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Adsorption of metal ions from aqueous solution onto microalga entrapped into Ca-alginate gel bead

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ABSTRACT

A microalga biomass was entrapped into gel bead using sodium alginate in the presence of Ca(II) ions. Firstly, adsorption of metal ions by the microalga entrapping alginate beads was studied in a batch system. The effects of initial metal concentration and pH on uptake of the metal ions were examined. The maximum experimental adsorption capacities of the microalga entrapping alginate beads of *Chlamydomonas reinhardtii* and *Anabena variabilis* were found to be 61.3 mmol-Cd/g-bead and 51.2 mmol-Cd/g-bead, respectively. The rate of metal adsorption was high, and approximately, 85% metal adsorption took place within 30 min. The adsorption equilibrium was well described by Langmuir adsorption isotherm. The adsorption capacity of the *C. reinhardtii* entrapping alginate beads was relatively high, and so it could be considered that the alginate beads were one of the suitable adsorbents for the removal of metal ions in wastewater treatment. In addition, it was possible that the adsorbents were reused at least three times in consecutive metal adsorption–desorption cycles without a significant loss in the adsorption capacity. Secondly a mutual separation between Cd(II), Cu(II), Zn(II), and Ni(II) was conducted using a column packed with the microalga entrapping alginate beads. As the result, it was suggested that the mutual separation of the metals was possible under a suitable operating condition.

Keywords: Adsorption; Calcium alginate bead; Immobilization; Metal adsorption; Microalgae; Packed bed bioreactor

1. Introduction

Adsorption process for the removal of metal ions possesses some advantages compared with other processes for the reasons of cheap cost of materials used and easiness of the operation. Recently, many biopolymers for adsorbing the metals have been developed, and the biopolymers have attracted practical interest from the viewpoints of recovery of valuable metals and removal of toxic metals.

Many workers have investigated the methods of metal adsorption on an adsorbent and the application to wastewater treatment. Agar [1], polyacrylamide [2], alginate [3,4], and κ-carrageenan [5,6] have been used for the materials of metal entrapment. Among these, the mechanical strength of agar is rather weak. Also, alginate gel does not have high mechanical strength, and so when using the alginate gel the addition of Ca

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(II) or Al(III) ion is required for stabilization of the gel. This treatment causes a drawback because these ions form a precipitate with phosphate ion [5,7].

The research of using polyvinylalcohol (PVA) as an immobilization support was initiated about 10 years ago [8]. PVA is a raw material of vinylon and can be produced rather cheaply in industry. PVA also offers various advantages over conventional immobilization methods, which are high durability, chemical stability, and non-toxicity to living things. Up to date, several immobilization methods using PVA have been reported. Among these, PVA-boric acid method [9] was widely used, for example, an activated sludge was immobilized using this method. However, the PVA-boric acid method has such a problem as hydration of immobilization biomass.

Recently, it has been reported that co-immobilization of *Chlorella vulgaris* with the plant growth-promoting bacterium, *Azospirillum brasilense*, which is used as an inoculator in agriculture, significantly increased the growth and pigment production of a microalga [10]. This is very similar to the effect of the bacterium on the growth of numerous terrestrial plants.

In this study, *Chlamydomonas reinhardtii* (IAM C-9) and *Anabena variabilis* (IAM M-3) were entrapped into Ca-alginate gel beads. These algae were used after the growth of microalgae attained steady state. The microalga entrapping alginate beads were used for the adsorption of the metal ions (Cd(II), Cu(II), Zn(II), and Ni(II)) from an aqueous solution in a batch system. The effect of pH on the adsorption capacity of the metals was examined by measuring the amount of metal ions adsorbed onto the alginate beads at various pH of the aqueous solution. The maximum adsorption capacities were determined by varying the initial concentration of the metal ions in the aqueous solution. The adsorption isotherms of the metal uptake and the adsorption rates of the metal ions were also examined. Hydrochloric acid solution could desorb the metal ions from the alginate beads. The microalga entrapping alginate beads were also used to study the adsorption behavior and the mutual separation of the metal ions from an aqueous solution in a continuous flow system using a packed column with the alginate beads.

2. Experimental

2.1. Entrapment of algae in Ca-alginate beads

The entrapment of *C. reinhardtii* and *A. variabilis* in the Ca-alginate beads was carried out as follows [4]. Na-alginate (1.6 g) was dissolved in distilled water (40 mL), and then, they were mixed with the microalgae. The mixture was introduced into $CaCl_2$ aqueous solution with a concentration of 0.1 mol/dm^3 in a beaker, and then, the solution was stirred to prevent the Ca-alginate beads entrapping the microalgae from aggregating. This is hereafter called microalga entrapping alginate beads. The microalga entrapping alginate beads were then rinsed twice with 200 mL distilled water. The beads were then transferred into the growth medium of the alga and were incubated for 7 days. After the incubation period, the microalga entrapping alginate beads were removed from the medium by filtration and rinsed twice with the distilled water. The beads were maintained at 4℃ in $CaCl_2$ solution until use. And the beads were dried in a drying oven just before the experiments.

2.2. Adsorption of metals

The adsorption of metal ions onto both the *C. reinhardtii* and *A. variabilis* entrapping alginate beads from an aqueous solution was investigated in a batch adsorption system. The effects of pH of the aqueous solution and initial concentration of the metal ions on the metal adsorption uptake were examined.

Further, the effect of pH on the metal adsorption rate to both microalga entrapping alginate beads was investigated at 30℃ in the pH range of 2.0–6.0. The pH was adjusted using the buffer solution of $HCl-CH_3COONa$ with a concentration of 0.1 mol/dm^3 at the beginning of the experiment and was not controlled afterwards. The aqueous solution containing the metal ion with a concentration of 10–200 mol/m^3 was prepared using distilled water. The nitrates of each metal were used as the metal source in this experiment. The microalga entrapping alginate beads were then transferred into the aqueous solution containing the metal ion.

The effect of the initial concentration of the metal ion on the adsorption rate was examined at pH 5.0. The concentration of metal ions in the aqueous solution was varied in the range of 30–600 mol/m^3.

2.3. Analytical procedure

After a designated period (approximately 120 min) since the metal adsorption experiment, the aqueous phase was separated from the adsorbents, and the metal concentration in the aqueous solution was measured by inductively coupled plasma spectrophotometer (Shimadzu ICPS-8000). The amount of metal ions adsorbed on the microalga entrapping alginate beads was calculated by the following equation.

$$q = [(C_0 - C)V]/M \quad (1)$$

In Eq. (1), q is the amount of metal ion adsorbed onto the unit adsorbents (mmol-metal ion per g-dry bead). C_0 and C are the initial concentration of the metal ion in the aqueous solution (mol/m^3) and the metal concentration after adsorption, respectively. V is the volume of the aqueous solution (m^3) and M is the amount of adsorbent used (g). A known quantity of the microalga entrapping alginate beads was used in the experiment. The experiment was carried out three times, and the results given below are the average value.

In order to examine the reusability of the microalga entrapping alginate beads, a consecutive metal adsorption–desorption cycle was repeated three times using the identical adsorbents. Desorption of the metal ions was performed by using 10 mol/m^3 HCl solution. The microalga entrapping alginate beads were placed in the desorption solution and these were stirred at 400 rpm for 60 min at 25°C. The final metal ion concentration in the aqueous phase after filtration was determined by ICPS as described earlier. The extent of metal desorbed from the adsorbents was calculated from both the amount of metal ions adsorbed on the beads and the residual metal ion concentration in the desorption solution.

2.4. Langmuir adsorption isotherm

Behavior of the metal adsorption onto the microalga entrapping alginate beads were analyzed by applying an adsorption isotherm to the experimental results. Among several adsorption isotherm equations, Langmuir adsorption isotherm was used, which is widely used to analyze various data for metal adsorption and wastewater treatment.

$$q_{eq} = q_{\max} K_{eq} C_{eq} / (1 + K_{eq} C_{eq}) \quad (2)$$

In Eq. (2), subscript *eq* means adsorption equilibrium. C is the metal concentration in the aqueous solution, K_{eq} is the Langmuir adsorption equilibrium constant, and $q_{\max}$ is the maximum adsorption capacity of the metals. Eq. (2) can be rewritten as follows.

$$1/q_{eq} = 1/q_{\max} + 1/(q_{\max} K_{eq} C_{eq}) \quad (3)$$

The plot of $1/q_{eq}$ vs. $1/C_{eq}$ according to Eq. (3) was employed to generate a straight line whose intercept is $1/q_{\max}$ and the slope is $1/(q_{\max} \cdot K_{eq})$.

2.5. Continuous flow system

Using a glass column with an inner diameter of 1.5 cm and a height of 12 cm, a continuous flow experiment for adsorption of the metals was also carried out. An aqueous solution at pH 5.0 containing each metal ion with a concentration of 10 mol/m^3 was pumped into the column at a flow rate of 2.0 mL/min. In the metal-coexisting system, an aqueous solution containing each metal ion with a concentration of 2.5 mol/m^3 was prepared. At a designated time, the outlet solution from the column was sampled by an auto-sampler. The metal concentration in the sample solution was analyzed by ICPS. After that, the metal desorption experiments were carried out using the hydrochloric acid solution as the eluent with a concentration of 0.1 mol/dm^3.

3. Results and discussion

3.1. Effect of pH on adsorption of metal

The pH of aqueous solution generally affects the ionization state of the functional groups (i.e., hydroxyl, carboxyl, phosphate, and amino groups) existing on the wall of algal cell. At acidic pH, metals exist as the free cations and they are available for its adsorption. Preparation of metal-containing aqueous solution at high pH generally causes some precipitation like insoluble metal hydroxides, and so they lower its availability for adsorption. Therefore, in this study, the initial pH of an aqueous solution was set so as not to form the precipitation. In order to clarify the effect of pH on the adsorption of metal ions onto the microalga entrapping alginate beads, batch equilibrium studies of the metal ions were carried out at various pHs in the range of 2.0–6.0.

Fig. 1 shows the effect of pH on the amount of metal adsorbed in the case of *C. reinhardtii* entrapping alginate beads. The adsorption behavior of the metal ions in Fig. 1 is discussed as follows. The amount of metal adsorbed is increased with pH in a low pH region and then attains the maximum value around pH between 4 and 5. Copper ion was most adsorbed among the four metals. This result is considered to be caused by the difference in the binding affinity between the four metals and the metal-binding functions existing at the wall of microalgal cell. The interaction of the metal ion with the alginate and with the wall of entrapped microalgal cell could primarily be through the carboxyl groups on both the alginate and the wall of microalgal cell. The wall of algal cell of *C. reinhardtii* mainly consists of a number of polymers containing various acidic groups, which may be deprotonated with increase in pH of the aqueous solution. Hence, the metal adsorption depends on whether these carboxyl groups are protonated or deprotonated. It is anticipated that the functional groups responsible for the metal adsorption are carboxyl groups whose

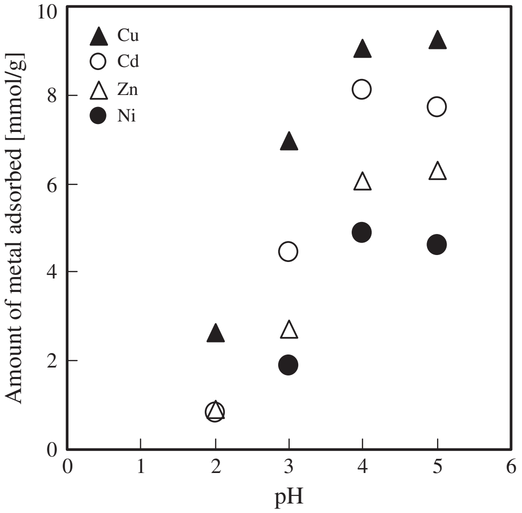

Fig. 1. Effect of pH on the amount of metal adsorbed (*C. reinhardtii*).

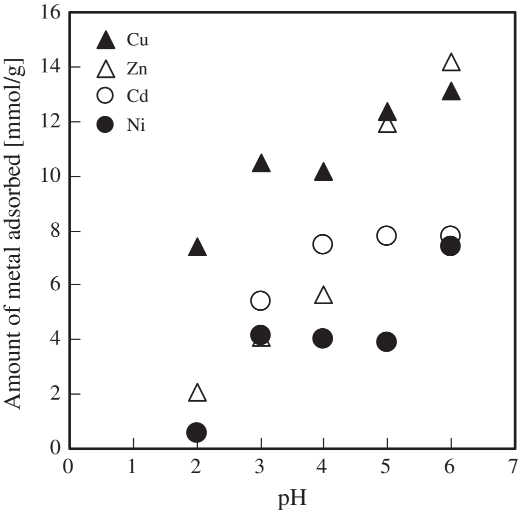

Fig. 2. Effect of pH on the amount of metal adsorbed (*A. variabillis*).

pK_a value is between 3 and 4. The increase in the amount of metal adsorbed that is seen around pH 4 reflects that the functional groups are deprotonated and negatively charged. This means that the negatively charged functional group attracts positively charged metal ions, which leads to a large amount of metal adsorption. It was known that a dead microalga entrapping beads exhibit a higher metal adsorption than that by a living microalga one at all tested pH values. Two mechanisms of metal ion binding on the microalgal cell can be considered. First, metal ion can be attracted by the negative charge of the cell wall component. This electrostatic binding is non-specific and it is mainly influenced by the valence of the ion. The second mechanism is a specific binding of the metal ion to the reactive sites at the cell wall. In our experiments, the reactive sites correspond to some functional groups existing at the algal cell wall, for example, carboxyl and hydroxyl groups. The adsorption of the metal ion on the microalgae would take place between the positively charged metal ion and the negatively charged algal cell surface. This is considered as the specific interactions between the metal ions and the anionic functional groups, depending on the metal property such as acidity or basicity.

Fig. 2 shows the effect of pH on the amount of metal adsorbed in the case of *A. variabilis* entrapping alginate beads. This result shows almost the same tendency as seen in Fig. 1.

3.2. Adsorption rates

Fig. 3 shows the changes in the amount of metal adsorbed with time in the case of *C. reinhardtii* entrapping alginate beads. The initial slope of the plots reflects the adsorption rate of the metal. It should be noted that there was no precipitation under the experimental conditions. A high metal adsorption rate was observed for Cd(II) and Cu(II). For example, approximately 85% Cd(II) adsorption took place within 30 min. Then, the adsorption rate was gradually reaching constant value, in other words, reaching its adsorption equilibrium. The information on the adsorption rates of heavy metal ions has been reported so far when using a variety of adsorbents. For example, in kinetic studies of polyvinyl alcohol–yeast and alginate–yeast adsorbent systems applied to copper adsorption, the adsorption equilibrium was attained in 12 and 24 h, respectively [11]. The adsorption equilibrium of Cr(VI) on the dead and immobilized biomass of *Rhizopus arrhizus* was attained in only 4 h [12]. The rate of lead adsorption on the cyanobacterium *Gloeocapsa* sp. was very fast and reached its equilibrium within 1 h [13]. The adsorption of Cd(II) onto pre-treated biomass of marine alga *Durvillaea potatorum* was studied to find out that the adsorption rate was very fast, almost 90% uptake of the metal taking place within 30 min [14,15]. It is anticipated from these results mentioned previously that there are several parameters which affect the adsorption rate, for example, stirring speed of the aqueous solution, structural properties of both the support and the adsorbent, amount of the adsorbent employed, properties of the metal ion such as ionic radius, initial concentration of the ionic species, and coexistence of other metal ions which may compete with the ionic species of interest. Therefore, it is too difficult to compare the reported adsorption rates with each other.

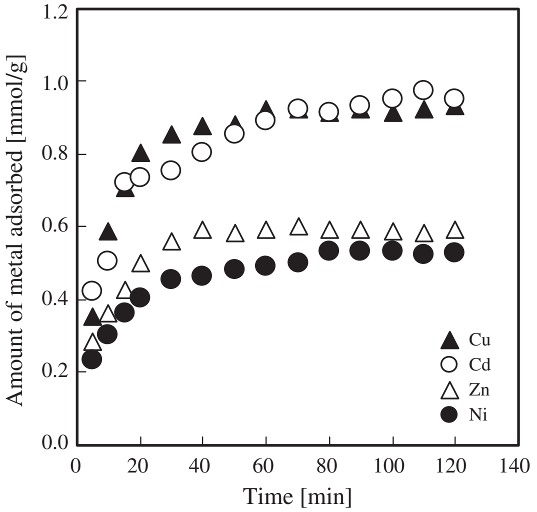

Fig. 3. Time course of the amount of metal adsorbed (*C. reinhardtii*).

Fig. 4 shows the changes in the amount of metal adsorbed with time in the case of *A. variabilis* entrapping alginate beads. This result shows almost the same tendency as seen in Fig. 3 in the sense that the adsorption equilibrium attains in about 80 min and that the maximum amount of metal adsorbed is about 1.0 mmol/g. But *A. variabilis* entrapping alginate beads possess a possibility to separate the metals as will be shown later.

3.3. Effect of initial metal ion concentration on amount of metal adsorbed

The amount of metal adsorbed on the microalga entrapping alginate beads are plotted against the equilibrium concentration of metal ions in the aqueous solution in Figs. 5 and 6 in the case of *C. reinhardtii* entrapping- and *A. variabilis* entrapping alginate beads, respectively. The amounts of metal ion adsorbed per unit mass of the adsorbent were increased as increase in the equilibrium concentration of metal ions. In order to attain the saturation state of the active sites with the metal, in other words, to obtain the maximum adsorption capacity of the microalga entrapping alginate beads for the metal ions, we used the metal aqueous solution with an initial concentration 300 mol/m^3. As seen in Fig. 5, the maximum adsorption capacity for *C. reinhardtii* entrapping alginate beads was found to be 61.3 mmol Cd(II)/g-bead. The adsorption of metal ion on dead *C. reinhardtii* entrapping alginate beads was found to be approximately 20% higher than that of the living cell entrapping one. It is considered that the increased metal adsorption capacity is caused by changes in the adsorptive characteristics of the algal surface due to the heat treatment in the dead *C. reinhardtii* entrapping alginate beads. From these results, it is confirmed that the surface properties of algal cell can be improved by the heat treatment as reported previously by other researchers. One explanation for this is that the heat treatment could erode the microalgal cell surface causing the wall to become leaky. This leads to a remarkable increase in the passive diffusion of the metal ions into the inner part of the cell wall.

Other adsorbents having a variety of adsorption capacities for heavy metal ions have been reported. For example, the heat treatment fungal biomass of *L. sajor-caju* was used for the adsorption of Cd(II) [4]. The adsorption capacity of the adsorbent was found

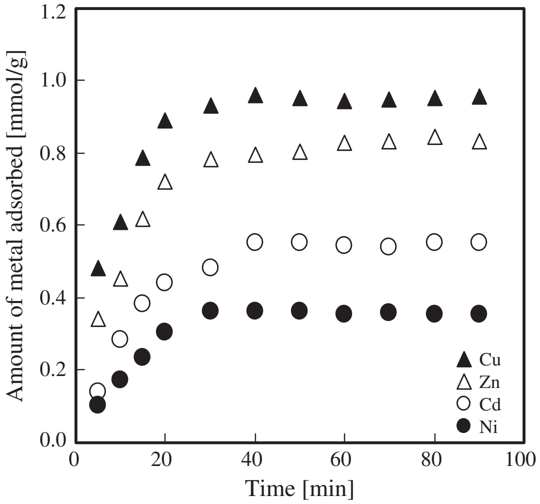

Fig. 4. Time course of the amount of metal adsorbed (*A. variabillis*).

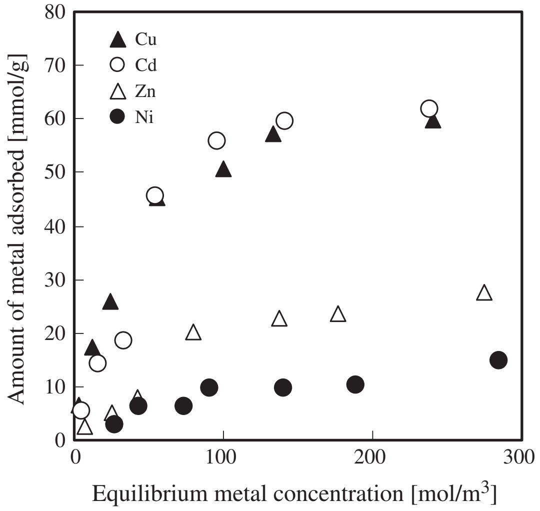

Fig. 5. Adsorption isotherm of the metal ions (*C. reinhardtii*).

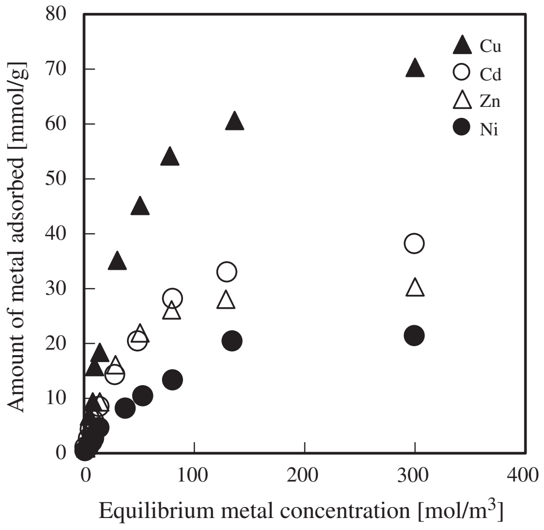

Fig. 6. Adsorption isotherm of the metal ions (*A. variabillis*).

to be 1.10 mmol Cd/g-dry biomass. The adsorption capacity of the dead *Fusarium flocciferum* mycelium was 1.71 mmol Cd(II)/g-dry biomass [16]. The Ca-pretreated alga, *D. Potatorum* was used for cadmium removal and it was reported that the adsorption capacity of the adsorbent was 1.01 mmol Cd(II)/g-dry biomass [14]. The cadmium adsorption capacity of NaOH-pretreated fungus biomass, *Aspergillus niger*, was 0.03 mmol Cd(II)/g-dry biomass [17]. The pretreated marine alga biomass, *Padina* sp., used for removal of cadmium from an aqueous solution had a capacity of 0.49 mmol Cd(II)/g-dry biomass [18]. The fungal biomass of white rot fungus, *Phanerochaete chrysosporium*, used for metal ion removal from artificial wastewater had a capacity of 0.21 mmol Cd (II)/g-dry biomass [19].

Summarizing these data mentioned above, it is found that *C. reinhardtii* entrapping alginate beads in our study is superior adsorbent to other ones especially for cadmium removal. However, we have not carried out the metal adsorption experiments using the Ca-alginate gel beads only. This subject is now under consideration. And the overall mechanism will be clarified in near future.

3.4. Adsorption isotherm equilibrium

In order to determine whether the microalga-entrapped adsorbent systems could be modeled using conventional adsorption isotherms, two typical adsorption isotherms, that is, Langmuir and Freundlich adsorption isotherms, used for adsorption of heavy metal ions were applied to our experimental results. As the result, the Langmuir adsorption isotherm explained the experimental results better than the Freundlich one. Figs. 7 and 8 show the reciprocal plots of the Langmuir adsorption isotherms, that is, $1/q_{eq}$ vs. $1/C_{eq}$, in the case of *C. reinhardtii* entrapping- and *A. variabilis* entrapping alginate beads, respectively. The straight lines are obtained in both cases. The intercept and slope of the straight lines give the Langmuir constants, $q_{\max}$ and K_{eq}. These are summarized in Tables 1 and 2 in the case of *C. reinhardti* entrapping- and *A. variabilis* entrapping alginate beads, respectively. It is found from these tables that Cu (II) is most adsorbed on both the alginate beads. Cd(II) is also well adsorbed on

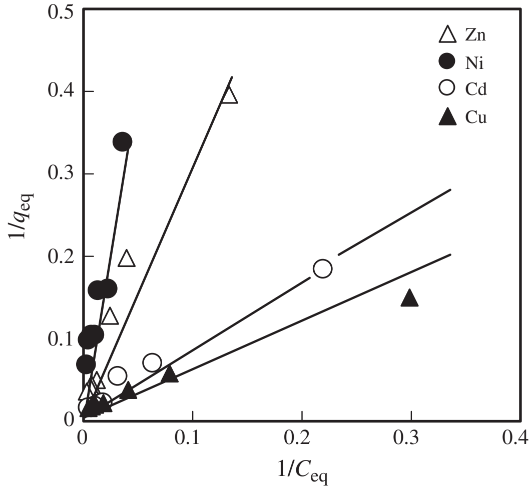

Fig. 7. Langmuir plot of the metal adsorption (*C. reinhardtii*).

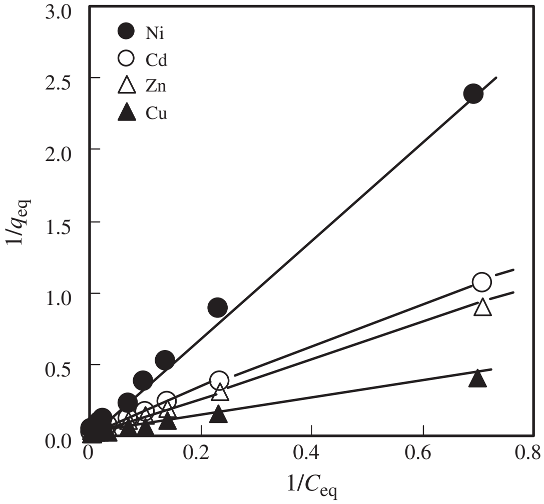

Fig. 8. Langmuir plot of the metal adsorption (*A. variabillis*).

Table 1
Parameters of Langmuir adsorption isotherm for *C. reinhardtii*

Metal	Ni	Cd	Cu	Zn
K_{eq} [m^3/mmol]	5.81×10^{-3}	3.86×10^{-2}	3.58×10^{-2}	1.31×10^{-2}
$q_{\max}$ [mmol/g]	2.35×10	6.13×10	6.85×10	2.73×10
R^2	0.999	0.997	0.998	0.997

Table 2
Parameters of Langmuir adsorption isotherm for *A. variabilis*

Metal	Ni	Cd	Cu	Zn
K_{eq} [m^3/mmol]	9.84×10^{-3}	1.31×10^{-2}	2.52×10^{-2}	1.54×10^{-2}
$q_{\max}$ [mmol/g]	2.96×10	5.12×10	7.04×10	5.21×10
R^2	0.993	0.997	0.998	0.999

Table 3
Parameters of Freundlich adsorption isotherm for *C. reinhardtii*

Metal	Ni	Cd	Cu	Zn
n	1.64	1.30	1.50	1.30
k	0.467	1.02	1.71	0.431
R^2	0.987	0.991	0.992	0.990

Unit of k is (mmol/g)(m^3/mmol)$^{1/n}$.

Table 4
Parameters of Freundlich adsorption isotherm for *A. variabilis*

Metal	Ni	Cd	Cu	Zn
n	1.43	1.39	1.54	1.57
k	0.414	1.03	2.80	1.41
R^2	0.968	0.961	0.943	0.927

Unit of k is (mmol/g)(m^3/mmol)$^{1/n}$.

C. reinhardtii entrapping alginate bead. These results agree well with the discussion mentioned above.

On the contrary, the Freundlich model could not explain enough the experimental results as shown in Tables 3 and 4 since the correlation coefficients, R, are smaller than those for the Langmuir model. This result is very reasonable since the metal adsorption in our case is considered to be due to a chemical interaction.

3.5. Adsorption of metal ions using a column packed with the alginate beads

First, a consecutive metal adsorption–desorption experiment was carried out in order to examine the reusability of the adsorbents. The results are shown in Tables 5 and 6. It was found that the adsorbents were reused at least three times in consecutive metal adsorption-desorption cycles without a significant loss in the adsorption capacity of the metals.

Fig. 9 shows the breakthrough curve in the column packed with *C. reinhardtii* entrapping alginate bead for a single-metal system. As shown in Fig. 9, it is found that the breakthrough point of Cu(II) emerged at around 300 mL of the effluent volume. This result means that Cu(II) is most adsorbed to the column, this is also recognized from the results mentioned in subsection 3.4. The breakthrough point of Cd(II) was about 200 mL of the effluent volume. This also agrees well with the results shown in Table 1. Fig. 10 shows the breakthrough curve in the column packed with *C. reinhardtii* entrapping alginate bead for metal coexisting system. In this case, the feed solution to the inlet of the column contains the four metal ions with the same concentration. Fig. 10 suggests a possibility of the separation of Cu(II) and Cd(II) group from Ni(II) and Zn(II) group.

Fig. 11 shows the elution curve of the metal ions in Ni(II)–Zn(II) binary system in the column packed with *A. variabilis* entrapping alginate beads. It is found that Zn(II) can be separated completely from Ni(II) at the point of 100 mL of the effluent volume. Fig. 12 shows the elution curve of the metal ions in Cd(II)–Cu(II) bin-

Table 5
Repeating experiment of metal adsorption–desorption cycles for *C. reinhardtii*

	Adsorption (1st) [mmol/g]	Desorption (1st) [mmol/g]	Adsorption (2nd) [mmol/g]	Desorption (2nd) [mmol/g]	Adsorption (3rd) [mmol/g]
Ni	5.21	5.03	5.01	5.01	4.99
Cd	8.41	8.21	8.11	8.12	8.10
Cu	9.21	9.00	8.97	8.94	8.92
Zn	6.34	6.21	6.05	6.03	6.04

Table 6
Repeating experiment of metal adsorption-desorption cycles for *A. variabilis*

	Adsorption (1st) [mmol/g]	Desorption (1st) [mmol/g]	Adsorption (2nd) [mmol/g]	Desorption (2nd) [mmol/g]	Adsorption (3rd) [mmol/g]
Ni	4.85	4.67	4.66	4.65	4.65
Cd	7.83	7.65	7.60	7.56	7.58
Cu	11.43	11.28	11.20	11.18	11.17
Zn	10.43	10.17	10.17	10.15	10.12

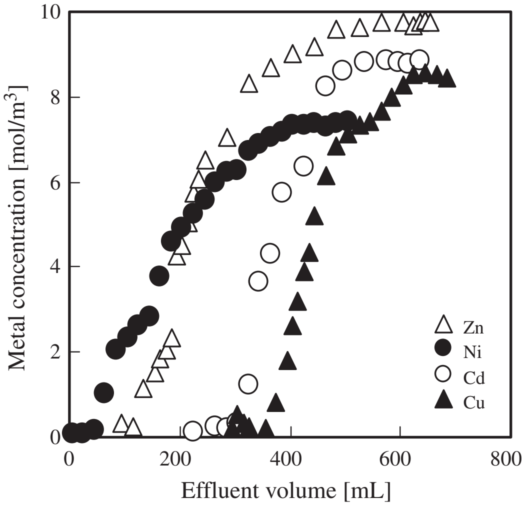

Fig. 9. Breakthrough curve of the metal ions (single-metal system, *C. reinhardtii*).

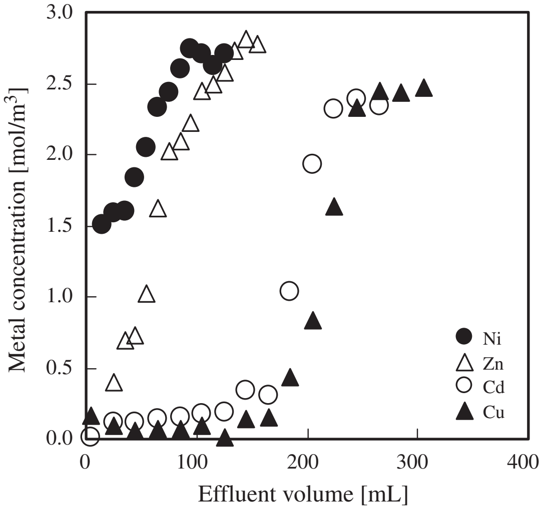

Fig. 10. Breakthrough curve of the metal ions (metal coexisting system, *C. reinhardtii*).

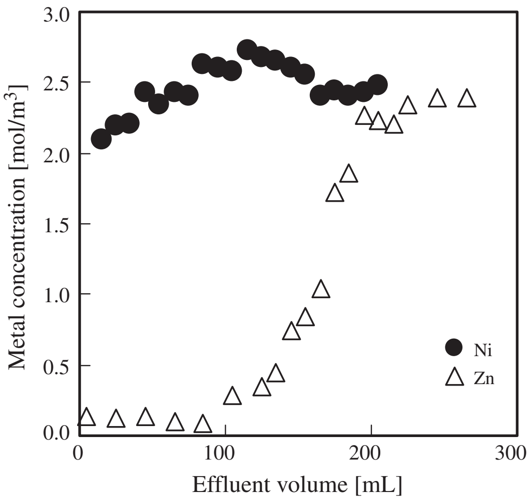

Fig. 11. Elution curve of the metal ions (Ni–Zn binary system, *A. variabillis*).

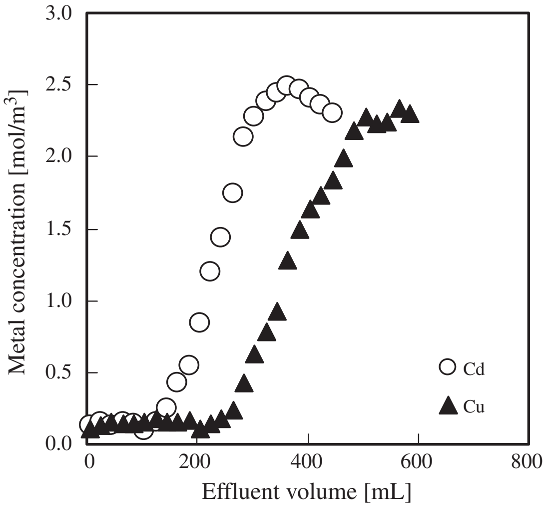

Fig. 12. Elution curve of the metal ions (Cd–Cu binary system, *A. variabillis*).

ary system. It is found that Cu(II) may be separated from Cd(II) at the point of 200 mL of the effluent volume. However, in the case, the complete separation between Cd(II) and Cu(II) is difficult. This problem may be improved by changing the operating condition.

Conclusively, the separation of Cu(II) and Cd(II) group from Ni(II) and Zn(II) group is possible. We are trying the separation of Zn(II) from Ni(II) and the separation of Cu(II) from Cd(II). This is further study which should be resolved and is now under consideration.

4. Conclusions

In this study, the adsorption of the metal ions, Cd (II), Cu(II), Zn(II) and Ni(II) on both the *C. reinhardtii*- and *A. variabilis*-entrapping alginate beads from an aqueous solution was investigated in the batch and the continuous flow adsorption systems. First the effect of pH on the adsorption of the metal ions on the microalga entrapping alginate beads was examined. The amount of metal adsorbed is increased with pH in a low pH region and then attains the maximum value around pH between 4 and 5. Copper ion was most adsorbed among the four metal ions. This is due to a specific interaction between the metal ion and the anionic functional groups on the microalgae.

Next the adsorption rate of the metal ion was examined. A high adsorption rate was observed for Cd(II) and Cu(II), especially approximately 85% Cd(II) adsorption took place within 30 min. The adsorption mechanism was also discussed. As the result, the Langmuir adsorption isotherm explained the experimental results better than the Freundlich one for all metal ions. The Langmuir constants and the maximum amount of the metal adsorbed were obtained for each metal ion.

Finally, the continuous flow experiment for adsorption of the metal ions was carried out using a glass column packed with the microalga entrapping alginate beads. As the result, a possibility of the separation of Cu(II) and Cd(II) group from Ni(II) and Zn (II) group was suggested. Further, it was found that Ni(II) can be separated from Zn(II) under an appropriate operating condition. But the complete separation between Cd(II) and Cu(II) was difficult. This is further study which should be resolved.

List of symbols

C — metal-ion concentration
C_{eq} — metal-ion concentration at equilibrium
C_0 — initial metal-ion concentration
K_{eq} — Langmuir adsorption equilibrium constant
M — amount of adsorbent used
q — amount of metal-ion adsorbed
q_{eq} — amount of metal-ion adsorbed at equilibrium
$q_{\max}$ — maximum adsorption capacity of metal ion
V — volume of aqueous phase

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