Biosorption of Heavy Metal Ions to Brown Algae, *Macrocystis pyrifera, Kjellmaniella crassiforia,* and *Undaria pinnatifida*

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(Abbreviated title: BIOSORPTION OF HEAVY METALS TO BROWN ALGAE)

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ABSTRACT

A fundamental study of the application of brown algae to the aqueous-phase separation of toxic heavy metals was carried out. The biosorption characteristics of cadmium and lead ions were determined with brown algae, *Macrocystis pyrifera*, *Kjellmaniella crassiforia*, and *Undaria pinnatifida*. A metal binding model proposed by the authors was used for the description of metal binding data. The results showed that the biosorption of bivalent metal ions to brown algae was due to bivalent binding to carboxylic groups on alginic acid in brown algae.

Key Words: biosorption; heavy metals; brown algae, *Macrocystis pyrifera*, *Kjellmaniella crassiforia*, *Undaria pinnatifida*

INTRODUCTION

The aqueous-phase separation of toxic heavy metal ions by biosorption has attracted much attention in recent years. Biosorption employs inexhaustible, inexpensive, nonhazardous materials, and generates low volumes of nonhazardous waste. Microorganisms (1-6), algae (7-10), and other types of biomass (11-18) have been investigated for use in this application. An abundant source potentially metal-sorbing biomass is marine algae. They are widely available and are ecologically acceptable. Moreover, marine algae can be used as biosorbents without intricate pretreatment such as centrifugation and immobilization.

Many studies have been carried out about the application of marine algae to the metal recovery from dilute aqueous solutions. In the earlier studies (7, 8, 10), the determination of adsorption parameters using the Langmuir adsorption model was attempted to assist in the comparison of biosorption performance. However, the adsorption models used in these studies could not predict the influence of pH, which may be one of the most important influencing factor, on biosorption.

In the present study, the biosorption characteristics of toxic heavy metals, lead and cadmium ions, in acidic media were investigated with brown algae,

Macrocystis pyrifera, *Kjellmaniella crassiforia*, and *Undaria pinnatifida*. These algae grow abundantly, densely, and rapidly. Especially, *Macrocystis pyrifera*, or giant kelp, is one of the largest and vastest marine plant. In this paper, a potentiometric titration was performed to determine the acid-dissociation characteristics of the acidic sites on the brown algae. Then we tried to apply a metal-complexation model proposed in our previous studies (17, 18) to the biosorption of lead and cadmium ions to the brown algae. Based on the model, the biosorption mechanism of these algae will be discussed.

MATERIALS

Cadmium nitrate, lead nitrate, sodium nitrate and sodium alginate were obtained from Wako Pure Chemical Industries (Japan). They were used as received.

A sun-dried sample of *Macrocystis pyrifera* (*MP*) was obtained from the Hopkins Marine Station, Stanford University, USA. *Kjellmaniella crassiforia* (*KC*) and *Undaria pinnatifida* (*UP*) were collected in Funka Bay, Japan. *KC* and *UP* were dried at room temperature for 3 days after collection. These algae were further dried at 60℃ for 2 days, and stored in a desiccator.

EXPERIMENTAL METHODS

Potentiometric Titration of Algae

A certain amount of dried algae was washed with a HNO_3 solution (0.01 mol dm^{-3}) and was cut into fragments (ca. 2 x 2 cm). The algae fragments were mechanically stirred in 0.3 dm^3 of $NaNO_3$ (0.1 mol dm^{-3}) solution at 30℃. To eliminate CO_2, N_2 gas was continuously bubbled through the system. After reaching thermal equilibrium, it was titrated with a volumetric standard solution of HNO_3 (0.1 mol dm^{-3}). The pH of the solution was measured by a pH meter (Oiron Research 720A). The number of protonated acidic groups of algae was determined from the difference between the bulk proton concentrations in the presence and in the absence of algae.

Biosorption of Metal Ions to Algae

A solution of $NaNO_3$ (0.1 mol dm^{-3}) containing a certain amount of $Cd(NO_3)_2$ or $Pb(NO_3)_2$ was prepared. The pH of the solution was adjusted to the desired value by HNO_3. After reaching thermal equilibrium at 30℃, a certain amount of algae fragments washed with a HNO_3 solution (0.01 mol dm^{-3}) was added to the solution. The solution was stirred for a necessary time to

attain the adsorption equilibrium. Then, the pH and metal concentration of the liquid phase were measured. The metal concentration was determined by an atomic absorption spectrophotometer (Hitachi A-1800). The amount of metal ion adsorbed to algae was determined from the difference between the metal concentrations in the initial and the equilibrium states.

RESULTS AND DISCUSSION

Acidic Sites on Brown Algae

Figure 1 shows the acid dissociation characteristics of the acidic sites on *MP*, *KC*, and *UP* in acidic media. Brown algae contain 20-40 % of alginic acid on a dry-weight basis. Alginic acid, a linear polysaccharide of β-D-mannuronic acid and α-L-guluronic acid, is a main cell-boundary constituent of brown algae (19). It contains about 4 mmol·g^{-1} of carboxylic groups (18, 20). Assuming that the major acidic sites on brown algae is carboxylic groups on alginic acid, the acid-dissociation reaction can be written as

$$\text{-COOH} \leftrightarrow \text{-COO}^- + \text{H}^+ \quad ;K \qquad [1]$$

The acid-dissociation constant K is defined as

$$K = \alpha[\text{H}^+]/(1-\alpha) \qquad [2]$$

where α is the degree of dissociation of carboxylic groups. The number of deprotonated carboxylic groups on 1 dry-g of brown algae, X_o, can be expressed as

$$X_0 = \quad N\,a \quad = \frac{NK}{K + [\mathrm{H}^+]}, \qquad [3]$$

where *N* is the number of carboxylic groups on brown algae. A nonlinear least-squares method was applied to find two constants, *K* and *N*, in Eq. [3]. These constants for *MP*, *KC*, and *UP*, which gave the best fit with the experimental data (in Fig.1), were listed in **Table 1**. The solid lines in Fig. 1 represent the theoretical curves calculated from Eq. [3] using the constants listed in Table 1. The correlation coefficients between the experimental and the predicted value were, respectively, 0.995 (*MP*); 0.999 (*KC*); and 1.000 (*UP*).

The acid-dissociation constants of three brown algae are almost the same, and agreed well with the acid-dissociation constants of carboxylic groups on alginic acid (*AA*) determined by the authors, p*K*=3.21 (18), and Jang *et al*., p*K*=3.28 (20). This result indicates that the acid properties of brown algae can be attributed to the carboxylic groups on *AA*.

Biosorption of Bivalent Metal Ions to Brown Algae

We previously investigated the binding of lead and cadmium ions to biopolymers such as alginic acid and humic acid, and proposed a metal-complexation model (17,18). The model gave good results for the description

of bivalent metal ion binding data. Assuming that the major metal binding site of brown algae is the carboxylic group on *AA*, the biosorption reaction of bivalent metal ions to brown algae can be written as

$$2(\text{-COO}^-) \; + \; \text{M}^{2+} \; \leftrightarrow \; (\text{-COO})_2\text{M} \qquad ; K_{\text{M}} \quad [4]$$

M^{2+} in Eq. [4] represents the bivalent metal ions. The metal binding constants K_{M} ($dm^3\ mol^{-1}$) in Eq. [4] is defined as

$$K_{\text{M}} = \frac{\theta}{\{(1-\theta)\alpha\}^2[\text{M}^{2+}]} = \frac{\theta}{\{(1-\theta)K/(K+[\text{H}^+])\}^2[\text{M}^{2+}]} \quad [5]$$

or

$$\theta = (P - \sqrt{P^2 - 4})/2 \qquad [6]$$

$$P \equiv 2 + \{K[\text{M}^{2+}]\{K/(K+[\text{H}^+])\}^2\}^{-1}$$

where θ represents the fraction of carboxylic groups occupied by metal ions. The number of metal ions bound to 1 dry-g of brown algae, X_{M}, can be expressed as

$$X_{\text{M}} = N\theta/2 \qquad [7]$$

Figures 2-4 show the pH dependence of lead adsorption to *MP*, *KC*, and *UP*, respectively. The ordinate, X_M, represents the equilibrium number of lead ions bound to the brown algae. A nonlinear least-squares method was applied to find lead binding constant, K_M, using Eqs. [6] and [7]. The obtained constants are listed in **Table 2**. In this calculation, the number of carboxylic groups, *N*, and acid-dissociation constant, *K*, obtained from the petentiometric titration (in Table 1) were used. The solid lines in Figs. 2-4 represent the theoretical curves calculated from Eqs. [6] and [7] using the constants listed in Tables 1 and 2. Figures 2-4 demonstrate a good agreement of the experimental data with the theoretical curves. The correlation coefficients between the experimental and the predicted value were, respectively, 0.998 (*MP*); 0.999 (*KC*); and 1.000 (*UP*). The lead binding constants of three brown algae are almost the same, and agreed well with the lead-complexation constant of *AA* determined by the authors, pK_M=-5.13 (18).

Figures 5-8 show the pH dependence of cadmium adsorption to *AA*, *MP*, *KC*, and *UP*, respectively. The detailed method of adsorption experiment with *AA* is given elsewhere (18). The cadmium binding constant, K_M, was determined in the same manner as those for lead adsorption, and they are listed in **Table 3**. The correlation coefficients between the experimental and the predicted value were, respectively, 0.999 (*AA*); 0.994 (*MP*); 0.997 (*KC*); and

0.996 (*UP*). The cadmium binding constants of three brown algae also agreed with the cadmium-complexation constant of *AA*.

CONCLUSION

Brown algae, *Macrocystis pyrifera*, *Kjellmaniella crassiforia*, and *Undaria pinnatifida*, were applied to the recovery of lead and cadmium ions. Potentiometric titration was performed to determine the number and acid-dissociation constants of acidic sites on the algae. The acid-dissociation constants of acidic sites on the algae were agreed well with the constant of carboxylic groups on alginic acid. A metal-complexation model proposed by the authors was used to determine the biosorption characteristics of lead and cadmium ions to brown algae. The metal-complexation model was applicable to the biosorption of bivalent metal ions to brown algae, and the model gave good results for the description of metal binding data. The metal binding constants of the brown algae also agreed well with the constants of alginic acid.

APPENDIX A: NOMENCLATURE

C_{AL} = concentration of brown algae (g dm^{-3})

C_{MI} = initial concentration of metal ions (mol dm^{-3})

K = acid dissociation constant of acidic sites (mol dm^{-3})

K_M = metal binding constant of acidic sites (dm^3 mol^{-1})

N = number of acidic sites (mol g^{-1})

X_0 = number of deprotonated acidic sites (mol g^{-1})

X_M = number of metal ions bound to brown algae (mol g^{-1})

α = degree of dissociation of acidic sites (-)

θ = fraction of acidic sites occupied by metal ions (-)

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Figure Captions

FIG. 1. Comparison of the number of deprotonated acidic groups determined experimentally and the number predicted from Eq.[3] using the parameters listed in Table 1 (solid lines). The number of deprotonated acidic groups was determined by potentiometric titrations for 300 cm^3 of a solution containing ca. 0.5 g of brown algae and $NaNO_3$ (0.1 $mol \cdot dm^{-3}$) with 0.1 HNO_3 at 30℃.

FIG. 2. pH dependence of lead adsorption to *MP* at 30℃. Concentration of $NaNO_3$ is 0.1 $mol \cdot dm^{-3}$. Concentration of algae, C_{AL}, and initial concentration of $Pb(NO_3)_2$, C_{MI}, are indicated in the figure. The solid lines represent the theoretical curves calculated from Eqs. [6] and [7].

FIG. 3. pH dependence of lead adsorption to *KC* at 30℃. Initial concentrations of $Pb(NO_3)_2$ and $NaNO_3$ are 4×10^{-4} $mol \cdot dm^{-3}$ and 0.1 $mol \cdot dm^{-3}$, respectively. Concentration of *KC* is 0.45 $g \cdot dm^{-3}$. The solid line represents the theoretical curve calculated from Eqs. [6] and [7].

FIG. 4. pH dependence of lead adsorption to *UP* at 30℃. Initial concentrations of $Pb(NO_3)_2$ and $NaNO_3$ are 2×10^{-4} $mol \cdot dm^{-3}$ and 0.1 $mol \cdot dm^{-3}$,

respectively. Concentration of *UP* is 0.37 g·dm^{-3}. The solid line represents the theoretical curve calculated from Eqs. [6] and [7].

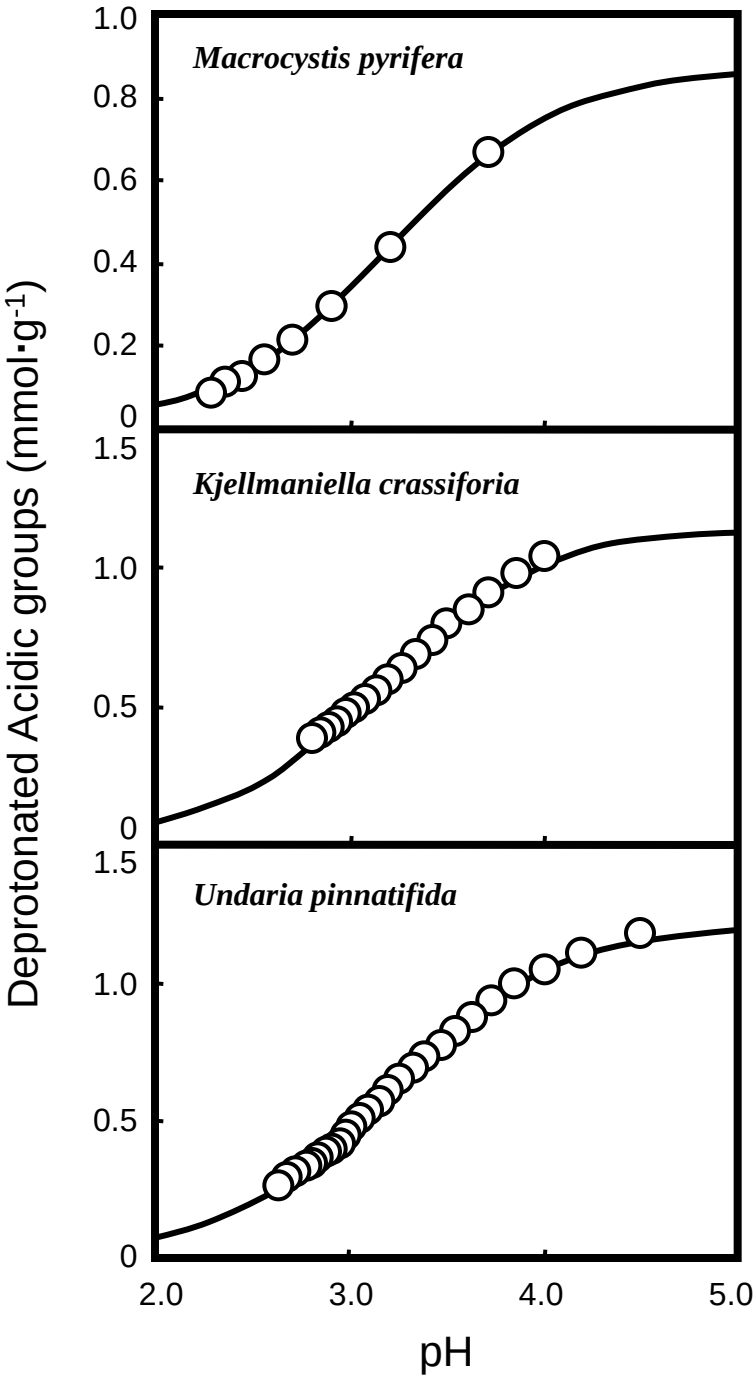
FIG. 5. pH dependence of cadmium adsorption to *AA* at 30℃. Initial concentrations of $Cd(NO_3)_2$ and $NaNO_3$ are 5×10^{-4} mol·dm^{-3} and 0.1 mol·dm^{-3}, respectively. Concentration of *AA* is 3.66 g·dm^{-3}. The solid line represents the theoretical curve calculated from Eqs. [6] and [7].

FIG. 6. pH dependence of cadmium adsorption to *MP* at 30℃. Concentration of $NaNO_3$ is 0.1 mol·dm^{-3}. Concentration of algae, C_{AL}, and initial concentration of $Cd(NO_3)_2$, C_{MI}, are indicated in the figure. The solid lines represent the theoretical curves calculated from Eqs. [6] and [7].

FIG. 7. pH dependence of cadmium adsorption to *KC* at 30℃. Concentration of $NaNO_3$ is 0.1 mol·dm^{-3}. Concentration of algae, C_{AL}, and initial concentration of $Cd(NO_3)_2$, C_{MI}, are indicated in the figure. The solid lines represent the theoretical curves calculated from Eqs. [6] and [7].

FIG. 8. pH dependence of cadmium adsorption to *UP* at 30℃. Concentration of $NaNO_3$ is 0.1 mol·dm^{-3}. Concentration of algae, C_{AL}, and initial

concentration of $Cd(NO_3)_2$, C_{MI}, are indicated in the figure. The solid lines represent the theoretical curves calculated from Eqs. [6] and [7].



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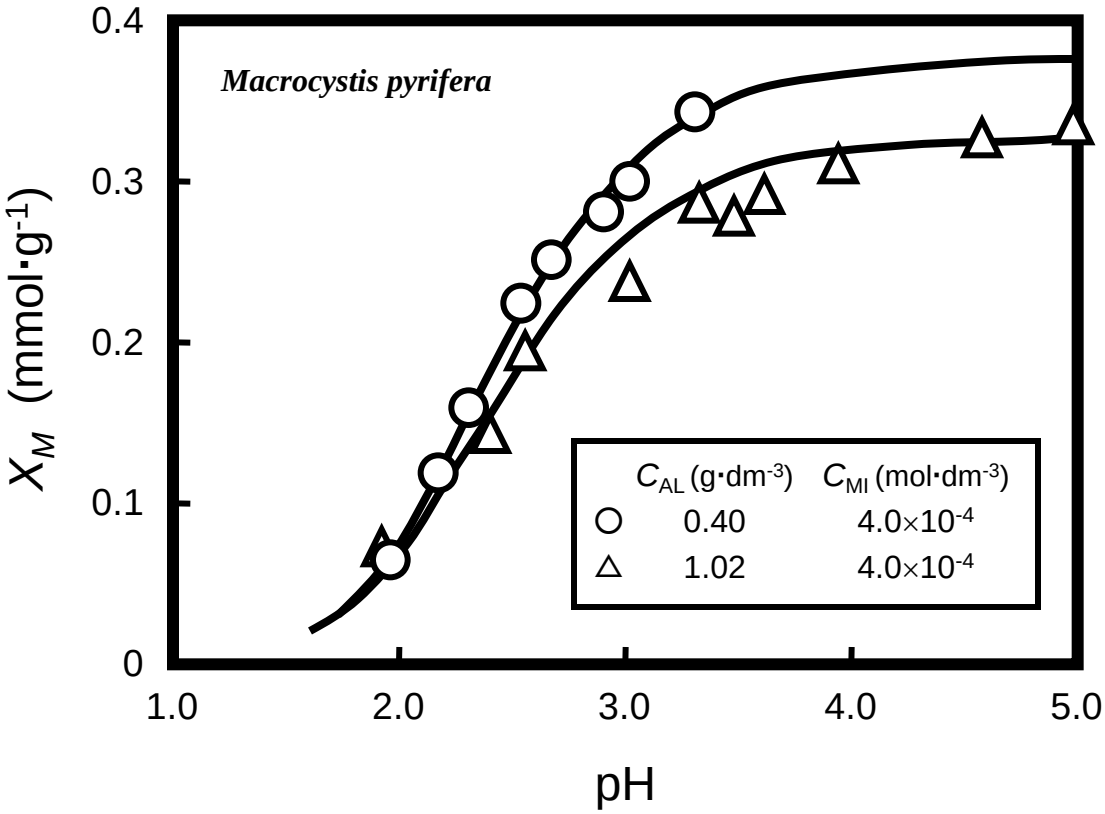

FIG. 2. pH dependence of lead adsorption to *MP* at 30℃. Concentration of $NaNO_3$ is 0.1 mol·dm^{-3}. Concentration of algae, C_{AL}, and initial concentration of $Pb(NO_3)_2$, C_{MI}, are indicated in the figure. The solid lines represent the theoretical curves calculated from Eqs. [6] and [7].

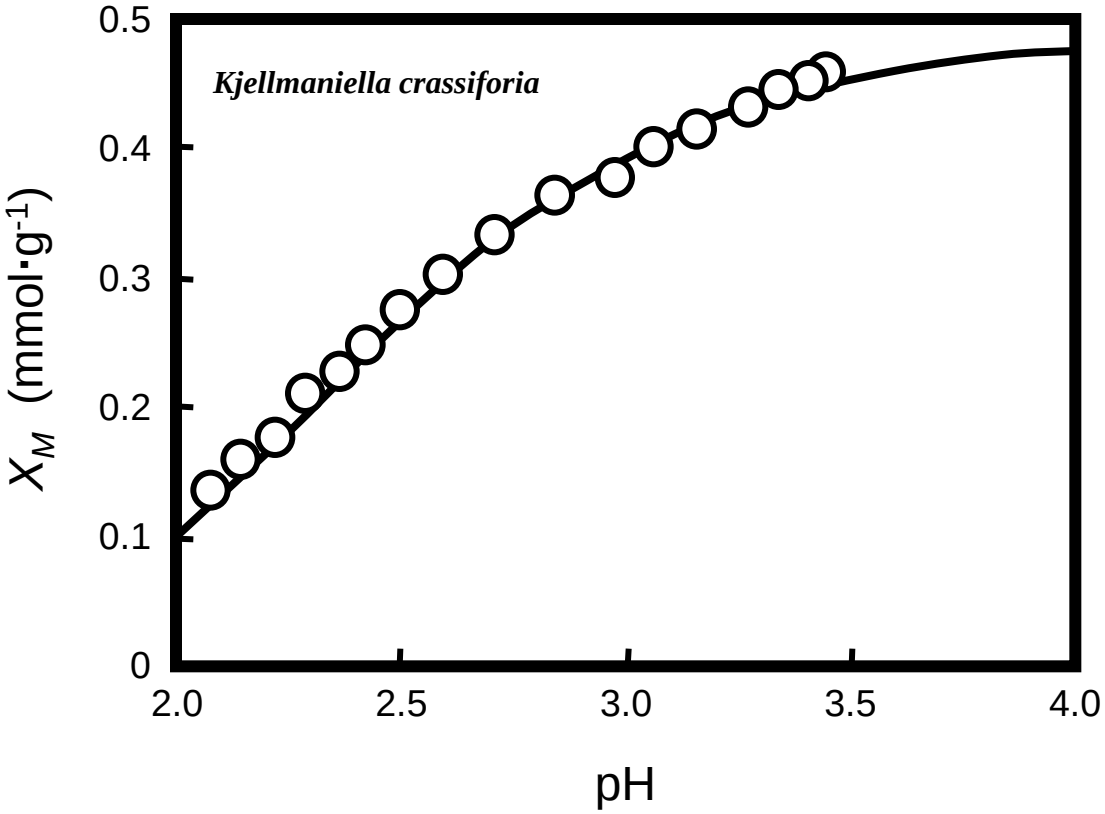

FIG. 3. pH dependence of lead adsorption to *KC* at 30℃. Initial concentrations of $Pb(NO_3)_2$ and $NaNO_3$ are 4×10^{-4} mol·dm^{-3} and 0.1 mol·dm^{-3}, respectively. Concentration of *KC* is 0.45 g·dm^{-3}. The solid line represents the theoretical curve calculated from Eqs. [6] and [7].

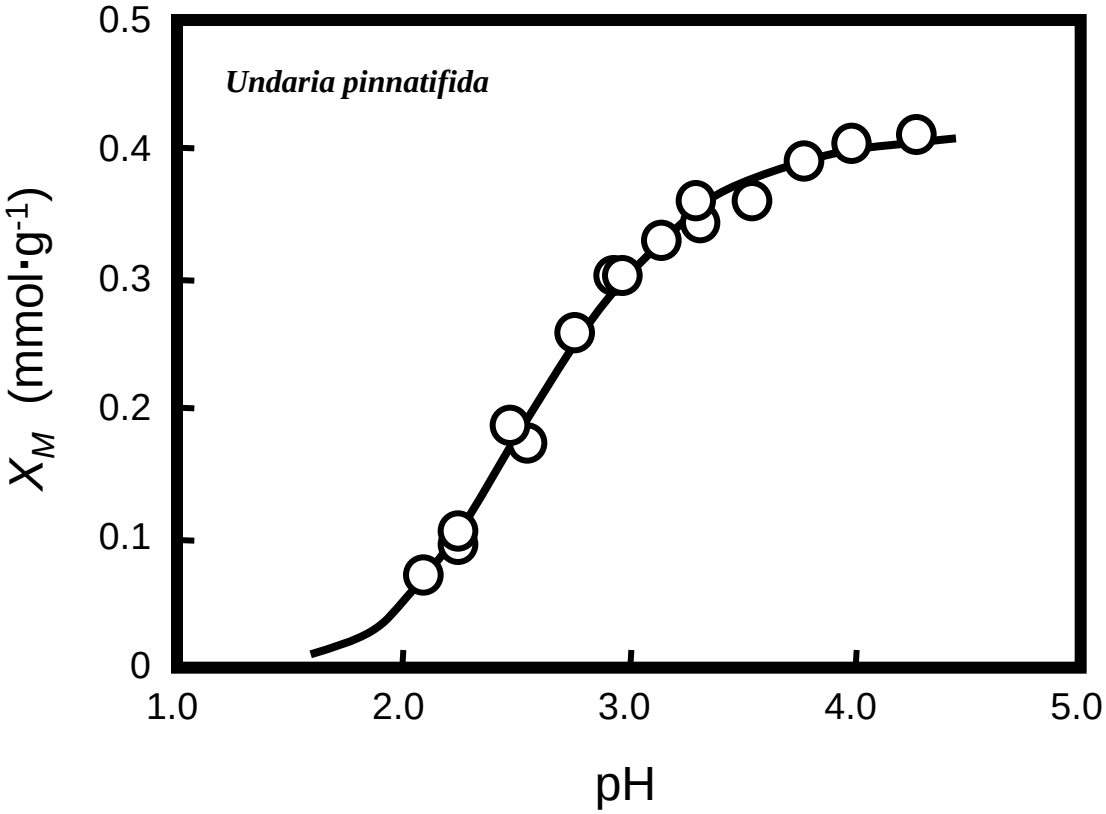

FIG. 4. pH dependence of lead adsorption to *UP* at 30℃. Initial concentrations of $Pb(NO_3)_2$ and $NaNO_3$ are 2×10^{-4} mol·dm^{-3} and 0.1 mol·dm^{-3}, respectively. Concentration of *UP* is 0.37 g·dm^{-3}. The solid line represents the theoretical curve calculated from Eqs. [6] and [7].

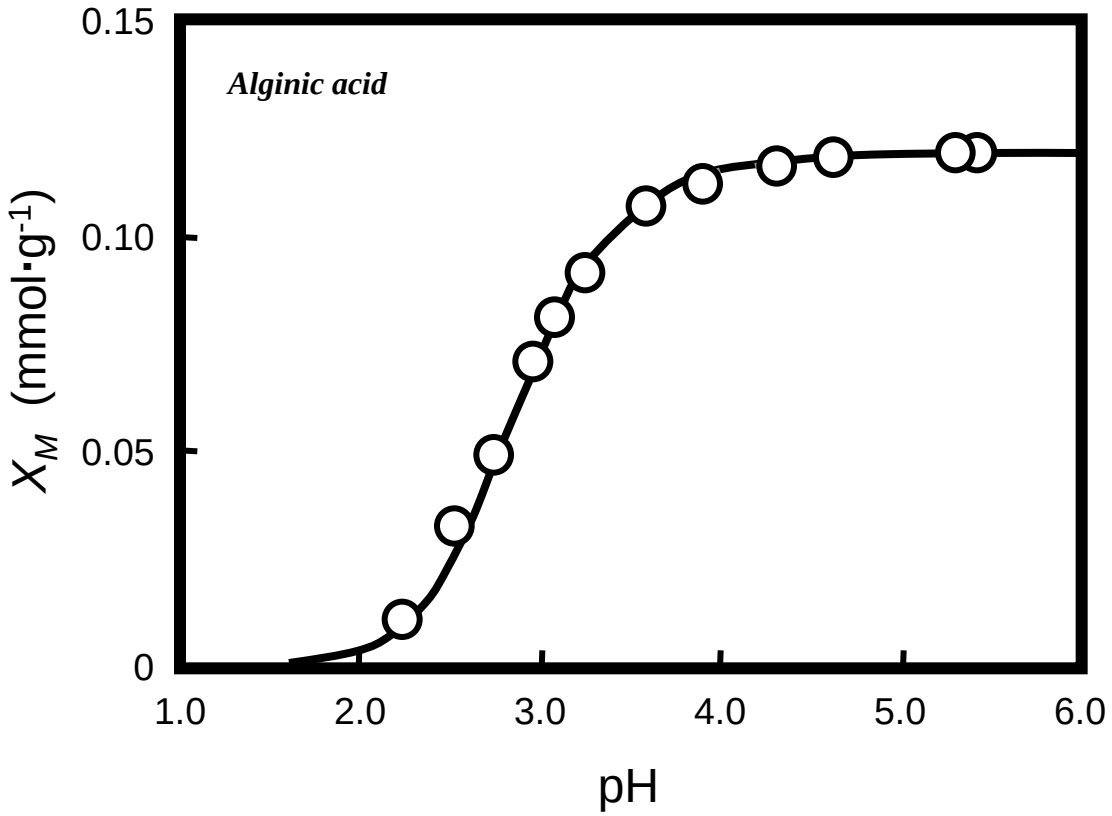

FIG. 5. pH dependence of cadmium adsorption to *AA* at 30℃. Initial concentrations of $Cd(NO_3)_2$ and $NaNO_3$ are 5×10^{-4} mol·dm^{-3} and 0.1 mol·dm^{-3}, respectively. Concentration of *AA* is 3.66 g·dm^{-3}. The solid line represents the theoretical curve calculated from Eqs. [6] and [7].

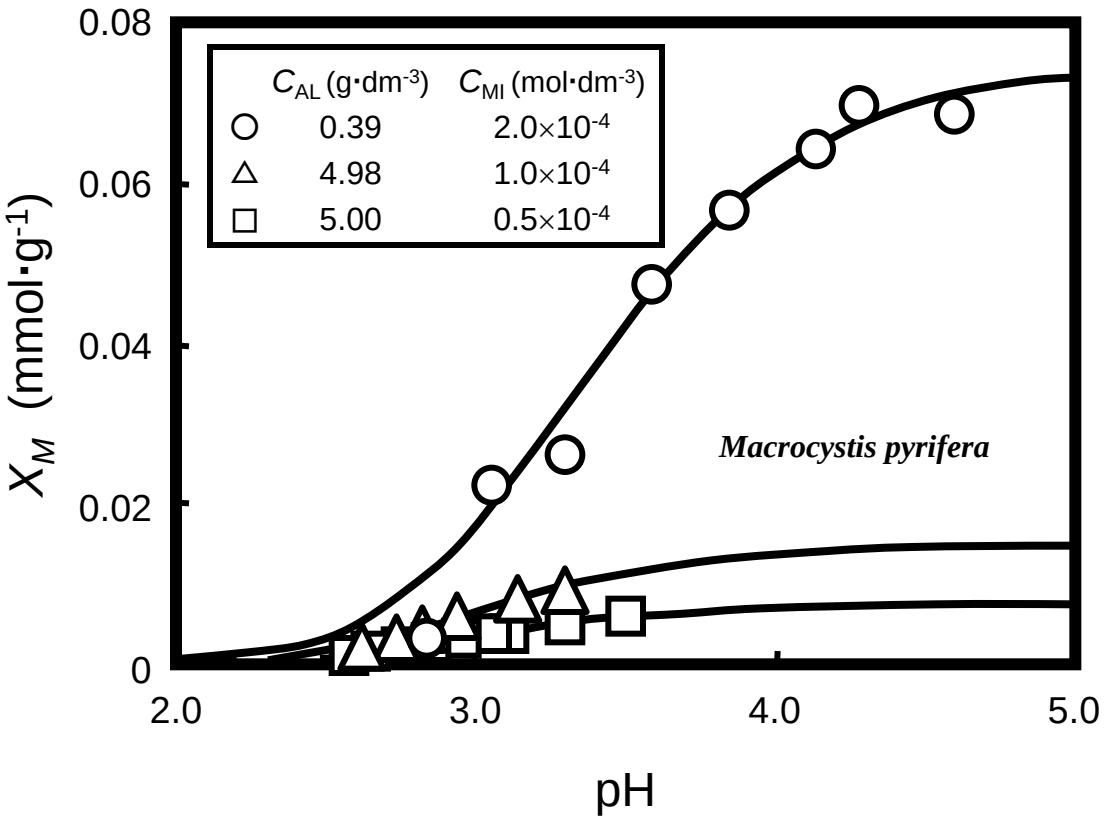

FIG. 6. pH dependence of cadmium adsorption to *MP* at 30℃. Concentration of $NaNO_3$ is 0.1 mol·dm^{-3}. Concentration of algae, C_{AL}, and initial concentration of $Cd(NO_3)_2$, C_{MI}, are indicated in the figure. The solid lines represent the theoretical curves calculated from Eqs. [6] and [7].

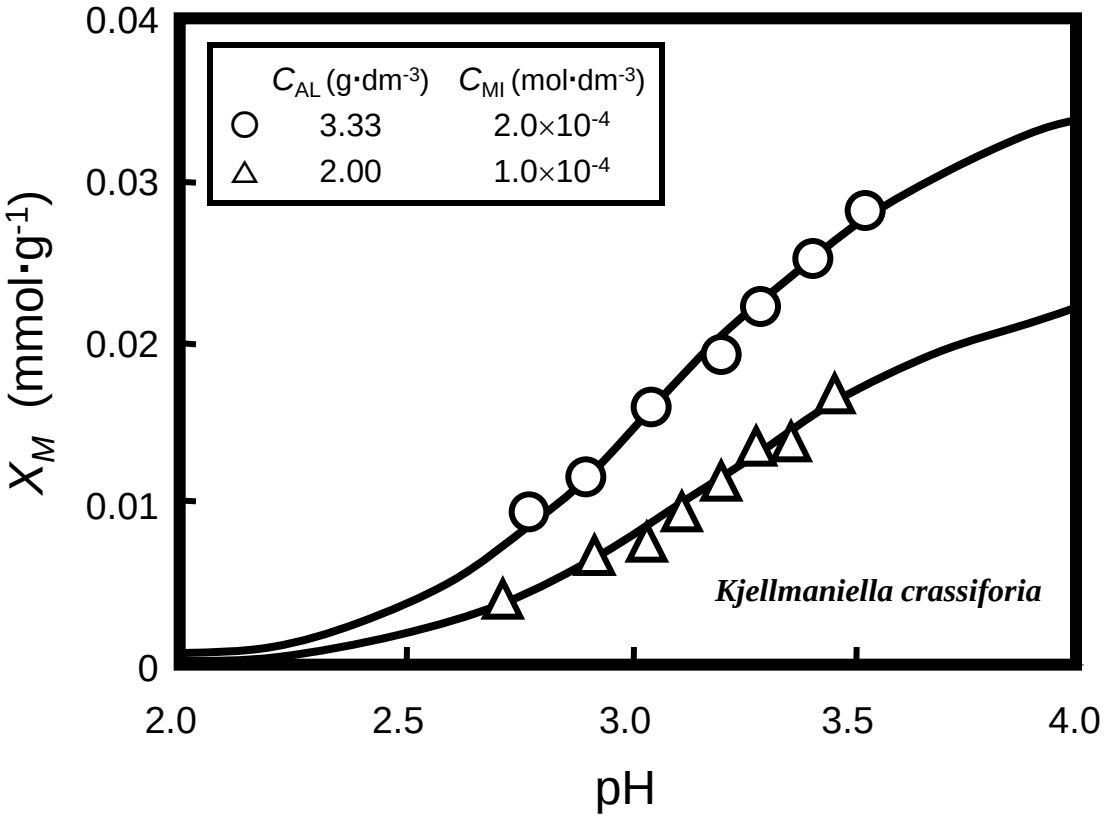

FIG. 7. pH dependence of cadmium adsorption to *KC* at 30℃. Concentration of $NaNO_3$ is 0.1 mol·dm^{-3}. Concentration of algae, C_{AL}, and initial concentration of $Cd(NO_3)_2$, C_{MI}, are indicated in the figure. The solid lines represent the theoretical curves calculated from Eqs. [6] and [7].

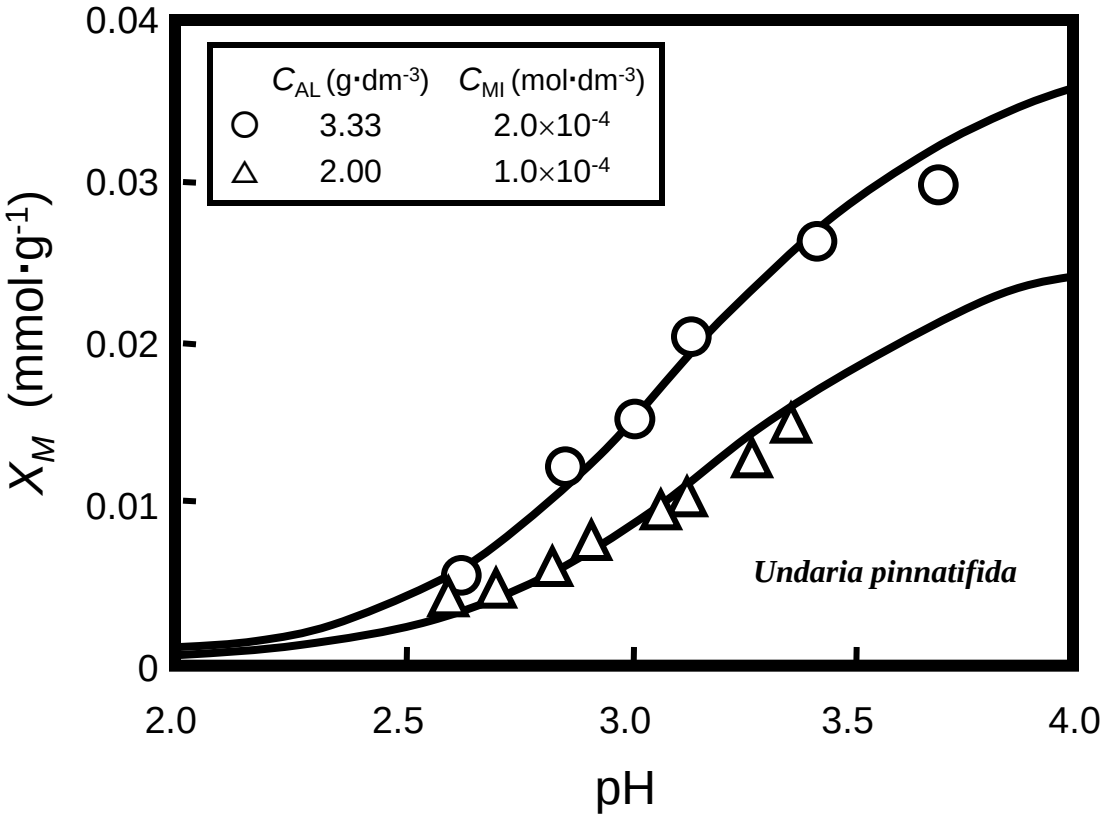

FIG. 8. pH dependence of cadmium adsorption to *UP* at 30℃. Concentration of $NaNO_3$ is 0.1 mol·dm^{-3}. Concentration of algae, C_{AL}, and initial concentration of $Cd(NO_3)_2$, C_{MI}, are indicated in the figure. The solid lines represent the theoretical curves calculated from Eqs. [6] and [7].

TABLE 1
Equilibrium Parameters for the Acid Dissociation of Brown Algae

	N (mol·g^{-1})	pK
MP	0.87×10^{-3}	3.19
KC	1.16×10^{-3}	3.14
UP	1.21×10^{-3}	3.20

TABLE 2
Equilibrium Parameters for Lead Adsorption of Brown Algae

	MP	*KC*	*UP*
pK_M	-5.28	-5.24	-5.22

TABLE 3
Equilibrium Parameters for Cadmium Adsorption of Brown Algae and Alginic Acid

	AA	*MP*	*KC*	*UP*
pK_M	-3.17	-3.16	-3.04	-3.06

Original Figures

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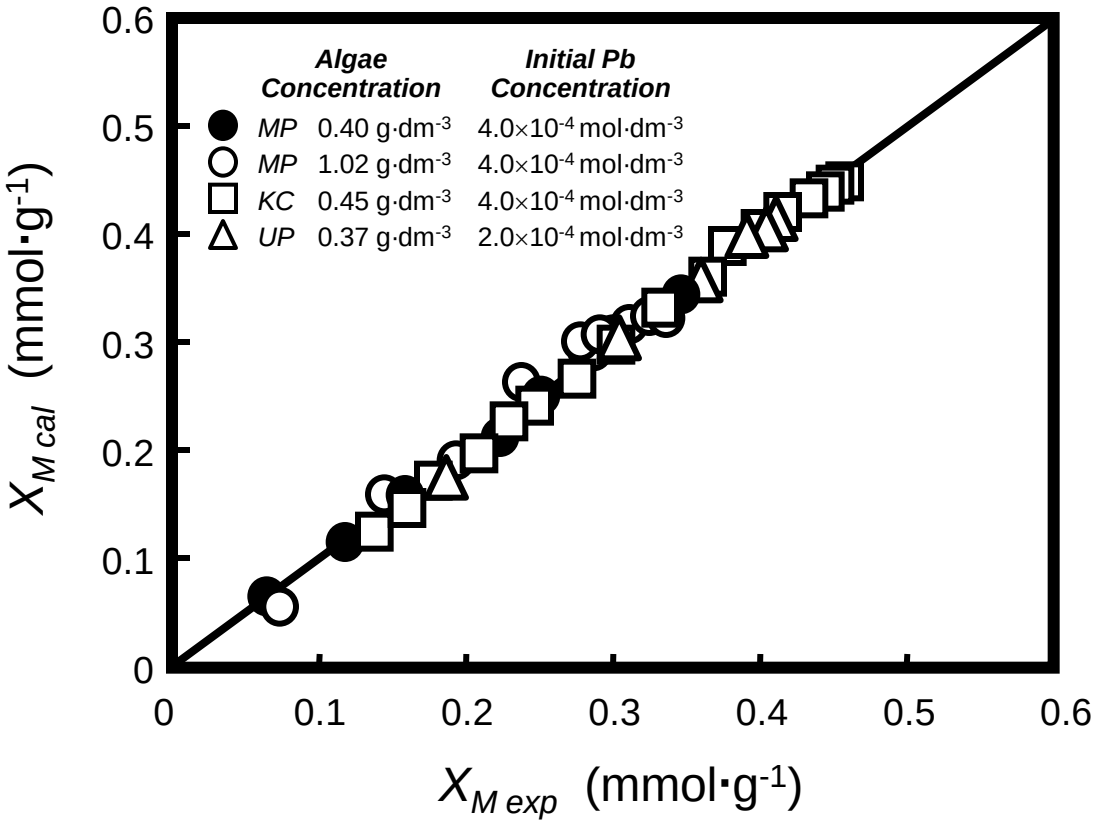

FIG. 3. Comparison of the experimental amount of lead adsorbed on algae and the amount calculated from Eqs. [*]-[*].

TABLE 1
Equilibrium Parameters for the Acid Dissociation of Brown Algae and Alginic Acid

	N (mol·g^{-1})	pK
MP	0.87×10^{-3}	3.19
KC	1.16×10^{-3}	3.14
UP	1.21×10^{-3}	3.20
AA*	-	3.21
AA**	-	3.28

* Seki and Suzuki (1996), ** Jang *et al*. (1989)

TABLE 2
Equilibrium Parameters for Lead Adsorption of Brown Algae and Alginic Acid

	MP	*KC*	*UP*	*AA**
pK_M	-5.28	-5.24	-5.22	-5.13

* Seki and Suzuki (1996)