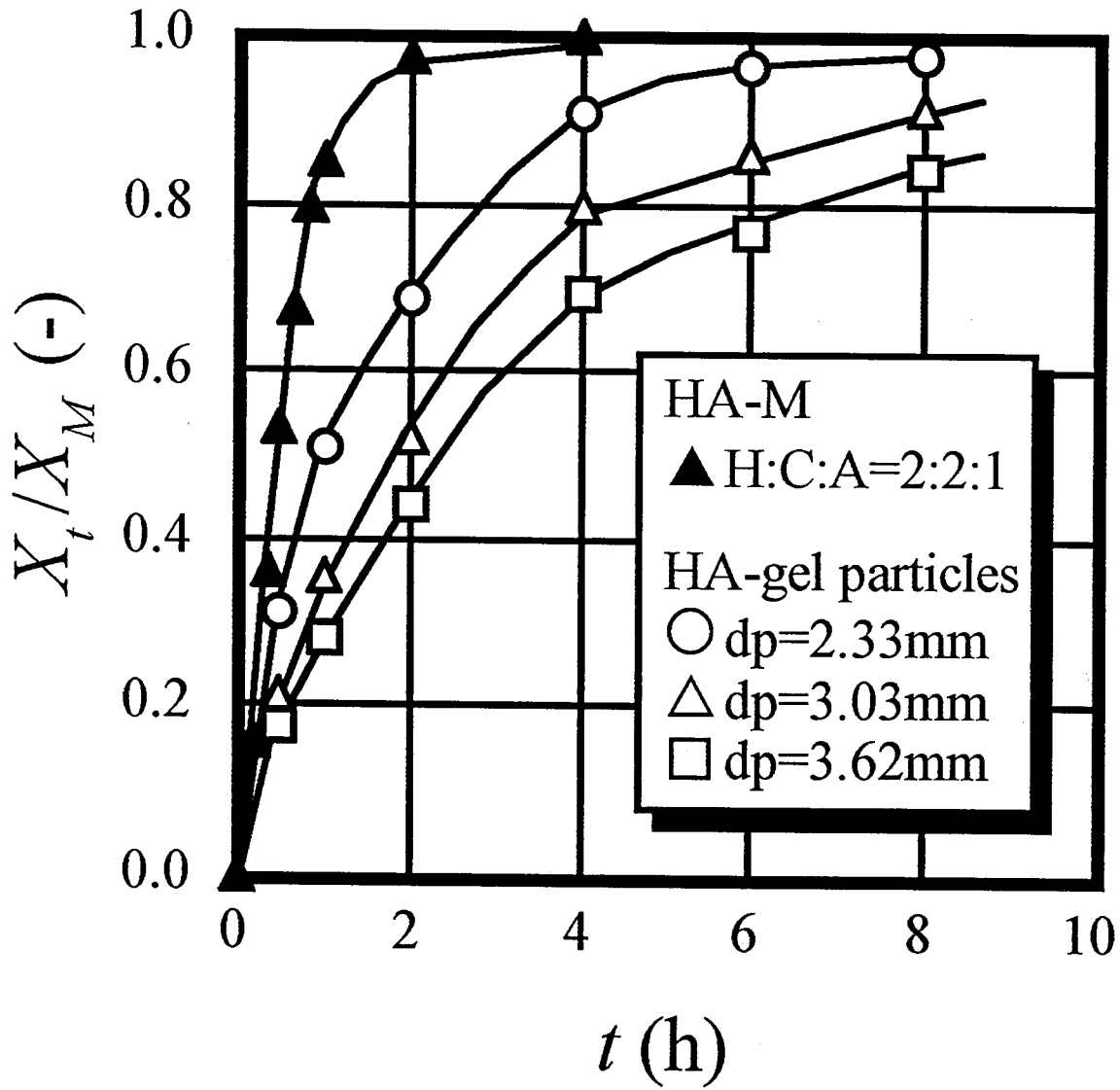


Fig4-6. Time dependence of lead adsorption on HA-gel particles and HA-M at 30°C. Initial concentration of lead ion, volume of the system, and equilibrium pH are $2.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$, 1.0 dm^3 , and pH 3.8, respectively.

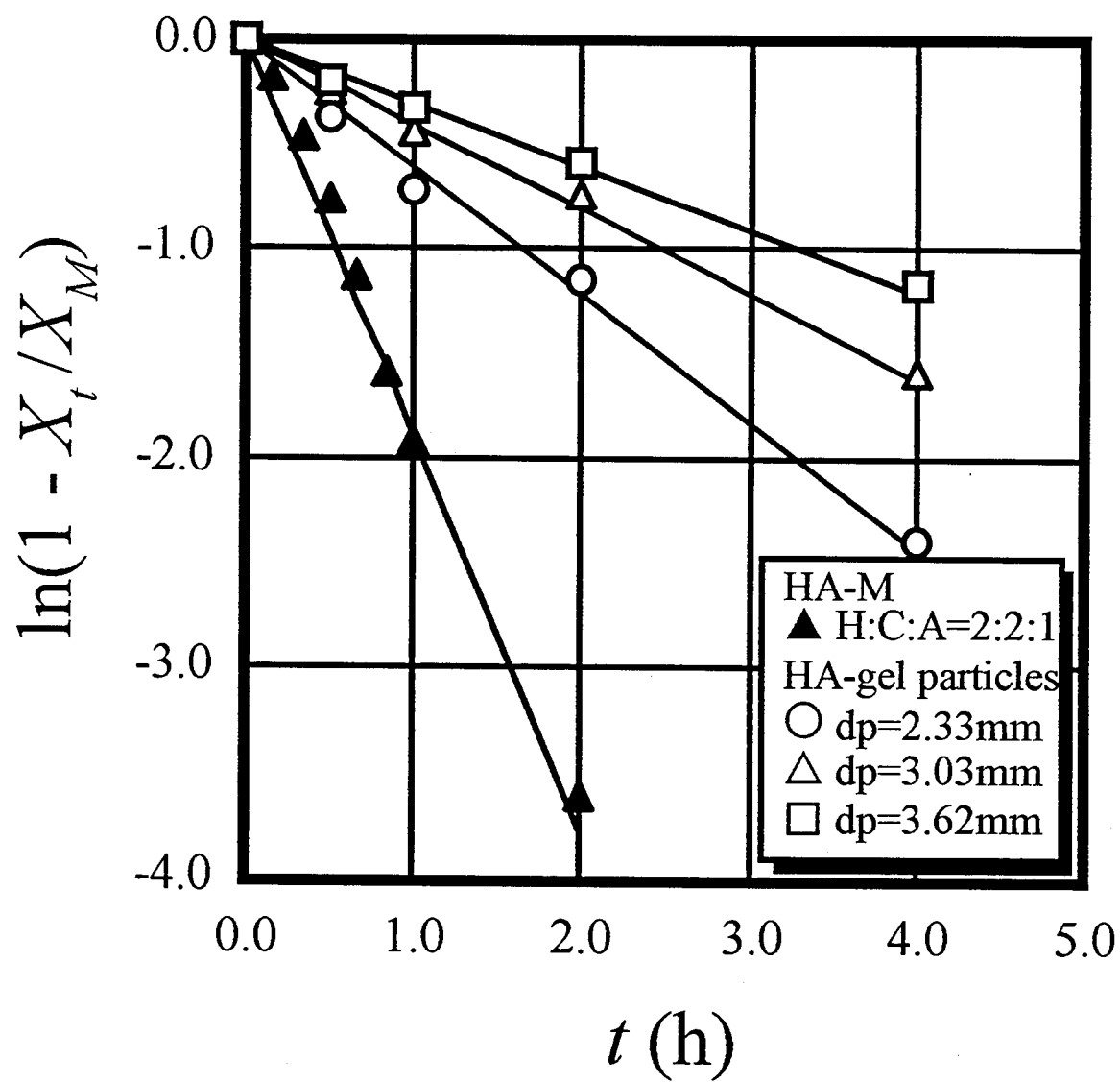


Fig.4-7. Fitting of the data of Fig.4-6 to Eq.[4-2].

4.3.5 Desorption of Lead from HA-M

Figure 4-8 shows the time course of lead desorption from HA-M (H:C:A = 2:2:1). HA-M, on which lead was adsorbed to the extent of about 60% of its adsorption capacity, was used in this experiments. The desorption experiments were carried out in 0.05, 0.10 and 0.50 M of HNO_3 solutions. The desorption of lead from HA-M proceeded rapidly and about 10 min or so were enough to attain the desorption equilibrium.

A convenient linear operating line for lead desorption was obtained from Eqs.[3-5]-[3-7] (shown in Fig.4-9). Figure 4-9 shows the relationship between the fractional coverage of lead on HA-M, α_M [-] , lead concentration in bulk phase and pH at equilibrium. The desorption conditions can be easily determined from the operating line.

4.4 Conclusions

A membranous HA-gel (HA-M) was developed in order to increase the adsorption rate and the HA content of the adsorbent on a wet-weight basis. The equilibrium and kinetic data of lead adsorption experiments onto HA-M were compared with a model previously proposed in the preceding chapter and with a mathematical expression for adsorption kinetics given in the present work, respectively. Furthermore, the lead desorption characteristics of HA-M was experimentally examined for the regeneration of metal adsorbed HA-M. On the basis of these results, the followings were concluded.

(1) A membranous HA-gel which has a thickness of about 0.3 mm was

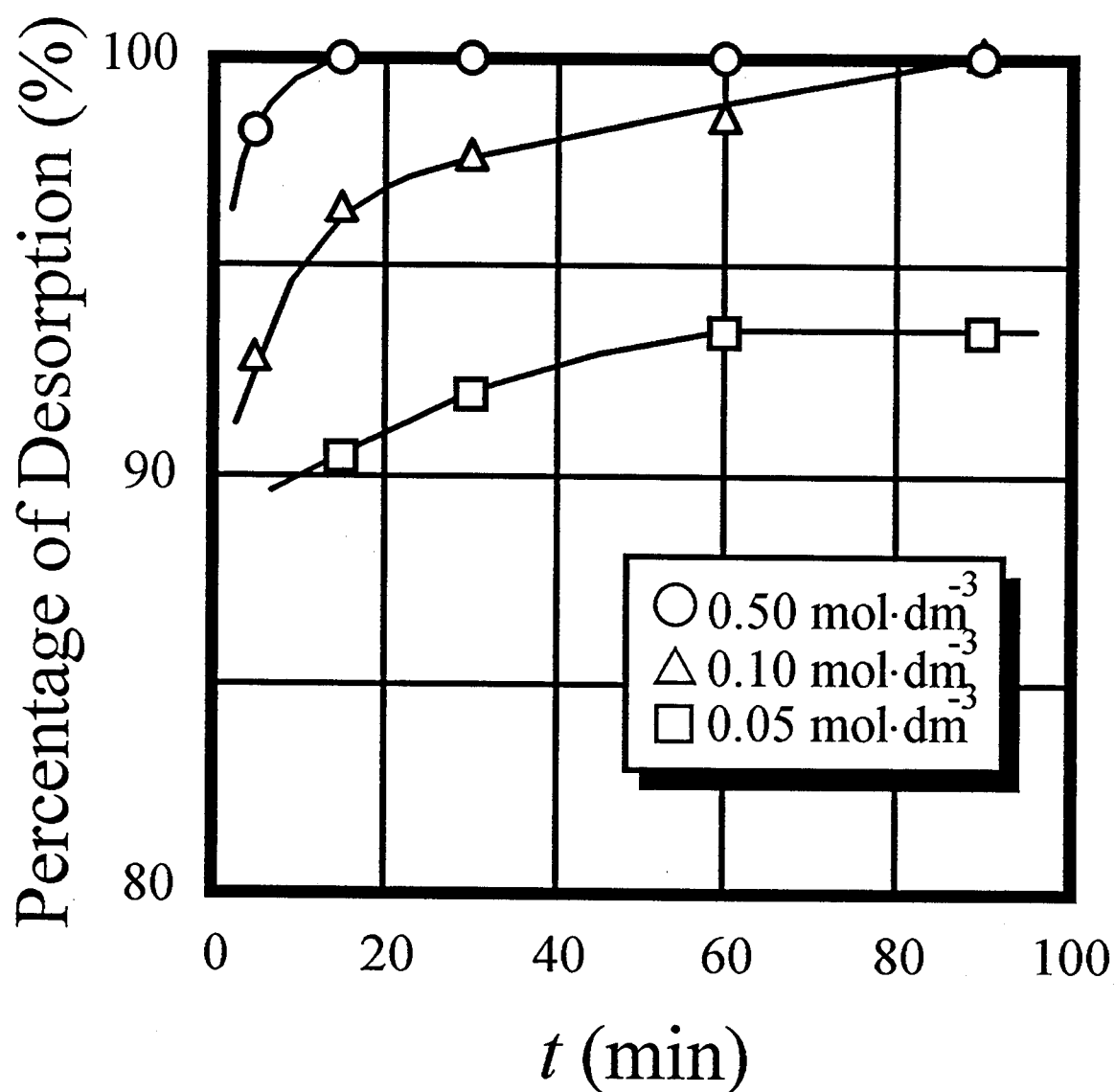


Fig.4-8. Time dependence of lead desorption from HA-M prepared from the mixture suspension containing 2% of HA, 2% of ACP, and 1% of AA. The desorption experiments were carried out in 0.05, 0.10, and 0.50M HNO₃ solutions at 30°C.

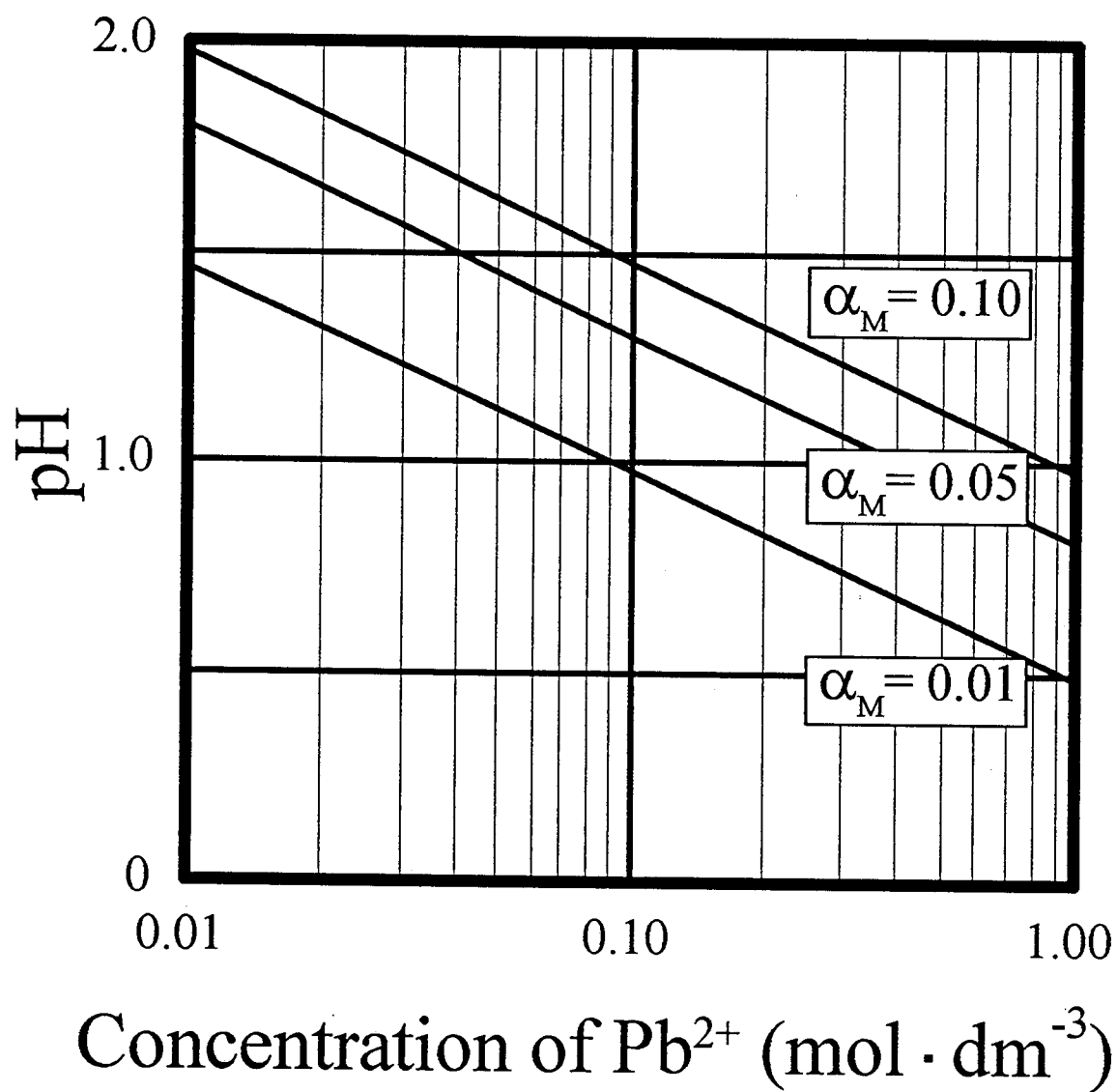


Fig.4-9. Operating line of lead desorption calculated from Eq.[3-5]-[3-7].

prepared from a mixture suspension containing AA (1 wt-%), HA (2 wt-%) and ACP (2 wt-%).

(2) The equilibrium data agreed well with the adsorption model. The complexation constants and the number of available sites for complexation were not influenced by immobilization.

(3) The number of available metal complexation sites for HA-M was estimated as $N_M = 1.42 \times 10^{-3} \text{ mol} \cdot \text{g}^{-1}$ on a dry-weight basis or $1.01 \times 10^{-3} \text{ mol} \cdot \text{g}^{-1}$ on a wet-weight basis, and 1.4 or 2.0 times larger than those of HA-gel particle.

(4) The kinetic adsorption data revealed that the rate of lead adsorption by the HA-M was much faster than that of the HA-gel particle.

(5) HA-M was rapidly regenerated by washing with 0.1 M HNO_3 .

4.5 Nomenclature

K = metal complexation constant of polymer (dm³·mol⁻¹)

N_M = number of acidic groups available for metal-complexation (mol·g⁻¹)

P = weight fraction of polymer in the gel (-)

X_M = amount of metal ions complexed with polymer (mol·g⁻¹)

X_t = amount of metal ions complexed with polymer at time t (mol·g⁻¹)

α_M = fraction of acidic groups complexed with metal ions (-)

Subscripts

AA = Values for alginic acid

HA = Values for humic acid

5 ADSORPTION OF METAL IONS ON INSOLUBILIZED HUMIC ACID

5.1 Introduction

New adsorbents of humic acid immobilized in spherical (HA-gel) and membranous (HA-M) calcium alginate gels in combination with activated carbon powder have been developed and investigated the adsorption of lead ions on the adsorbents (Chapters 2, 3 and 4). This technique enabled the immobilization of HA with retention of metal complexing ability. However, the mechanical strength of calcium alginate gel is affected by pH and ionic strength in aqueous phase. Therefore, these adsorbents may be only available in a limited condition, that is, in acidic and/or high ionic strength solutions.

The adsorption property of metal ions on HA prepared by the oxidation of coal and bituminous coal have been investigated (21,24,2,3). HA extracted from coal was insolubilized by heating treatment and was use for the recovery of divalent metal ions (23). In these studies, however, the metal complexation mechanism of HA and the effect of insolubilization on the metal complexing ability of HA were not quantitatively discussed. In this chapter, another HA insolubilized by heating treatment was prepared, and it will be applied to the recovery of cadmium and lead ions. Furthermore, a general metal-complexation model will be derived to determine the numbers of proton binding and metal binding acidic groups and the acid-dissociation and metal-complexation constants of HA and insolubilized humic acids (IHA). Based on

these parameters, the effect of insolubilization on the metal-complexation ability of humic acid will be also discussed.

5.2 Experimental

5.2.1 HA Calcium Salt

HA was insolubilized by heating treatment. As the heating of raw HA caused too rapid dehydration (condensation) between acidic groups, HA was pretreated with CaCl_2 solution and was converted from sodium salt to calcium. A certain concentration of CaCl_2 solution and the same volume of HA solution (30 wt-%) were mixed and stirred for 10 min at room temperature. Then, precipitated HA calcium was separated from the liquid phase in a centrifuge (KOKUSAN H-1500F) at 4,000 rpm for 10 min and dried at 70 °C. The concentration of HA in the supernatant was measured by a spectrophotometric method at 300 nm.

5.2.2 Insolubilization of HA

HA calcium salt was insolubilized by heating treatment at 100, 200, 250, 330, 550 and 800 °C in a muffle furnace for 1 h. Thus obtained insolubilized HA (IHA) was ground in agate mortar with a pestle, and was washed repeatedly with a 1M HNO_3 solution and hot distilled water. Finally, IHA was converted from the hydrogen form to sodium form with 1M NaNO_3 solution, and it was rinsed with distilled water and dried at 70°C.

5.2.3 Effectiveness of Insolubilization

(1) A 0.05 g IHA was mechanically stirred in a 0.5 dm³ distilled water at various temperature for 24 h. The concentration of HA in bulk phase was measured in order to determine the percentage of dissolution. (2) A 0.05 g HA was mechanically stirred in a 0.5 dm³ solution containing a certain amount of HNO₃ or NaOH at 30°C for 24 h. The concentration of HA and pH in bulk phase was measured.

5.2.4 Potentiometric Titration of HA and IHA

A 0.3 dm³ of solution containing 0.2 g of HA/ IHA and NaNO₃ (0.1 M) was titrated with a standard solution of HNO₃ (0.1 M) at 30°C. The pH of the solution was measured by a pH meter (ORION RESEARCH 520-A). The number of protonated acidic groups on HA/IHA was determined from the difference between the bulk proton concentrations in the presence and in the absence of HA/IHA. The other experimental procedures and condition were almost same as the conductometric titration.

5.2.5 Complexation between HA and Metal ions

A 90 cm³ of NaNO₃ solution (0.1M) containing a certain amount of Cd(NO₃)₂ or Pb(NO₃)₂ was prepared. The pH of the solution was adjusted to a desired value by HNO₃. After reaching the thermal equilibrium at 30°C, a 10 cm³ of HA solution (10 g·dm⁻³) was added to the solution and the complexation reaction was initiated. The solution was stirred for a necessary time to attain the complexation equilibrium and then HA was separated from the liquid

phase in a centrifuge (KOKUSAN H-1500F) at 10,000 rpm for 20 min. The pH and metal ion concentration of the supernatant were measured. The metal ion concentration was determined by atomic absorption spectrophotometer (HITACHI A-1800). The amount of metal ion complexed with HA was determined from the difference between the metal ion concentrations in the initial and the equilibrium states.

5.2.6 Adsorption of Metal ions on IHA

A 0.1 dm³ (for Cd adsorption) or 0.5 dm³ (for Pb adsorption) of NaNO₃ (0.1 M) solution containing a necessary amount of Cd(NO₃)₂ or Pb(NO₃)₂ was prepared. The pH of the solution was adjusted to a desired value by HNO₃. After reaching the thermal equilibrium at 30°C, 0.1g of IHA was added to the solution. The suspension was stirred for a necessary time to attain the adsorption equilibrium and then IHA was separated from the liquid phase in a centrifuge at 10,000 rpm for 10 min. The pH and metal ion concentration of the supernatant were measured.

5.3 Results and Discussion

5.3.1 Conditions for Preparing IHA

Figure 5-1 shows the effect of CaCl₂ concentration on the percentage of HA remaining in supernatant solutions after centrifugation. Percentage of remaining HA abruptly decreased with the increase of CaCl₂ concentration and HA can be almost completely precipitated with 1.0 M CaCl₂ solution. **Figure 5-2**

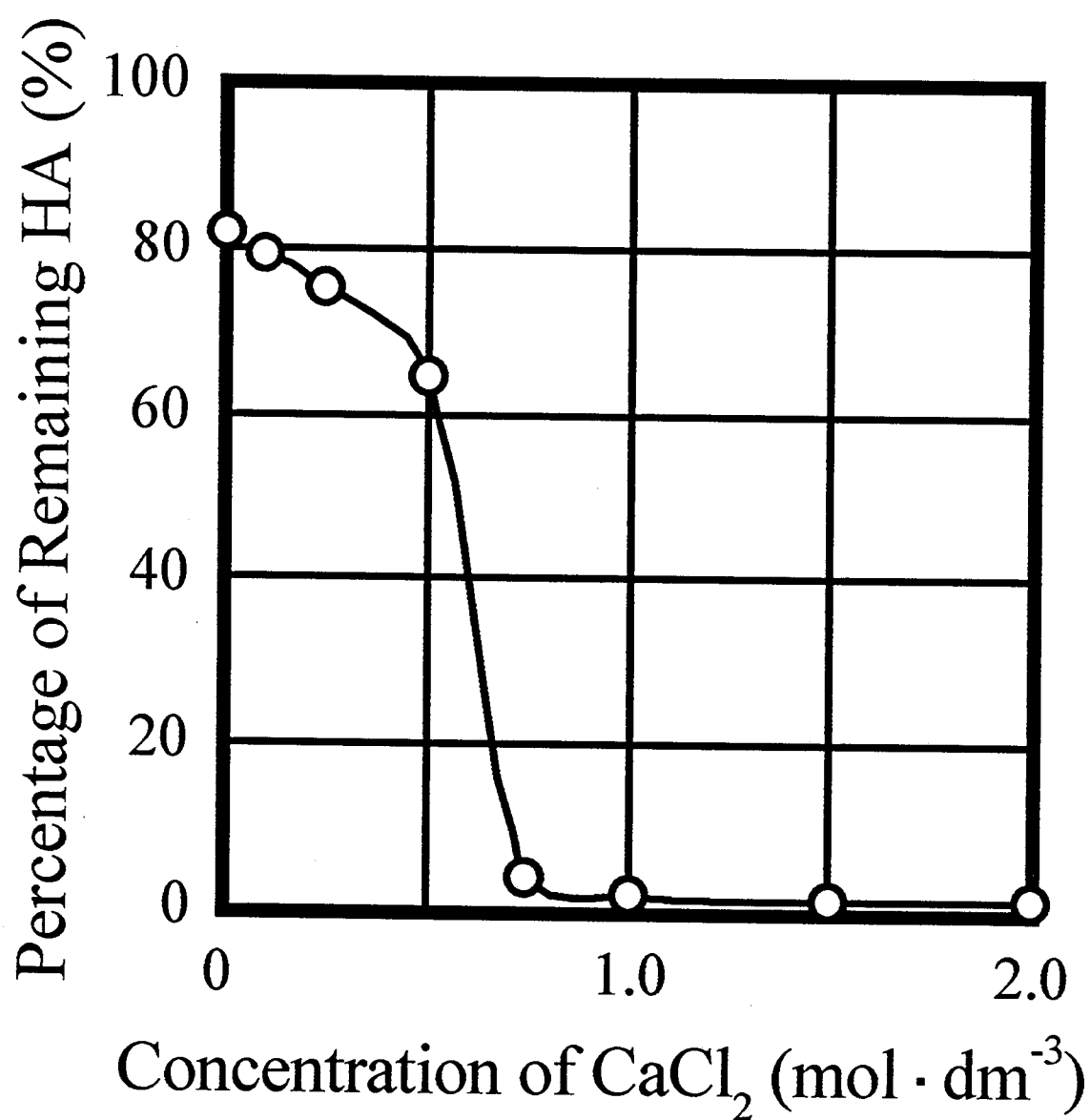


Fig.5-1. Effect of CaCl₂ concentration on the percentage of HA remaining in supernatant solutions after centrifugation.

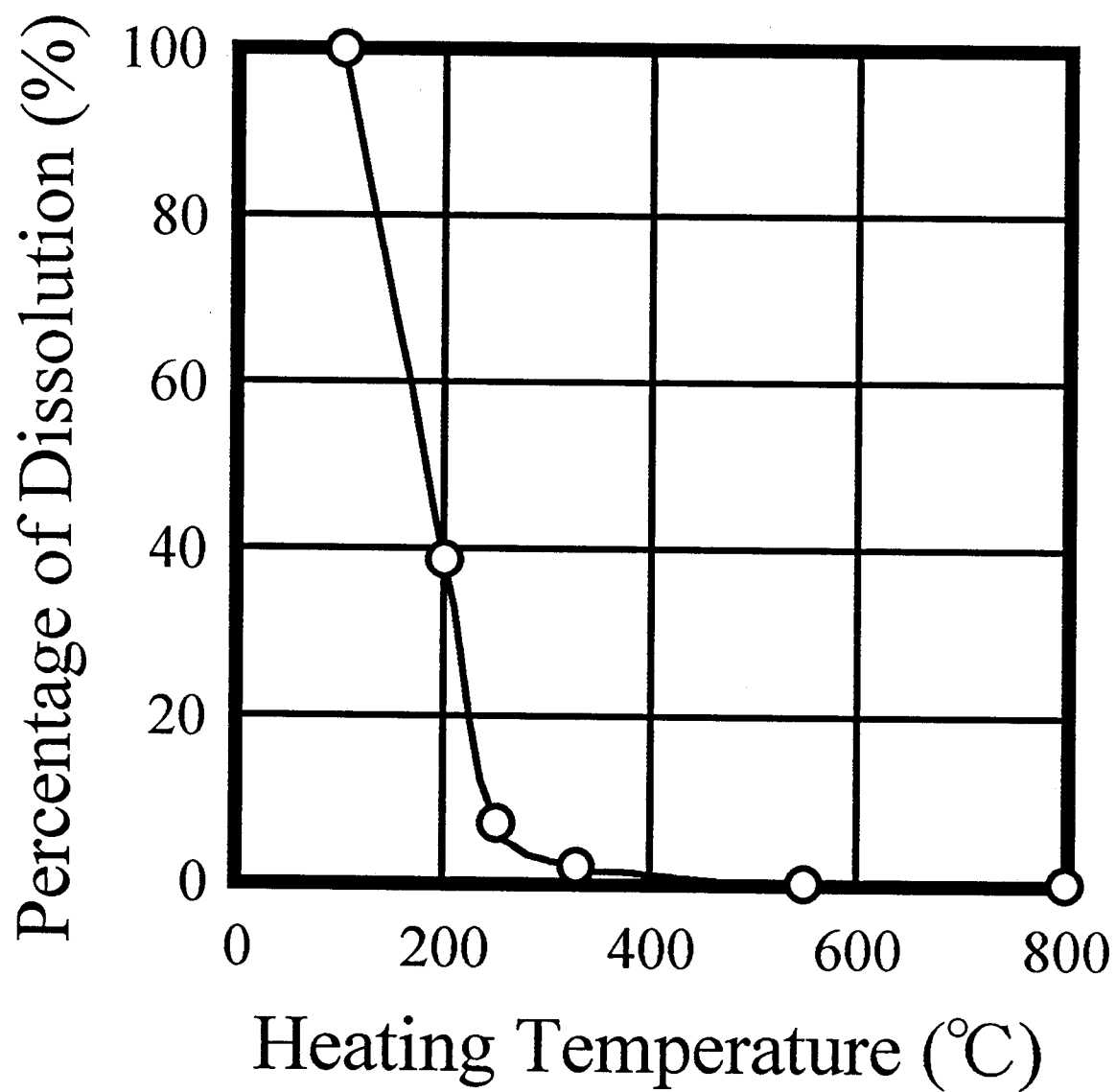


Fig.5-2. Effect of heating temperature on the percentage of IHA dissolution in distilled water at 30°C.

shows the effect of heating temperature on the insolubility of IHA. The percentage of dissolution abruptly decreased with the increase of heating temperature and the dissolution of IHA prepared at 330 °C was virtually negligible. From the results, the CaCl_2 concentration for HA calcium preparation and the temperature for insolubilization were determined as 0.1 M and 330°C.

5.3.2 Dissolution Characteristics of IHA

Figure 5-3 shows the percentage of IHA dissolution in various temperature of distilled water. IHA prepared at 250 °C and 330 °C were used in this experiment. The dissolution gradually increased with the increase of temperature, IHA prepared at 330°C exhibited an excellent insolubility over the wide temperature range. IHA prepared at 330°C dissolved only about 5 % even in a boiling water, while IHA prepared at 250°C dissolved about 15 %. **Figure 5-4** shows the pH dependence of the percentage of IHA dissolution. IHA prepared at 330°C exhibited a excellent insolubility even in an alkaline solution of pH 11. From the results, the IHA prepared at 330 °C was used in the following experiments.

5.3.3 Influence of Insolubilization on Acid-Base Properties of HA

HA is insolubilized by condensation of acidic groups (23) such as aromatic carboxyl groups and phenolic hydroxyl groups (32), which are probably the sites for metal complexation. Therefore, it is presumable that the number of acidic groups and acid-dissociation constant of IHA are lowered by heating

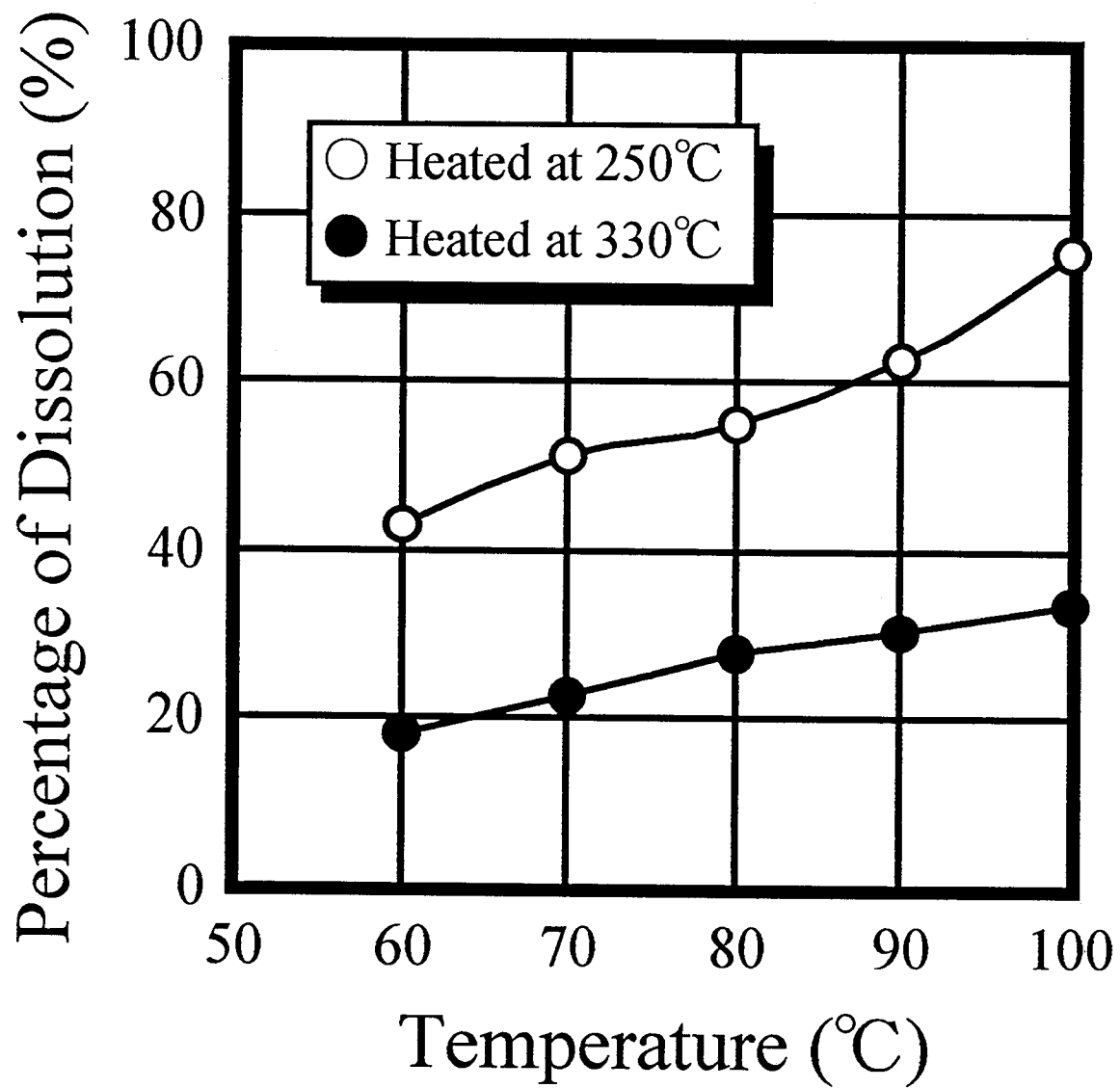


Fig.5-3. Dissolution of IHA prepared at 250°C(○) and 330°C(●) in various temperature of distilled water.

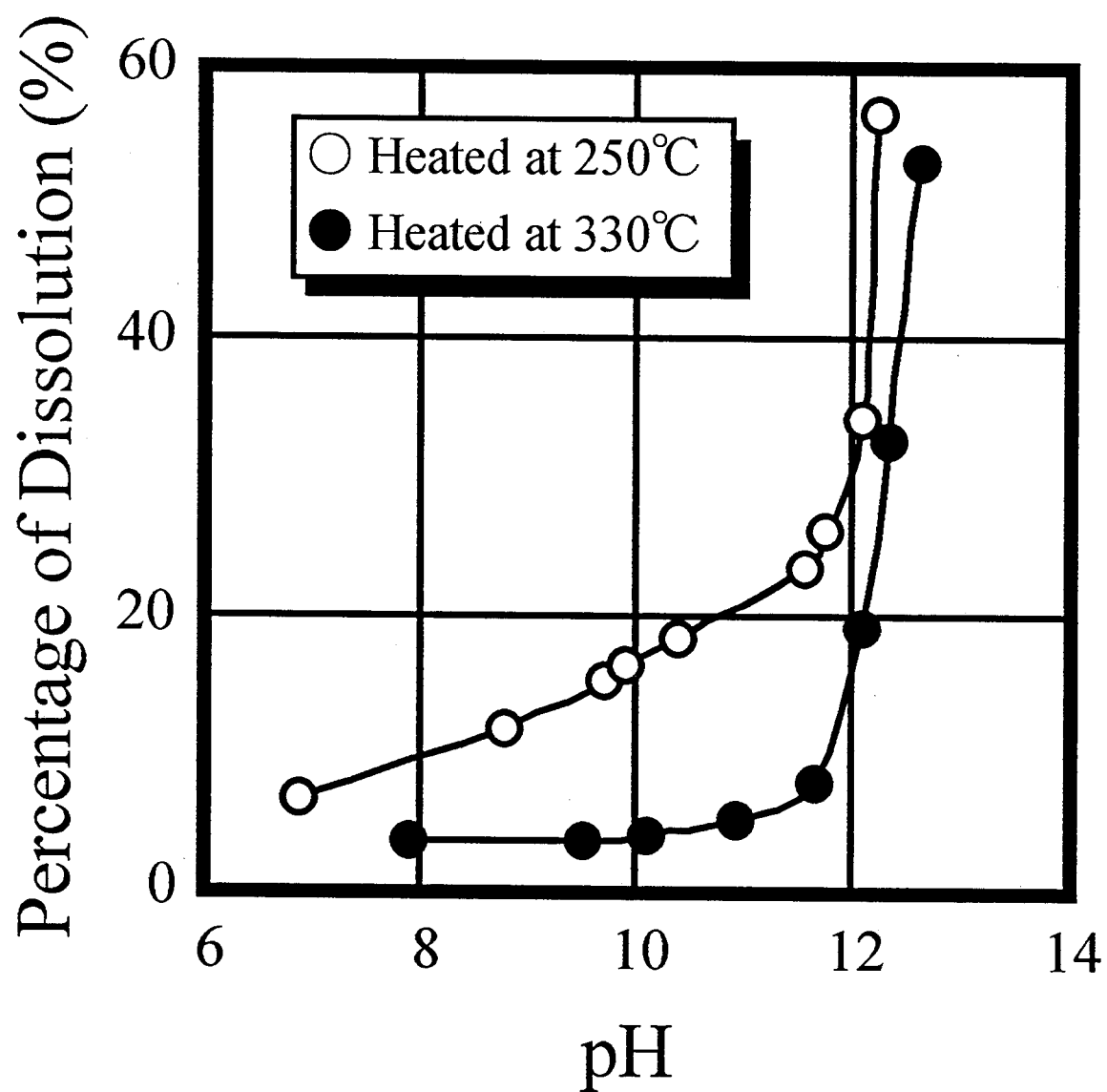


Fig.5-4. Dissolution of IHA prepared at 250°C(○) and 330°C(●) in various pH of solutions at 30°C.

treatment, as compared with those of HA. **Figure 5-5** shows the results of conductometric titration of HA (○) and IHA (□) with 0.1M HNO₃. The titration curve gives the end point by the intersection of two straight lines (12). No end point was obtained from the titration with 0.1M NaOH. The total number of acidic groups on HA and IHA were determined from these titration curves as 3.40×10^{-3} and 2.60×10^{-3} mol·g⁻¹, respectively. In other words, about 25% of the acidic groups on HA disappeared by the condensation reaction.

Figure 5-6 shows the protonation characteristics of the acidic groups on HA and IHA obtained from the potentiometric titration. The titration curves of humic substances are usually broad and ill-defined thus reflecting the diversity in acidic groups. Wilson and Kinney (36) investigated the acid-base properties of lake water and marine humic substances, and determined two acid-dissociation constants. Assuming that the similar relation hold in the present HA, the acid-dissociation reactions of HA can be written as



-S₁ and -S₂ represent the type 1 and 2 acidic groups on HA, respectively. The acid-dissociation constants K_{H1} and K_{H2} are defined as

$$K_{H1} = \alpha_1 [H^+] / (1 - \alpha_1) \quad [5-3]$$

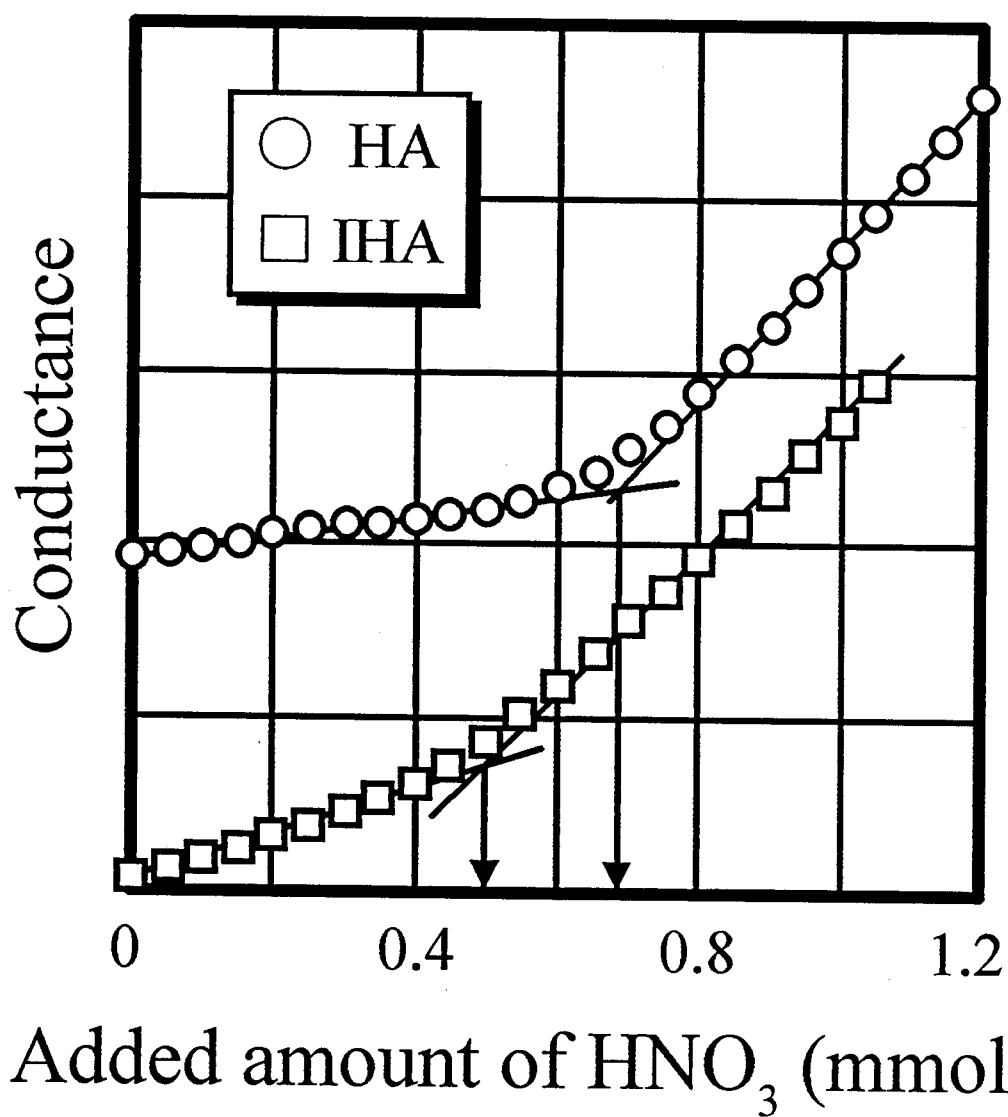


Fig.5-5. Conductometric titration curves for 300 cm³ of a solution containing 0.2g of HA or IHA with 0.1 mol·dm⁻³ HNO_3 at 30°C.

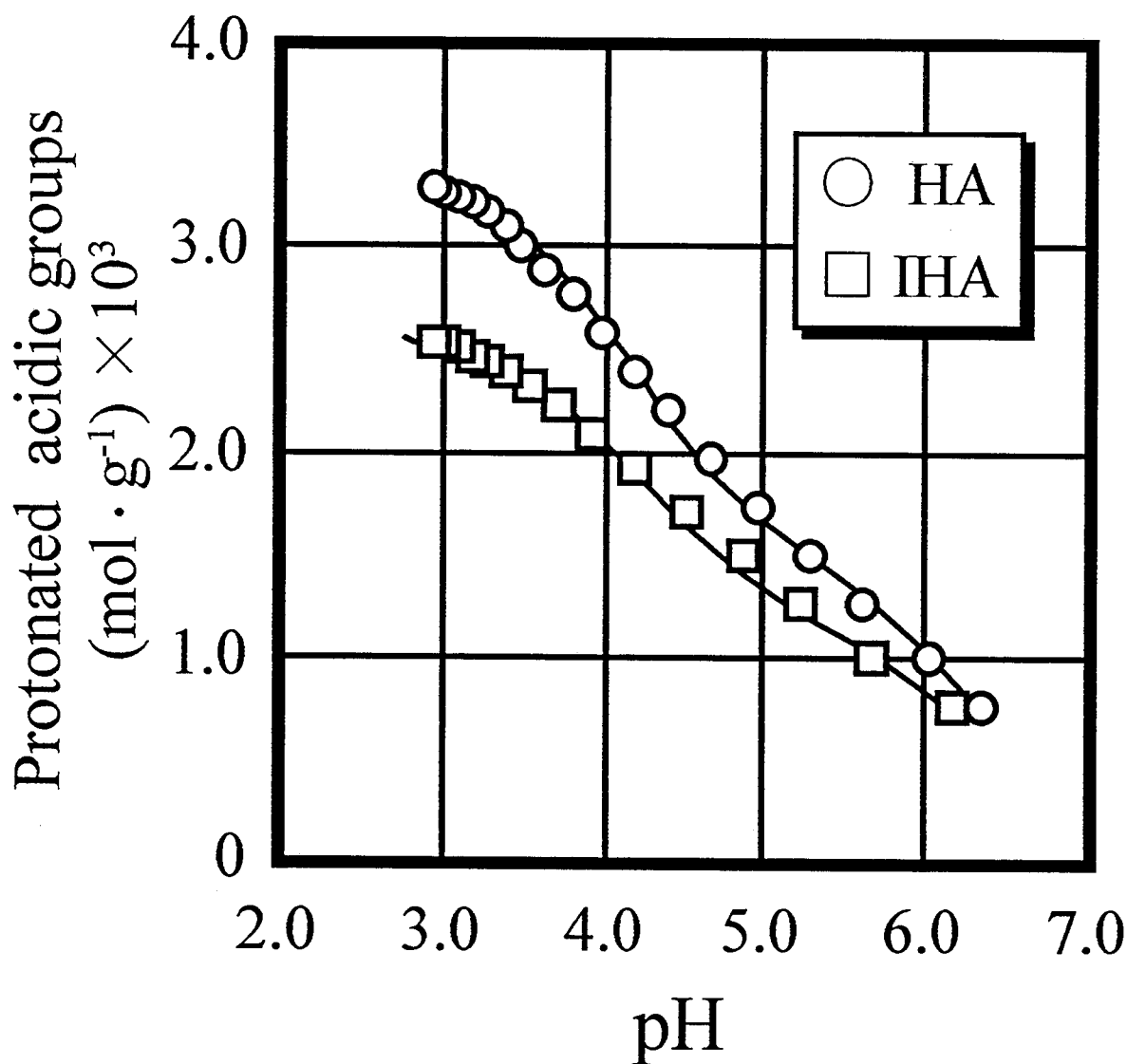


Fig.5-6. Number of protonated acidic groups on HA and IHA as a function of pH. The number of protonated acidic groups was determined by potentiometric titrations for 300 cm³ of a solution containing 0.2g of HA or IHA and NaNO₃ (0.1 mol·dm⁻³) with 0.1 mol·dm⁻³ HNO₃ at 30°C.

$$K_{H2} = \alpha_2 [H^+] / (1 - \alpha_2), \quad [5-4]$$

where α_1 and α_2 are the degree of dissociation of type 1 and 2 acidic groups, respectively. Eqs.[5-3] and [5-4] are modified to

$$\alpha_1 = K_{H1} / \{K_{H1} + [H^+]\} \quad [5-5]$$

$$\alpha_2 = K_{H2} / \{K_{H2} + [H^+]\}. \quad [5-6]$$

The amount of proton bound to acidic groups on 1 g of HA, X_H , can be expressed as

$$X_H = N_{H1}(1 - \alpha_1) + N_{H2}(1 - \alpha_2), \quad [5-7]$$

where N_{H1} and N_{H2} are the number of type 1 and 2 acidic groups, respectively. A nonlinear least-square method was applied to find four constants, K_{H1} , K_{H2} , N_{H1} and N_{H2} , in Eqs.[5-3] and [5-4]. These constants for HA and IHA, which gave the best fit with the experimental data (in Fig.5-6), were listed in **Table 5-1**. In this calculation, the total number of acidic groups obtained from the conductometric titration, $3.40 \times 10^{-3} \text{ mol} \cdot \text{g}^{-1}$ (HA) and $2.60 \times 10^{-3} \text{ mol} \cdot \text{g}^{-1}$ (IHA) were used. **Figure 5-7** shows the comparison between the experimental amount of proton bound to acidic groups, $X_{H(\text{exp})}$, and the calculated from Eq.[5-5]-[5-7] using the constants listed in Table5-1, $X_{H(\text{cal})}$. The experimental data agreed well with the calculated. From the results listed in Table5-1, the

TABLE 5-1 Equilibrium Parameters for Acid-Dissociation of HA and IHA

	N_{H1} (mol·g ⁻¹)	N_{H2} (mol·g ⁻¹)	pK_1	pK_2
HA	1.93×10^{-3}	1.47×10^{-3}	4.17	6.34
IHA	1.45×10^{-3}	1.15×10^{-3}	4.22	6.39

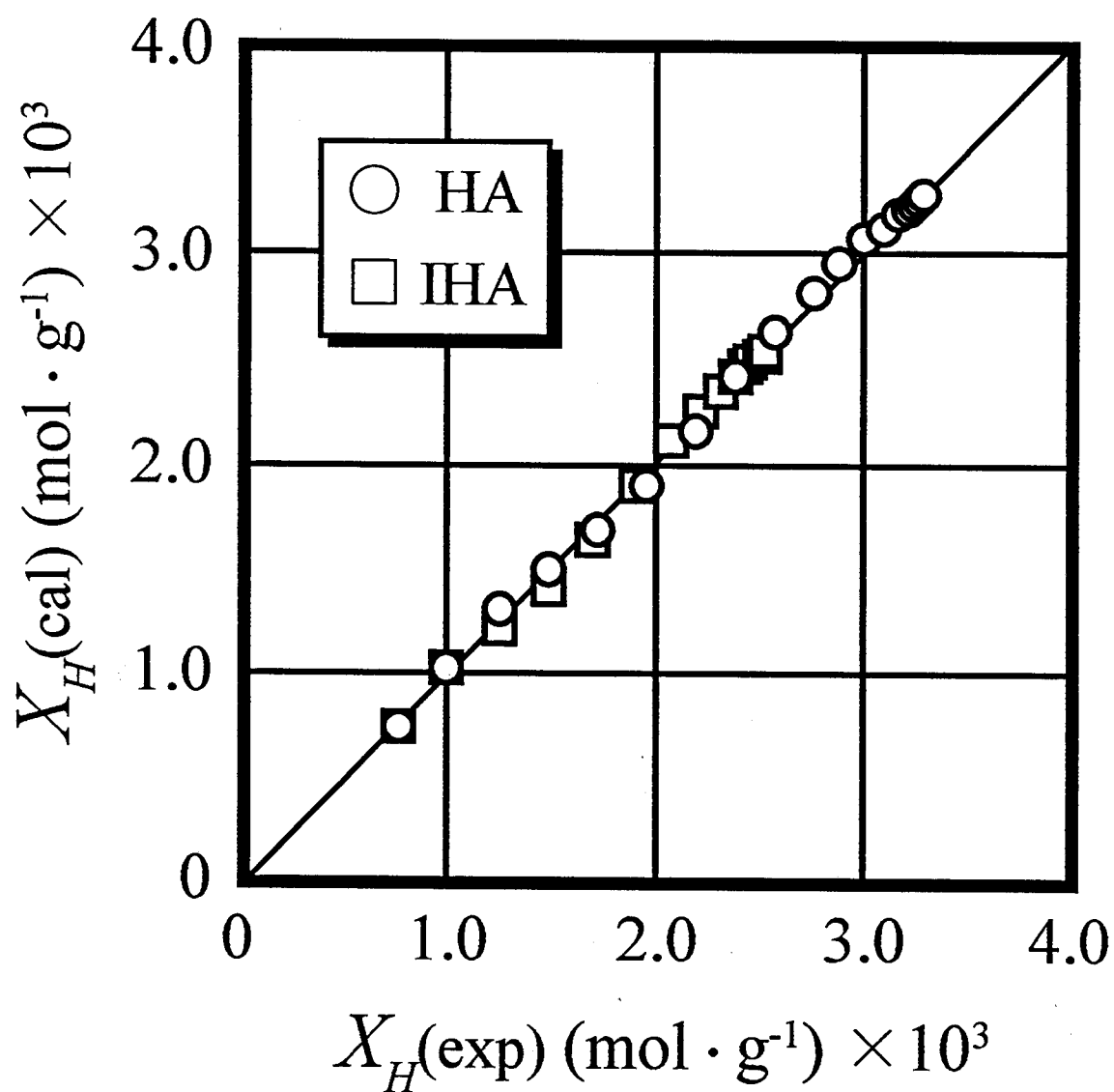
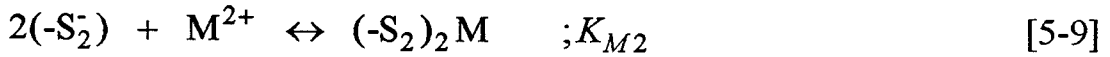
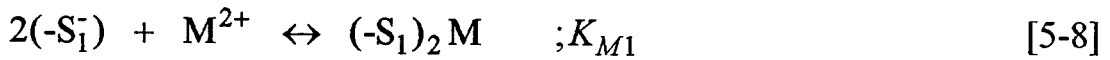


Fig.5-7. Comparison of the number of protonated acidic groups between the experimental and the calculated from Eqs.[5-5]-[5-7].

effect of the insolubilization on the acid-base properties of type 1 and 2 acidic groups can be clarified. 25% of type 1 and 22% of type 2 acidic groups are lost by the present insolubilization. The acid-dissociation constants, K_{H1} and K_{H2} , are scarcely influenced.

5.3.4 Influence of Insolubilization on Metal-HA Complexation

Figure 5-8 shows the acid-dissociation curves of acidic groups on HA calculated from Eq.[5-5]-[5-7]. The acid-dissociation constants K_{H1} and K_{H2} are different about two orders, and the acid-dissociation curves of type 1 and 2 acidic groups are clearly distinguished. Therefore, two equilibria were proposed to explain the complexation of divalent metal ions with HA:



M^{2+} in Eqs.[5-8] and [5-9] represents the divalent metal ions. The complexation constants K_{M1} and K_{M2} ($\text{dm}^3 \cdot \text{mol}^{-1}$) are defined as

$$\begin{aligned} K_{M1} &= \alpha_{M1} / \left[\{(1 - \alpha_{M1})\alpha_1\}^2 [M^{2+}] \right] \\ &= \frac{\alpha_{M1}}{\left\{ (1 - \alpha_{M1})K_{H1} / (K_{H1} + [H^+]) \right\}^2 [M^{2+}]} \end{aligned} \quad [5-10]$$

$$K_{M2} = \alpha_{M2} / \left[\{(1 - \alpha_{M2})\alpha_2\}^2 [M^{2+}] \right]$$

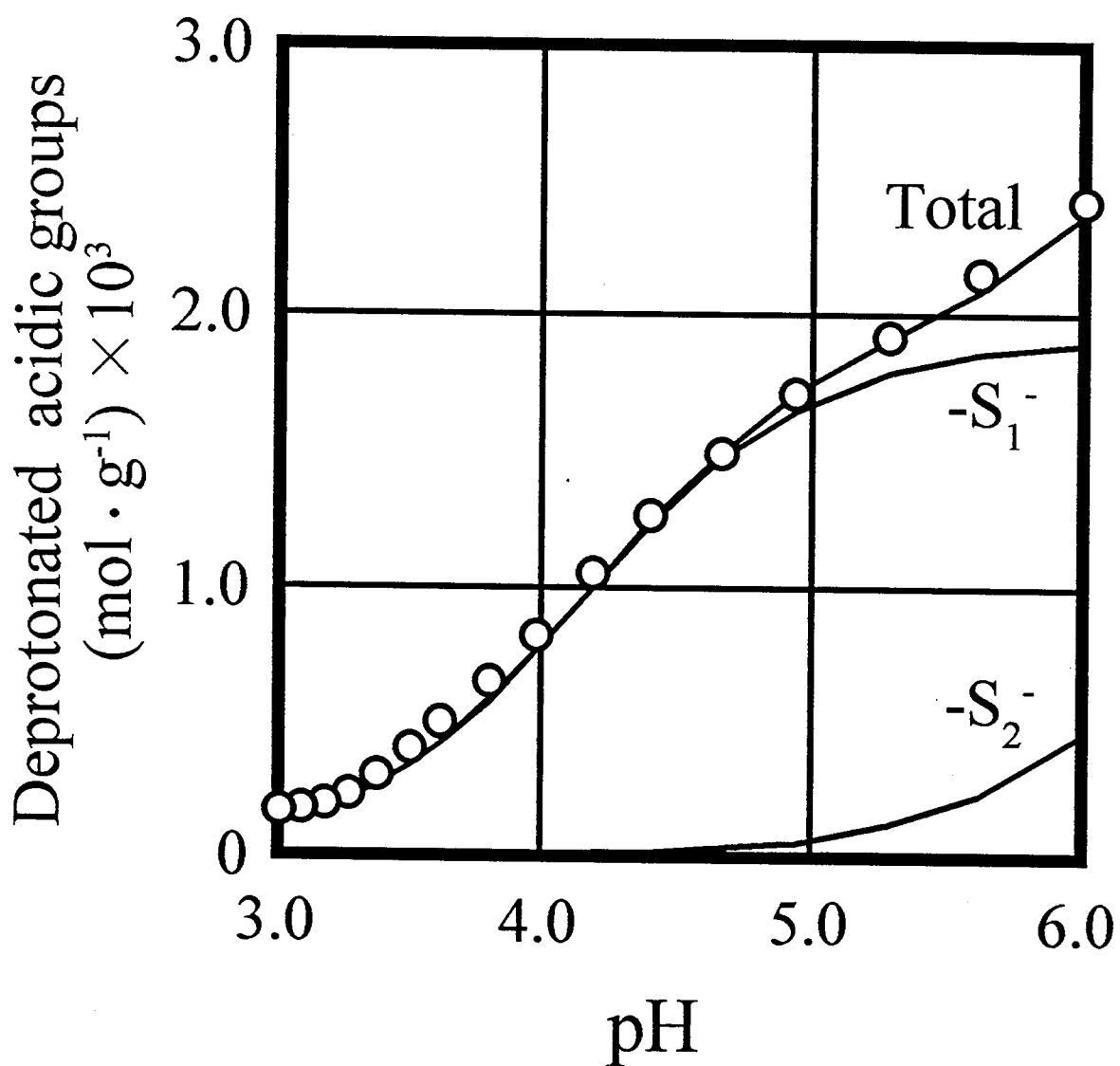


Fig.5-8. Acid-dissociation curves of acidic groups on HA. The solid lines represent the theoretical curves calculated from Eqs.[5-5]-[5-7].

$$= \frac{\alpha_{M2}}{\{(1-\alpha_{M2})K_{H2} / (K_{H2} + [H^+])\}^2 [M^{2+}]}, \quad [5-11]$$

where α_{M1} and α_{M2} represent the fraction of type 1 and 2 acidic groups complexed with metal ions, respectively. Eqs.[5-10] and [5-11] are modified to

$$\alpha_{M1} = (P_1 - \sqrt{P_1^2 - 4}) / 2 \quad [5-12]$$

$$P_1 \equiv 2 + \{K_{M1}[M^{2+}]\{K_{H1} / (K_{H1} + [H^+])\}^2\}^{-1}$$

$$\alpha_{M2} = (P_2 - \sqrt{P_2^2 - 4}) / 2 \quad [5-13]$$

$$P_2 \equiv 2 + \{K_{M2}[M^{2+}]\{K_{H2} / (K_{H2} + [H^+])\}^2\}^{-1}$$

The amount of metal ions complexed with 1 g of HA, X_M , can be expressed as

$$X_M = (N_{M1}\alpha_{M1} + N_{M2}\alpha_{M2}) / 2. \quad [5-14]$$

N_{M1} and N_{M2} represent the number of type 1 and 2 acidic groups available for metal-complexation, respectively.

The pH dependence of the amount of cadmium (○) and lead ions (●) complexed with HA is presented in **Fig.5-9**. The ordinate of Fig.5-9, X_M , represents the equilibrium amount of metal ions complexed with HA. Figure 5-9 shows that the pH increase of the complexation system resulted in more

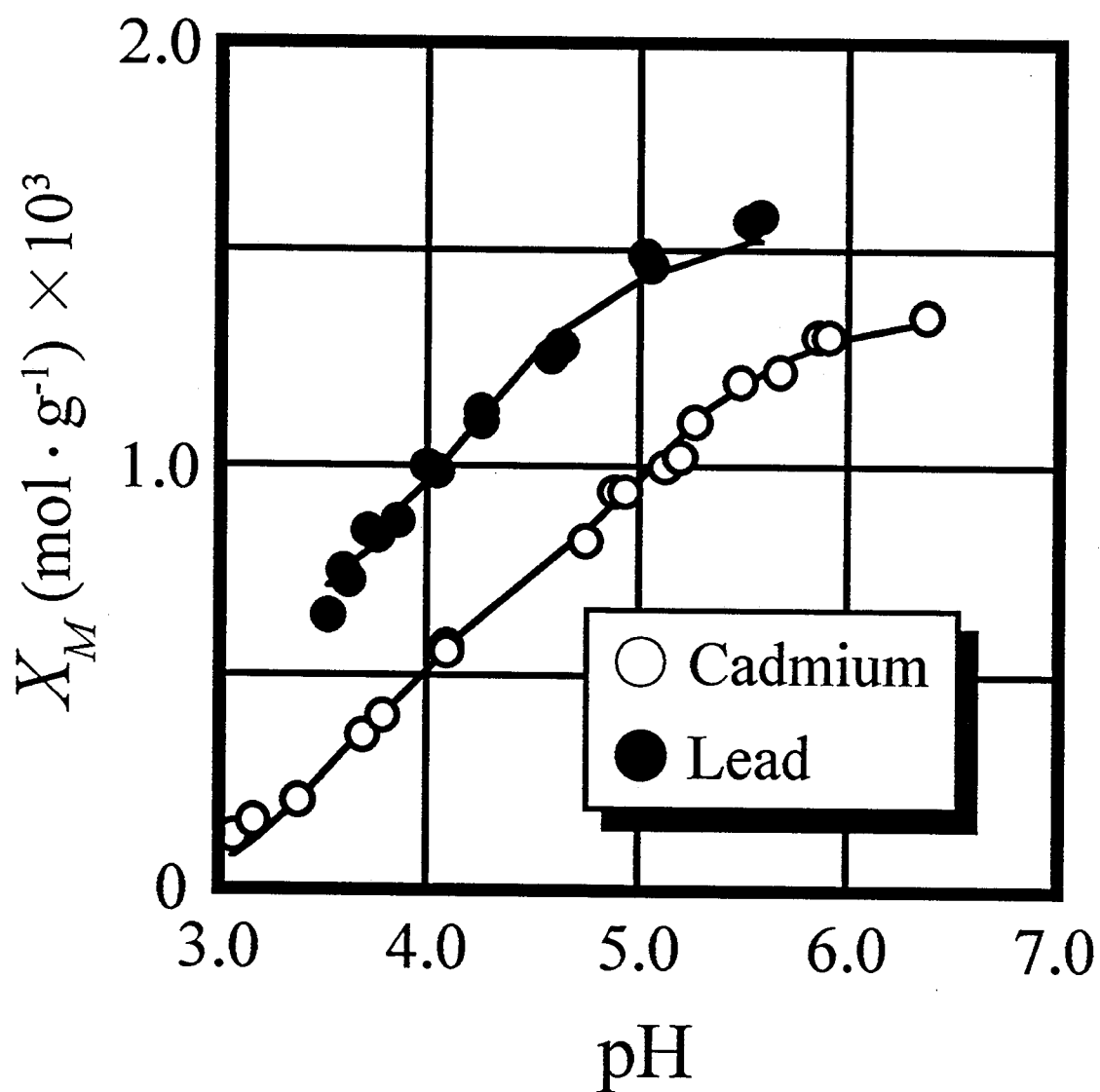


Fig.5-9. pH dependence of metal-HA complexation at 30°C. Initial concentrations of HA, NaNO_3 , $\text{Cd}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_2$ are $1 \text{ g} \cdot \text{dm}^{-3}$, 0.1, 1.0×10^{-3} and $4.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$, respectively.

formation of metal-HA complexes, and the formation of Pb-HA complex occurs even in low pH region compared to Cd-HA system. A nonlinear least square method was applied to find four constants, K_{M1} , K_{M2} , N_{M1} and N_{M2} , in Eqs.[5-12]-[5-14]. The obtained constants are listed in **Table 5-2**. **Figure 5-10** shows the comparison between the experimental amounts of metal ions complexed with HA and the amount calculated from Eqs.[5-12]-[5-14] using the constants listed in Table 5-2. Figure 5-10 demonstrates a good agreement of the experimental data with the present metal-HA complexation model. The number of acidic groups available for metal-complexation, N_{M1} and N_{M2} , are in fair agreement with the number of acidic groups on HA, N_{H1} and N_{H2} , determined from the potentiometric titration (Table 5-1). This means that all the acidic groups on HA are available for metal-complexation.

The pH dependence of the amount of cadmium ($\square$) and lead ions ($\blacksquare$) complexed with IHA is presented in **Fig.5-11**. The four constants, K_{M1} , K_{M2} , N_{M1} and N_{M2} , for IHA were determined in the same manner as HA, and they are listed in **Table 5-3**. **Figure 5-12** shows the comparison between the experimental amounts of metal ions adsorbed on IHA and the calculated from Eqs.[5-12]-[5-14] with the values in Table 5-3. It is seen that the calculated is in good accordance with the experimental. In the case of IHA (Table 5-3), the number of type 1 acidic groups available for metal complexation, N_{M1} , almost coincided with the number of acidic groups, N_{H1} (Table 5-1). However, 20% of type 2 acidic groups was unavailable for metal-complexation. The insolubilization process scarcely influenced on the complexation constants, K_{M1} and K_{M2} .

TABLE 5-2 Equilibrium Parameters for Metal-HA Complexation

	N_{M1} (mol·g ⁻¹)	N_{M2} (mol·g ⁻¹)	pK_{M1}	pK_{M2}
Cadmium	1.93×10^{-3}	1.47×10^{-3}	-3.78	-5.33
Lead	1.93×10^{-3}	1.47×10^{-3}	-5.89	-7.96

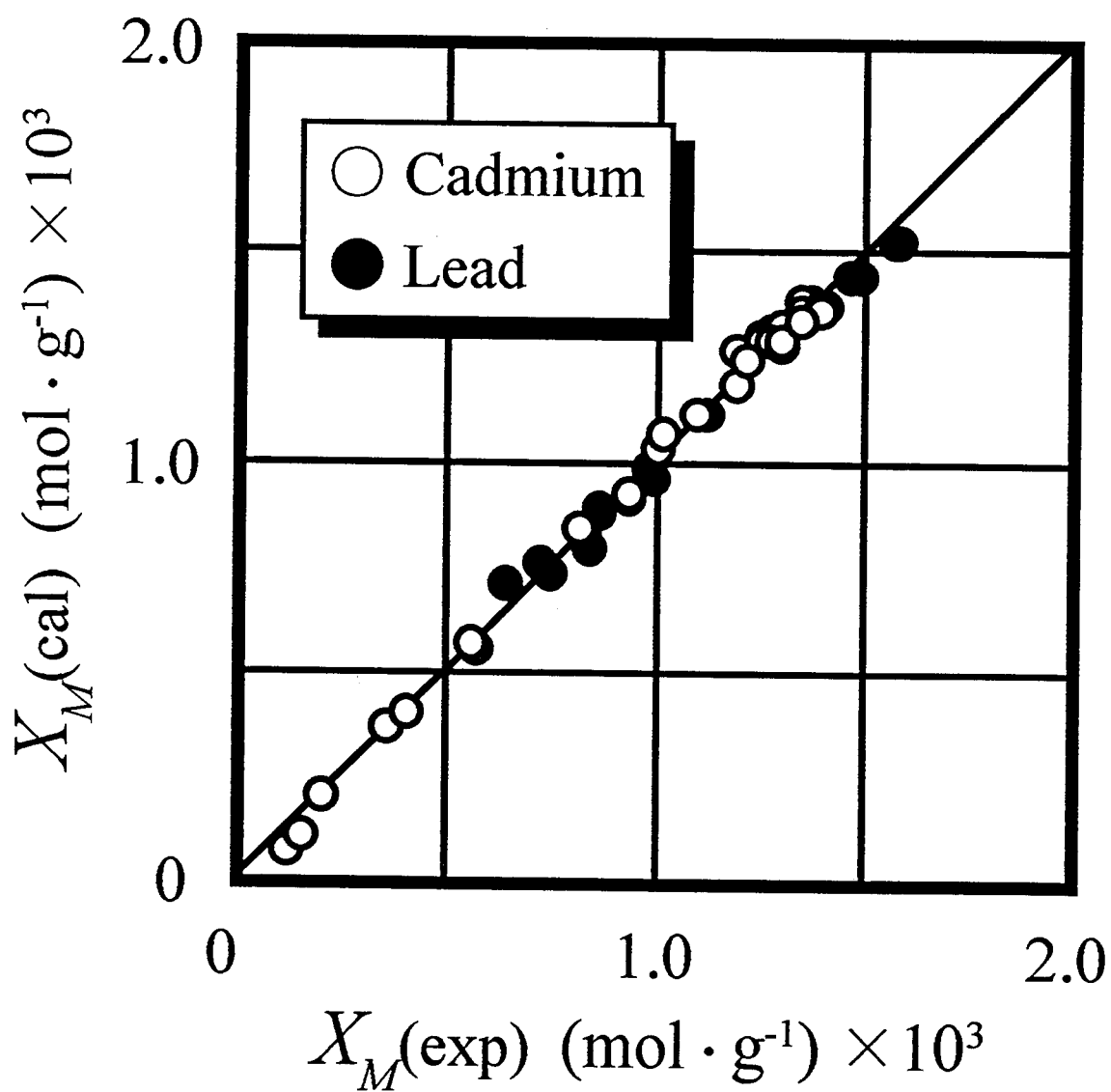


Fig.5-10. Comparison of the amounts of metal-complexation between the experimental and the calculated from Eqs.[5-12]-[5-14].

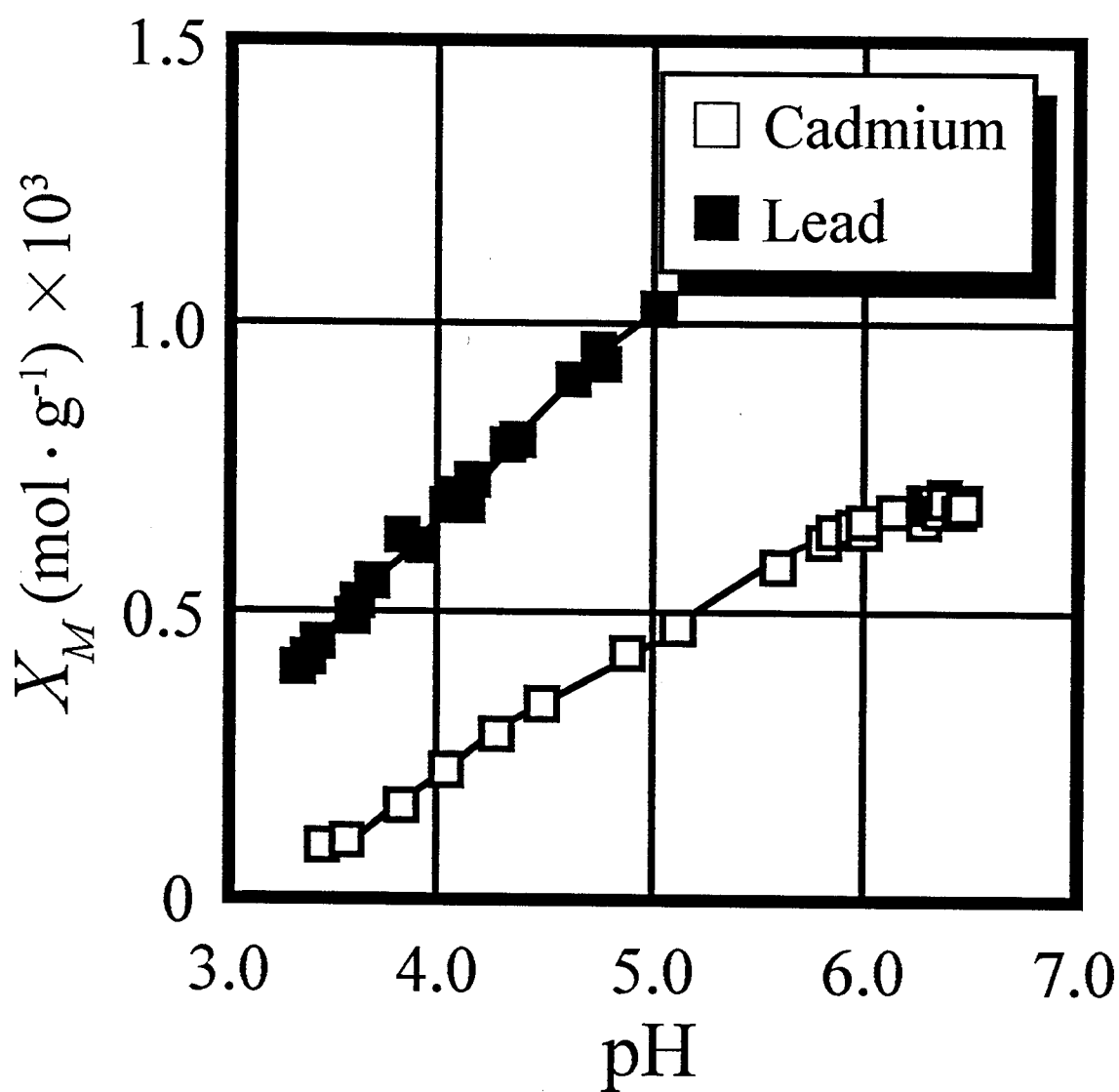


Fig.5-11. pH dependence of metal-IHA complexation at 30°C. Experimental conditions are identical to those described in Fig.5-5.

TABLE 5-3 Equilibrium Parameters for Metal-IHA Complexation

	$N_{M1}(\text{mol}\cdot\text{g}^{-1})$	$N_{M2}(\text{mol}\cdot\text{g}^{-1})$	$\text{p}K_{M1}$	$\text{p}K_{M2}$
Cadmium	1.45×10^{-3}	0.90×10^{-3}	-3.67	-5.37
Lead	1.45×10^{-3}	0.96×10^{-3}	-5.71	-7.56

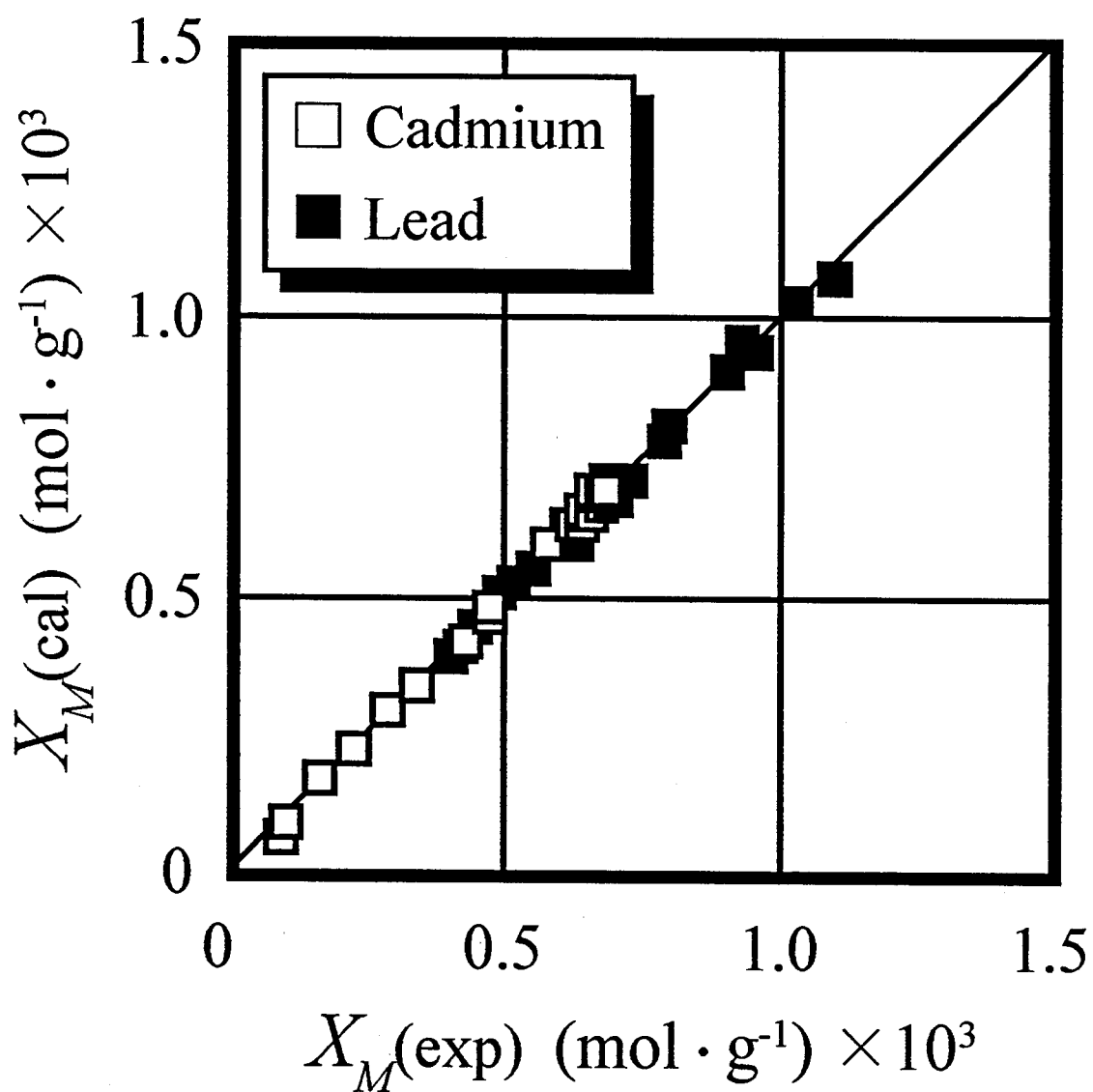


Fig.5-12. Comparison of the amounts of metal-complexation between the experimental and the calculated from Eqs.[5-12]-[5-14].

5.4 Conclusions

Humic acid, which has an excellent complexing ability with heavy metal ions, was applied to the recovery of cadmium and lead ions. It was insolubilized by heating treatment and was used as an adsorbent material. A metal-complexation model was proposed to determine the number of proton binding and metal binding acidic groups and acid-dissociation and metal-complexation constants of HA and IHA. The model was confirmed by the potentiometric titrations and metal-complexation experiments. On the basis of these results, the followings were concluded.

- (1) IHA was obtained by heating of HA calcium salt at 330°C for 1 h.
- (2) IHA prepared in this method was virtually insoluble in water up to pH 10 at 30°C and was virtually insoluble even in boiling distilled water.
- (3) The broad and ill-defined titration curves of HA and IHA were attributed to two different types of acidic groups.
- (4) The number and the acid-dissociation constants of type 1 and 2 acidic groups, N_{H1} , N_{H2} , K_{H1} and K_{H2} , were determined from the model. The acid-dissociation constants, K_{H1} and K_{H2} , scarcely influenced by the insolubilization. However, 25% of N_{H1} and 22% of N_{H2} were lost by the insolubilization.
- (5) The model was successfully applied to both metal-HA and metal-IHA systems. The available number and the metal-complexation constants of type 1 and 2 acidic groups, N_{M1} , N_{M2} , K_{M1} and K_{M2} , were determined.
- (6) All the acidic groups on HA were available for the metal-complexation, but 20% of type 2 acidic groups on IHA was unavailable.
- (7) The metal-complexation constants of IHA agreed with the constants of HA.

5.5 Nomenclature

K_{Hi}	= acid-dissociation constant of type i acidic groups	(dm ³ ·mol ⁻¹)
K_{Mi}	= metal-complexation constant of type i acidic groups	(dm ³ ·mol ⁻¹)
N_{Hi}	= number of type i acidic groups	(mol·g ⁻¹)
N_{Mi}	= number of type i acidic groups available for metal-complexation	(mol·g ⁻¹)
X_{Hi}	= amount of proton bound to type i acidic groups	(mol·g ⁻¹)
X_{Mi}	= amount of metal ions complexed with type i acidic groups	(mol·g ⁻¹)
α_i	= degree of dissociation of type i acidic groups	(-)
α_{Mi}	= fraction of type i acidic groups complexed with metal ions	(-)

6. GENERAL CONCLUSIONS

Application of humic acid(HA), which has an excellent complexing ability with heavy metals, to the aqueous-phase separation of metal ions was investigated. For this purpose, new adsorbents of immobilized HA were developed. Based on a simple model for the complexation of divalent metal ions on organic polymers in acidic media, the adsorption mechanism and the ability of this newly developed adsorbents were quantitatively discussed using lead ions as an adsorbate(in Chapters 2, 3 and 4).

In Chapter 5, another humic acid insolubilized by heating treatment was employed for the recovery of lead and cadmium from dilute solutions. Based on a general complexation model, the adsorption characteristics of insolubilized humic acid (IHA) was compared with those of HA. The general conclusions are:

(1) HA was immobilized by a combination of alginate gel and activated carbon powder(ACP). HA was almost completely entrapped by the addition of the HA's weight in ACP.

(2) This immobilizing technique enabled the preparation of an adsorbent comprising as much as about 50 wt-% HA on dry-weight basis or 15 wt-% on wet-weight basis.

(3) The complexation constants of the lead-HA system and the number of available sites for complexation of HA was not influenced by the immobilization.

(4) The alginate gel used as an immobilizing agent affected the rate of

adsorption to a remarkable extent.

(5) The membranous adsorbent(HA-M) was obviously superior to the spherical adsorbent(HA-gel) in both terms of adsorption kinetics and capacity on wet-weight basis.

(6) Insolubilized humic acid(IHA) prepared by heating treatment of HA calcium salt at 330°C for 1 h was virtually insoluble in water up to pH 10.

(7) HA had two different types of acidic groups. The acid-dissociation and metal complexation constants of type 1 and 2 acidic groups scarcely influenced by the insolubilization. However, 25% of type 1 and 22% of type 2 acidic groups were lost by the insolubilization.

(8) All the acidic groups on HA were available for the metal-complexation, but 20% of type 2 acidic groups on IHA was unavailable.

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LIST OF FIGURES

PART I

Chapter 2

Fig.2-1. Titration curves for 300 cm³ of a solution containing 1.0×10^{-2} mol·dm⁻³ NaOH and 0.1 mol·dm⁻³ NaNO₃ in the absence (○) and in the presence (●) of 0.22g of hydrous titanium(IV) oxide at 25°C.

Fig.2-2. Replot of Fig.2-1 data by Eq.[2-13].

Fig.2-3. Uptake of divalent metal ions in acidic solutions as a function of adsorption time at 25°C. Hydrous titanium(IV) oxide (ca. 0.05g) was used as the adsorbent. Initial concentrations of the metal ions are 1.0×10^{-4} mol·dm⁻³ for all the runs.

Fig.2-4. Effect of equilibrium pH on uranium adsorption in acidic solutions at 25°C. Hydrous titanium(IV) oxide (ca. 0.05g) was used as the adsorbent. Initial concentrations of uranyl nitrate for symbols ○, △ and ● are 1.0, 1.5 and 2.0×10^{-4} mol·g⁻¹, respectively.

Fig.2-5. Fitting of uranium adsorption in acidic solutions to the theoretical

isotherm (Eq.[2-15]).

Fig.2-6. Fitting of lead adsorption in acidic solutions to the theoretical isotherm (Eq.[2-15]).

Fig.2-7. Fitting of cadmium adsorption in acidic solutions to the theoretical isotherm (Eq.[2-15]).

Fig.2-8. Fitting of zinc adsorption in acidic solutions to the theoretical isotherm (Eq.[2-15]).

Fig.2-9. Effect of initial concentration of sodium hydrogencarbonate on uranium adsorption at 25 °C . R denotes the mole ratio of sodium hydrogencarbonate to uranium nitrate initially added. Hydrous titanium(IV) oxide (ca. 0.04g) was used as the adsorbent. Initial concentration of uranium nitrate is $1.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$.

Fig.2-10. Calculated concentrations of uranyl and uranyl tricarbonate ions in carbonate solutions. The stability constants listed in Table 2-2 were used for the calculation after they were corrected for actual conditions by Debye-Huckel's limiting law.

Fig.2-11. Fitting of uranium adsorption in basic (carbonate) solutions to the theoretical isotherm (Eq.[2-16]).

Fig.2-12. Change in surface uranium species ($-\text{SO}\cdot\text{UO}_2^+$ or $-\text{SO}\cdot\text{UO}_2\cdot\text{OH}$) on hydrous titanium(IV) oxide with the solution pH.

Chapter 3

Fig.3-1. Time-course of vacuum-dehydration process of hydrous titanium(IV) oxide at room temperature.

Fig.3-2. Effect of the equilibrium pH on uranium adsorption at 30°C. Initial concentration of uranium is $1\times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$.

Fig.3-3. A typical fitting of the equilibrium adsorption data to Eq.[2-15] for T-400 adsorbent.

Fig.3-4. Relation between adsorbent's moisture content and the number of available sites for uranium, N_M , determined from the plot of Fig.3-3.

Fig.3-5. Relation between adsorbent's moisture content and the adsorption constant, $K_M(0)$, determined from the plot of Fig.3-3.

Fig.3-6. Conductometric titration curve of a 200-cm³ suspension by 0.02M HNO_3 solution. The suspension contained 0.1g of T-400 adsorbent.

Fig.3-7. Relation between adsorbent's moisture content and the number of

total adsorption sites (surface hydroxyl groups), N_H .

Fig.3-8. Time dependence of uranium adsorption at 30 °C . Initial concentration of uranium is $1.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$.

Fig.3-9. Comparison of the data of Fig.3-8 with a first-order kinetic model (Eq. [3-2]).

Fig.3-10. Variation of the amounts of macro-, meso- and micro-pore sites in hydrous titanium(IV) oxide with moisture content.

Fig.3-11. Adsorption rate constants of uranium onto meso-pore sites in hydrous titanium(IV) oxide with various moisture contents.

PART II

Chapter 2

Fig.2-1. Conductometric titration curves for 300 cm³ of a solution containing 0.2g of AA or HA with $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ HNO}_3$ at 30°C.

Fig.2-2. Time dependence of the percentage of HA discharged from calcium alginate gel (in the absence of ACP) in distilled water at 30 °C . H and A

represent the weight percentages of HA and AA initially contained in the wet gel, respectively.

Fig.2-3. Effect of AA concentration on the percentage of HA discharged from calcium alginate gel containing 5 wt-% HA (in the absence of ACP) in distilled water at 30°C.

Fig.2-4. Effect of ACP concentration on the percentage of HA discharged from HA-gels in 0.1M CaCl_2 solution at 30°C. R represents the weight ratio of ACP to HA initially contained in the HA-gels.

Fig.2-5. The percentages of HA discharged from HA-gels in solutions of various CaCl_2 concentrations at 30 °C. H , C , and A represent the weight percentages of HA, ACP and AA initially contained in the wet gel, respectively.

Fig.2-6. The percentages of HA discharged from HA-gels with various gelation times, t [min], in distilled water at 30°C. Prior to this experiments, the gels were immersed in 0.1M CaCl_2 solutions for various time periods.

Chapter 3

Fig.3-1. Typical excitation and emission spectra of HA. Excitation spectra are for an emission wavelength of 450 nm and emission spectra for an excitation wavelength of 370 nm.

Fig.3-2. Time dependence of lead-HA complexation at 30 °C . Initial concentrations of lead ion and HA are $5.0 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$ and $0.02 \cdot \text{dm}^{-3}$ (Δ), and $1.0 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ and $0.16 \text{ g} \cdot \text{dm}^{-3}$ ($\circ$), respectively.

Fig.3-3. Effect of equilibrium pH on lead-HA complexation at 30°C. Initial concentrations of lead ion and HA are $1.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ and $0.05 \text{ g} \cdot \text{dm}^{-3}$, respectively. The solid line represents the theoretical curve calculated from Eq.[3-6].

Fig.3-4. Fitting of the data of Fig.3-3 to Eq.[3-4].

Fig.3-5. Effect of equilibrium pH on lead-AA complexation at 30°C. Initial concentrations of lead ion and HA are $1.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ and $0.033 \text{ g} \cdot \text{dm}^{-3}$, respectively. The solid line represents the theoretical curve calculated from Eq.[3-7].

Fig.3-6. Fitting of the data of Fig.3-5 to Eq.[3-4].

Fig.3-7. Time dependence of lead adsorption on HA gels containing 5%($\bullet$), 10%($\circ$), and 15% ($\blacksquare$) of HA at 30°C. All the HA-gels contain 1% AA and HA's weight in ACP. Initial concentration of lead ion is $1.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$.

Fig.3-8. The pH dependence of lead adsorption on HA-gels containing

0%(Δ), 5%($\bullet$), 10%($\circ$), and 15% ($\blacksquare$) of HA at 30°C. Initial concentration of lead ion is $2.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$.

Fig.3-9. Fitting of the data of Fig.3-8 to Eq.[3-4].

Fig.3-10. Comparison between the experimental amounts of lead adsorbed on several kinds of HA-gels and calculated from Eqs.[3-5]-[3-7]. The symbols are the same as those in Fig.3-8.

Chapter 4

Fig.4-1. Effect of AA concentration on the percentage of HA discharged from calcium alginate gel membranes prepared from mixture solutions containing 2% of HA and 0.5-3.0% of AA (in the absence of ACP) in distilled water at 30°C.

Fig.4-2. Effect of ACP concentration on the percentage of HA discharged from HA-M in 0.1M CaCl_2 solution at 30°C. R represents the weight ratio of ACP to HA initially contained in the HA-M. H and A represent the weight percentages of HA and AA in mixture suspensions from which the HA-M are prepared.

Fig.4-3. Comparison between the experimental amounts of lead adsorbed on

several kinds of HA-M and calculated from Eqs.[3-5]-[3-7]. H, C, and A represent the weight percentages of HA, ACP, and AA in the mixture suspensions, respectively.

Fig.4-4. Time dependence of lead adsorption on HA-M at 30 °C . Initial concentration of lead ion, volume of the system, and equilibrium pH are $2.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$, 1.0 dm^3 , and pH 3.8, respectively.

Fig.4-5. Fitting of the data of Fig.4-4 to Eq.[4-2].

Fig.4-6. Time dependence of lead adsorption on HA-gel particles and HA-M at 30°C. Initial concentration of lead ion, volume of the system, and equilibrium pH are $2.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$, 1.0 dm^3 , and pH 3.8, respectively.

Fig.4-7. Fitting of the data of Fig.4-6 to Eq.[4-2].

Fig.4-8. Time dependence of lead desorption from HA-M prepared from the mixture suspension containing 2% of HA, 2% of ACP, and 1% of AA. The desorption experiments were carried out in 0.05, 0.10, and 0.50M HNO_3 solutions at 30°C.

Fig.4-9. Operating line of lead desorption calculated from Eq.[3-5]-[3-7].

Chapter 5

Fig.5-1. Effect of CaCl_2 concentration on the percentage of HA remaining in supernatant solutions after centrifugation.

Fig.5-2. Effect of heating temperature on the percentage of IHA dissolution in distilled water at 30°C .

Fig.5-3. Dissolution of IHA prepared at 250°C (○) and 330°C (●) in various temperature of distilled water.

Fig.5-4. Dissolution of IHA prepared at 250°C (○) and 330°C (●) in various pH of solutions at 30°C .

Fig.5-5. Conductometric titration curves for 300 cm^3 of a solution containing 0.2g of HA or IHA with $0.1\text{ mol}\cdot\text{dm}^{-3}\text{ HNO}_3$ at 30°C .

Fig.5-6. Number of protonated acidic groups on HA and IHA as a function of pH. The number of protonated acidic groups was determined by potentiometric titrations for 300 cm^3 of a solution containing 0.2g of HA or IHA and NaNO_3 (0.1M) with $0.1\text{ mol}\cdot\text{dm}^{-3}\text{ HNO}_3$ at 30°C .

Fig.5-7. Comparison of the number of protonated acidic groups between the experimental and the calculated from Eqs.[5-5]-[5-7].

Fig.5-8. Acid-dissociation curves of acidic groups on HA. The solid lines represent the theoretical curves calculated from Eqs.[5-5]-[5-7].

Fig.5-9. pH dependence of metal-HA complexation at 30 °C . Initial concentrations of HA, NaNO₃, Cd(NO₃)₂ and Pb(NO₃)₂ are 1 g·dm⁻³, 0.1, 1.0 ×10⁻³ and 4.0×10⁻⁴ mol·dm⁻³, respectively.

Fig.5-10. Comparison of the amounts of metal-complexation between the experimental and the calculated from Eqs.[5-12]-[5-14].

Fig.5-11. pH dependence of metal-IHA complexation at 30°C. Experimental conditions are identical to those described in Fig.5-5.

Fig.5-12. Comparison of the amounts of metal-complexation between the experimental and the calculated from Eqs.[5-12]-[5-14].

LIST OF TABLES

PART I

Table 2-1 Adsorption constants of UO_2^{2+} , Pb^{2+} , Cd^{2+} and Zn^{2+} to hydrous titanium(IV) oxide.

Table 2-2 Stability constants of uranyl complexes.

Table 3-1 Summary of adsorption characteristics of adsorbents used in this work.

PART II

Table 5-1 Equilibrium parameters for acid-dissociation of HA and IHA.

Table 5-2 Equilibrium parameters for metal-HA complexation.

Table 5-3 Equilibrium parameters for metal-IHA complexation.