Enhancement of metal ion fractionation by adding alginate in batch foam separation

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Abstract

The influence of the addition of alginate on the separation rate, the recovery efficiency, and the fractionation of metal ions (Pb^{2+}, Cu^{2+}, and Cd^{2+}) in a batch foam separation was investigated in the coexisting system. Sodium dodecyl sulfate (SDS) was employed as an ion collector and a foaming agent. The separation rate was evaluated by the rate constant, *k*, which was obtained by fitting of the data to a first-order kinetic equation. By adding alginate, the fractionation effect relatively affected up to 0.05 g/L of alginate. In particular, the separation of Pb^{2+} was significantly affected by adding alginate in terms of the separation rate and the recovery efficiency. Pb^{2+} remained more in the liquid phase within the column with increasing the amount added of alginate. The optimum experimental condition was found in the range of the initial concentration of metal ion over 3.0×10^{-5} mol/L and concentration of alginate over 0.199 g/L for the effective fractionation of Pb^{2+} and Cd^{2+}. This fractionation could be considered to be caused by the difference between the binding strength of Pb^{2+} and Cd^{2+} to the carboxyl and the sulfate functional groups included in alginate and SDS, respectively.

KEYWORDS: adsorption, foam separation, heavy metal ion removal, fractionation, alginate.

1. Introduction

The recovery of metal ions from water is an extremely important issue for industry, environmental protection, and human health. Various methods have been proposed for this purpose, for example, chemical precipitation, photocatalysis, flotation, ion exchange, remediation, electrochemical treatment, adsorption, membrane technologies, and coagulation/flocculation [1]. In particular, the removal of dilute metal ions is even more important for complying with water quality standards. Adsorption separation is one of the most widely used methods. Recently there have been many reports using polymer-based adsorbents [2]. In the case of using a general solid adsorbent, desorption and adsorbent regeneration operations have been required to reuse the adsorbent and the metal ion recovered.

On the other hand, adsorptive bubble separation based on gas-liquid interfacial adsorption does not require secondary treatment of adsorbent and has been known to be a separation operation method suitable for the separation and recovery of dilute dissolved substances from an aqueous environment. Metal ions removal by adsorptive bubble separation has been known as ion flotation, which was first introduced by Sebba [3]. Recently studies about adsorption dynamics at the gas-liquid interface have been reported, for example, as modeling of adsorption dynamics [4,5], considerations using thermodynamics [6,7], and so on. It has been reported that the combined results indicated that the interaction between hydration shells of adsorbed ions and the H-bonds network of surface water plays a critical role in ionic adsorption [8].

Many removal techniques of metal ions by adsorptive bubble separation have been reported as ion and precipitation flotation, sorptive as biosorptive flotation, hybrid flotation, and so on [9,10]. In these reports, many researchers have focused on and made efforts for

developing flotation to the following points; kinds of objective metal ions (Al/Cu [11], Cr/Cu/Zn [12], CrO_4^- [13], Cd [14-16], Hg [17], Zn [18], Ni/Co/Cu [19], Cu/Ni/Cr(III) [20], Zn/Mn [21,22], Zn/Cd [23,24], I [25], Cd/Zn/Sr [26], Ni/Zn [27], Nd/Al [28], Li/Na/K/Rb/Cs [29]); kinds of surfactant (sodium dodecyl sulfate (SDS) [11,12,15,16,28,29], cetyltrimethylammonium bromide (CTAB) [13,18], sodium oleate [30], surfactin derived from *Bacilus subtilis* [17], polyoxyethylene(20) nonylphenyl ether (PONPE20) [31-34], dimethyldodecylamine-N-oxide [26]); kinds of additive reagents as chelating, liganding, and capturing agents (polyethylene glycols [25], side-armed lariat ether-type derivatives of diphosphaza-16-crown-6 ethers [22], m-dodecylphosphoric acid 32 and m-tetradecylphosphoric 33 acid [21], bis(2-ethylhexyl) phosphoric acid (D2EHPA) [35], aminopolycarboxylic chelating surfactant [26], triethylenetetramine (Trien) [27], NaF [28]), kinds of operations or apparatus (sorption-flotation [30], continuous counter-current [32-34], continuous multistage column with bubble-cap trays [16]). Moreover, the selective separation of metal ions has attracted much attention. In particular, some reports about selective metal ion separation based on affinity and binding strength between metal ions and surfactants have also been reported [31-34]. Kinoshita et al. reported a strong affinity between Au, Ga, and PONPE20 and the selective separation of Au and Ga.

In addition, several reports on the removal of toxic heavy metal ions using common adsorbents and biosorbents suggest that the ability to bind metal ions varies depending on the type of functional group which acts as the adsorption site [36]. The comparison of these adsorption strengths could be judged from some indicators, i.e., the differences in amounts adsorbed of the objective metal ions [37], equilibrium adsorption constants estimated by well-established adsorption model [38], and so on, although the difference in the adsorption strength would be recognized as a relative scale. These differences in adsorption strength could be originated from the difference in the binding strength of metal ions and functional

groups existing on the surface of the adsorbent, which can be regarded as adsorption sites. In particular, some studies about the adsorption of heavy metal ions using biomaterial adsorbents such as polysaccharides [37-39], bacteria [40], and marine algae [41] suggest that there is a very strong binding ability between lead ions and carboxyl functional groups. These differences reported in the literature suggest that adsorption fractionation can be done by using an adequate selection of a combination of two kinds of adsorbents, which have different functional groups from each other. We focused on the fact that the binding ability of metal ions to carboxyl and sulfone groups differs depending on the type of divalent metal ion. The use of inedible brown and red algae possessing these two functional groups as adsorbents may enable the development of environmentally friendly metal ion fractionating processes with low energy costs by using inexpensive biosorbents. The method proposed in this study is better than methods that add chelating agents, which are generally expensive, because the proposed method is relatively low-cost and is a naturally occurring, environmentally friendly, biodegradable material.

In this study, we attempted to fractionate metal ions (Cd^{2+}, Cu^{2+}, and Pb^{2+}) by adding alginate (Alg) to the treated solution in a batch foam separation technique. In addition, sodium dodecyl sulfate (SDS) was employed as a foaming agent. Alg and SDS have carboxyl and sulfonic groups respectively, and SDS should much adsorb onto the bubble surface than Alg. We investigated experimentally influence of coexisting two functional groups (carboxyl and sulfonic) on the fractionation of metal ions in foam separation technique and discussed the results.

2. Materials and methods

2.1. Materials

Cadmium nitrate tetrahydrate, copper sulfate pentahydrate, sodium alginate, and hydrochloric acid were purchased from Kanto Chemical Co. Inc. (Japan). Lead nitrate, sodium dodecyl sulfate, and sodium hydroxide were purchased from Fujifilm Wako Pure Chemical Co. (Japan). All purchased reagents were used without further purification.

2.2. Experimental setup

A transparent cylindrical acrylic pipe was used as a bubble column (70 cm in length, 4.4 cm in inside diameter). A sintered glass filter (10-15 μm average pore diameter) was equipped at the bottom of the column as a gas distributor. A sampling tap is equipped near the gas distributor at the outside wall. Pressure taps are also equipped along the outside wall at intervals of 25 cm to measure static pressure.

2.3. Experimental procedure

Foam separation experiments were conducted with a batch mode in this study. A solution including desired concentrations of metal ions, sodium alginate (Alg), and sodium dodecyl sulfate (SDS) was prepared. The dissolved metal ions were used alone or as coexisting (two or three) solutions. In most experiments, concentrations of metal ions were employed as 1.5×10^{-5}, 3.0×10^{-5}, and 6.0×10^{-5} mol/L, and concentrations of Alg were varied up to 0.2 g/L. The concentration of SDS was constant, at 7.5×10^{-4} mol/L, which was determined from

preliminary experiments to avoid foaming of the whole solution within the column. The prepared solution was set in the column, and then aeration was started at a constant volumetric flow rate (50 cm^3/min), which corresponds to 0.0537 cm/s, as a superficial gas velocity. The solution within the column was taken from a sampling tap at the desired time. All experiments were conducted at pH 5.5-5.8. The concentration of metal ions was determined by an atomic spectrophotometer (AAnalyst 200, Perkin Elmer, U.S.).

3. **Results and Discussion**

3.1. Influence of dose of alginate on separation rate and recovery efficiency of metal ions

The typical time course of the metal ion concentration within the column was shown in Figs. 1a and b. The ordinate of Figs. 1a and 1b represent the residual fraction, C/C_i. C represents the concentration of the metal ions, and the subscript, "i", represents the initial condition. In the case of without adding Alg (Fig. 1a) of coexisting system, all Pb^{2+} and Cd^{2+} ions were removed from the liquid within the column until 45 min. As for Cu^{2+}, almost an amount of Cu^{2+} was also removed until 90 min and its residual fraction, C/C_i, was 0.039, which corresponds to 1.18×10^{-6} mol/L. On the other hand, in the case of adding Alg (Fig. 1b, 0.0922 g/L), Cd^{2+} only was removed entirely from the liquid within the column at ca. 400 min, which indicated that the separation rate became slower than that without adding Alg (Fig. 1a). Pb^{2+} and Cu^{2+} were not entirely removed and remained in the liquid within the column as the equilibrium residual concentration. In this case, C/C_i was 0.3 and 0.67 for Cu^{2+} and Pb^{2+}, respectively. Moreover, it was confirmed that a lot of time was needed to reach the equilibrium residual concentration. Judging from the typical results shown in Figs. 1a and 1b, by adding Alg, it is considered that the separation rate and the residual fraction became slower and larger than those in the case of without adding Alg. For evaluation of the influence of adding Alg, in particular, its concentration on the separation rate and the removal efficiency more quantitatively, the separation rate constant was employed as an indicator to evaluate the separation rate. The separation rate constant was determined by following a first-order rate equation.

$$\ln(C/C_i) = -kt \qquad (1)$$

Where, *k*, represents the separation rate constant. Fig. 1c shows the typical result of the fitting of the data shown in Fig. 1b to Eq. (1). In most experiments, until 40 min, good linear relationships were confirmed, therefore *k* could be determined by Eq. (1).

Fig. 2 shows the influence of the concentration of Alg on the separation rate constant, *k*, (Fig. 2a), and the removal efficiency, *R*, (Fig. 2b) for the coexisting system. The removal efficiency, *R* was defined as follows.

$$R = 1 - C/C_i \quad (2)$$

In Fig. 2, the open and solid symbols correspond to the results obtained in the coexisting and the single system, respectively. As for *k*, all metal ions were affected by adding Alg. In particular, Pb^{2+} was significantly affected, and *k* for Pb^{2+} decreased abruptly with increasing the Alg concentration up to 0.05 g/L. The *k* value of Pb^{2+} without adding Alg was 0.0936 min^{-1}, and the average value of *k* in the range of 0.05-0.2 g/L Alg concentration was 6.89×10^{-4} min^{-1}, which corresponded to 1/136 times of 0.0936. The *k* values of Cd^{2+} and Cu^{2+} decreased gradually with increasing Alg concentration up to 0.15 g/L. As for *R*, Pb^{2+} was also affected significantly. *R* for Pb^{2+} decreased abruptly with increasing the Alg concentration up to 0.05 g/L, and Pb^{2+} was hardly removed from the solution at Alg concentration of 0.2 g/L. On the other hand, Cd^{2+} was not mostly affected by adding Alg, and even at Alg concentration of 0.2 g/L, *R* was 0.902. The *R* of Cu^{2+} decreased slowly to 0.6 with the addition of 0.2 g/L of Alg. The results obtained from the single system mostly agreed with those obtained from the coexisting system although some scatters were observed in the results for Pb^{2+}. This suggests that the removal tendency and behavior of each metal ion were not affected by the interaction between metal ions, but might be affected by the binding strength between functional groups

(carboxyl and sulfonate) and metal ions.

3.2. Influence of initial concentration of metal ion and molar ratio of carboxyl group to metal ion on separation rate and recovery efficiency of metal ions

Fig. 3 shows the influences of the initial molar ratio of the carboxyl group including in Alg molecule and metal ion, and the initial metal ion concentration on *k* (Figs. 3a-c) and *R* (Figs. 3d-f). Since the carboxyl groups per unit mass of Alg were determined to be 3.92×10^{-3} mol/g by a conductivity titration in our previous study [42,43], the value was used for conversion from Alg concentration to carboxyl group concentration. As seen in Figs. 3a-c, *k* decreased up to the molar ratio of 13 regardless of the kinds of metal ions, and the decrease in *k* for Pb^{2+} was significantly affected by the molar ratio. In the range of the molar ratio over 13, *k* seemed to be mostly constant for all metal ions. On the other hand, as for *R* (Figs. 3d-f), the influence of the molar ratio was observed to be quite different depending on the kind of metal ion and its initial concentration. The *R* of Cd^{2+} was little affected by the molar ratio and the initial concentration (Fig. 3f), and The *R* values were almost always above 0.9. As for *R* of Pb^{2+} and Cu^{2+}, *R* decreased abruptly with increasing the molar ratio at higher the initial concentration of metal ion (> 3.0×10^{-5} mol/L). When Pb^{2+} and Cu^{2+} were compared at the same initial concentration, the *R* value of Pb^{2+} was lower than that of Cu^{2+}, even at the same molar ratio. Judging from these behaviors of *R*, it is suggested that the order of adsorption affinity of Alg (carboxyl group) to metal ions might be $Pb^{2+} > Cu^{2+} > Cd^{2+}$.

3.3. Influence of initial concentration of metal ion and molar ratio of carboxyl group to SDS on separation rate and recovery efficiency of metal ions

Fig. 4 shows the influences of the initial concentration of metal ions and the molar ratio of carboxyl group to SDS on *k* (Fig. 4a-c) and *R* (Fig. 4d-f). As for Cu^{2+} (Figs. 4b and 4e) and Cd^{2+} (Figs. 4c and 4f), it was not sufficiently recognized the influence of the difference in the initial concentration of metal ions on *k* and *R*. As for Pb^{2+} (Figs. 4a and 4d) in the range up to the molar ratio of about 0.25, the influence of the difference in initial concentration of metal ion could not be confirmed, and *k* and *R* rapidly decreased. In the range over the molar ratio of 0.25, the values of *k* and *R* for Pb^{2+} did not vary abruptly, although there were some scatters depending on the initial concentration of Pb^{2+}. For comparison, in the case of the initial metal concentration of 3.0×10^{-5} mol/L, when the molar ratio varied from 0 to 0.25, the value of *k* for Pb^{2+} became about 0.013 times smaller. On the other hand, in the same case, the values of *k* for Cu^{2+} and Cd^{2+} became 0.65 and 0.36 times smaller.

Judging from the results shown in Figs. 2-4, it is considered that in the range of the initial concentration of metal ion over 3.0×10^{-5} mol/L and concentration of Alg over 0.199 g/L, most of all Cd^{2+} was removed from the liquid phase due to binding to SDS, and Pb^{2+} was mostly remained in the liquid phase due to binding to Alg. Thus, in those experimental conditions, fractionation of Pb^{2+} and Cd^{2+} could be achieved, and the addition of Alg could enhance the fractionation.

The driving force of transport from the liquid within the column should be considered as adsorption of SDS, which binds with metal ions, on the bubble surface. The adsorption of surfactant at air-liquid interface has been important issue for fundamental and practical aspects such as wetting, detergency, foaming, and emulsification [44]. In particular, the mechanisms of adsorption of surface-active substances at the air-liquid interface have been studied using dynamic surface tension measurements. In a pioneering model, Ward and Tordai (1946) assumed that the adsorption is limited by diffusion, resulting in an asymptotic decay as the inverse square root of time [45]. However, with the improved accuracy achieved in recent

years, some measurements have been reported suggesting that diffusion is not the only dominant factor [46]. Corti et al. (2015) measured the dynamic surface tension with the resonance response of the bubble surface oscillation and reported that SDS adsorbed at the air-water interface of a bubble could not be removed even at extremely low initial bulk concentration although when the surrounding solution was gently replaced by pure water, and on the contrary, at high coverage the monolayer dissolution kinetics is extremely fast at high an initial bulk concentration [47], which is consistent with previous hypotheses and observations that have been repeatedly reported in the literature [48,49]. Corti et al. (2015) also reported that interfacial SDS molecules may be in a gas-like state [47]. It is considered that their observed fact, which desorption from the bubble surface occurs less frequently when the bubble surface coverage is low and more frequently when the coverage is high, is almost consistent with the assumption of the Langmuir adsorption kinetic process.

Seki et al. [40,41] have reported that biosorbents using bacteria and marine algae had three types of adsorption sites for metal ions, in particular, the metal-binding constant of the calboxyl group for Pb^{2+} was larger than that for Cd^{2+}. Khan et al. [39] reported that adsorption experiments were conducted using lignocellulose derived from agricultural waste modified with dodecyl sulfate chains and that the adsorption constants, which were estimated by applying Langmuir isotherm, of Pb^{2+} were larger about 1.58 times larger than those of Cd^{2+} in the range of temperature (298-328 K). This suggests that the binding strength between the sulfate group and Pb^{2+} should be stronger than that of Cd^{2+}. Aranilla et al. [38] conducted adsorption experiments using carboxymethyl kappa carrageenan hydrogels, which have sulfate groups as adsorption sites and reported that in the pH range of 3-9, the amount adsorbed of Cu^{2+} was about 3.3-4.5 times larger than that of Pb^{2+}. Son et al. [37] reported that alginate has a higher adsorption affinity of Pb than of Cu and Hg in both single and coexisting systems. Moreover, Hasan Ehrampoush et al. (2001) reported that the order of the selectivity

of some divalent metal ions was $Pb^{2+} > Ca^{2+} > Cd^{2+} > Zn^{2+} > Cu^{2+}$ in the case of using SDS in flotation [50]. Huang and Talbot (1973) reported that the order of removal of the metal ions from the solution was $Pb^{2+} > Cd^{2+} > Cu^{2+}$ using sodium dodecylbenzene sulfonate in flotation [51]. Yuan et al. (2008) reported that the order of the selectivity was $Pb^{2+} > Cu^{2+} > Cd^{2+}$ in the case of using tea-derived saponin due to the carboxyl groups included in the saponin in ion flotation [52]. These results also support our results shown in Figs. 1a-b, Fig. 2, and Fig. 4.

The values of *k* calculated from Fig. 1a (without Alg addition) are 0.0936, 0.0773, and 0.0342 min^{-1} for Pb^{2+}, Cd^{2+}, and Cu^{2+} respectively. This order of *k* is in agreement with the reported results [50,51]. However, when Alg is added to the system (Fig. 1b), Pb^{2+} and Cu^{2+} were clearly not removed from the solution within the column. In addition, it also takes about 400 minutes for all Cd^{2+} to be removed from the solution within the column, which is about eight times longer than the time required without Alg (Fig. 1a). This trend is similar to the result reported by Yuan et al. [52]. When sulfonic and carboxyl groups coexist in the system, Pb^{2+} ions bind more easily to carboxyl groups than to sulfonic groups, indicating that the binding strength is much stronger than that of Cd^{2+} and Cu^{2+}. In addition, when Cu^{2+} and Cd^{2+} are compared, Cu^{2+} probably has stronger binding strength to the carboxyl group. As a result, Cd^{2+}, which has the weakest relative binding strength to carboxyl groups, is more likely to bind to sulfone groups. This difference in relative binding strength to the carboxyl groups may have caused Pb^{2+} to remain in the solution and Cd^{2+} to be transported out of the system by flotation.

Several previous reports suggested that the binding strength between the carboxyl group and Pb^{2+} was greater than that of Cd^{2+}, although we could not measure the difference in the binding strength between two functional groups (carboxyl and sulfate) and metal ions (Cd^{2+}, Cu^{2+}, and Pb^{2+}). Judging from these facts, the difference in the binding strength of the functional groups and metal ions could become a driving force of the present fractionation by

the batch foam separation method.

4. Conclusions

In this study, the removal of metal ions (Cd^{2+}, Cu^{2+}, and Pb^{2+}) from the aqueous phase was conducted and investigated in batch foam separation by adding alginate as a capture reagent of metal ions. we attempted to fractionate these metal ions by utilizing the difference in the binding strength or affinity between carboxyl (included in alginate molecule) and sulfonic (included in sodium dodecyl sulfate (SDS) molecule) functional groups and divalent metal ions (Cd^{2+}, Cu^{2+}, and Pb^{2+}). In particular, the fractionation of Pb^{2+} and Cd^{2+} has been achieved in some specific conditions described below. In the range of the initial concentration of metal ion over 3.0×10^{-5} mol/L and concentration of alginate over 0.199 g/L, most of all Cd^{2+} was removed from the liquid phase due to binding to SDS as a foaming agent, which adsorbed onto bubble surface, and Pb^{2+} was mostly remained in the liquid phase due to binding to alginate. Therefore, in those experimental conditions, the fractionation of Pb^{2+} and Cd^{2+} could be achieved, and the addition of alginate could enhance the fractionation of Pb^{2+} and Cd^{2+}.

In a further study, we will investigate which combination of metal ions affects to fractionate by this proposed method, what kinds of additive agents affect to fractionate metal ions, and the influences of some operating conditions (superficial gas velocities, column dimensions, and so on) in foam separation technique. In addition, we would also consider the effective utilization of inedible marine algae, for example, brown and red algae, which mainly contain carboxyl and sulfonic groups, respectively, for the adsorptive separation and fractionation of heavy metal ions.

Credit authorship contribution statement

Hideo Maruyama: Planning the experiments of this research, Assisting the experiments, Analysis of the experimental data, Writing original manuscript. Hideshi Seki: Advising experimental method, Discussions about results, Writing-Reviewing and Editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Nomenclature

C	= concentration of metal ion within the column	[mol/m^3]
C_i	= initial concentration of metal ion within the column	[mol/m^3]
k	= separation rate constant defined in Eq. (1)	[min^{-1}]
R	= removal efficiency of metal ion	[-]

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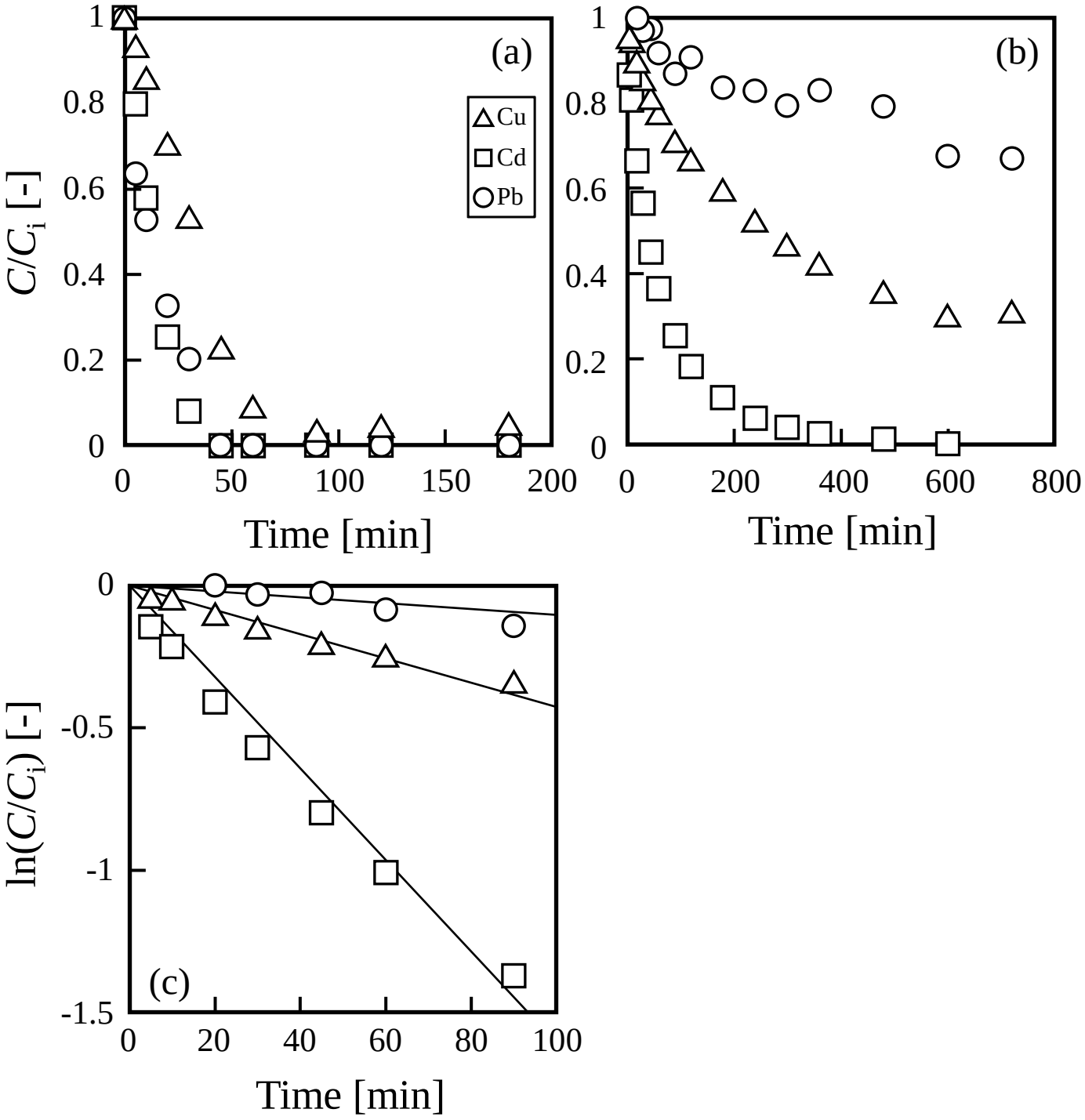
Figures captions

Fig. 1. (a) Typical time course of metal ion concentration within the column without adding alginate. (b) Typical time course of metal ion concentration within the column with adding alginate. (c) Typical result of fitting of the data to Eq. (1) to determine the separation rate constant, *k*. The experimental conditions: the initial concentration of metal ions, 3×10^{-5} mol/L; concentration of SDS, 7.5×10^{-4} mol/L; concentration of alginate, 0.0922 g/L.

Fig. 2. Influence of concentration of alginate on (a) the separation rate constant, *k*, and (b) the removal efficiency, *R*. The open and solid symbols correspond to the results of the coexisting (Pb^{2+}/Cu^{2+}/Cd^{2+}) and the single systems, respectively. The experimental conditions: the initial concentration of metal ions, 3×10^{-5} mol/L; concentration of SDS, 7.5×10^{-4} mol/L; concentration of alginate, 0.0922 g/L.

Fig. 3. Influence of the molar ratio of carboxyl group and metal ion in the initial condition and the initial metal concentration on the separation rate constant, *k*, and the removal efficiency, *R*. The experimental conditions: concentration of SDS, 7.5×10^{-4} mol/L; concentration of alginate, 0.0922 g/L.

Fig. 4. Influence of the molar ratio of carboxyl group and sulfate group in the initial condition and the initial metal concentration on the separation rate constant, *k*, and the removal efficiency, *R*. The experimental conditions: concentration of SDS, 7.5×10^{-4} mol/L; concentration of alginate, 0.0922 g/L.



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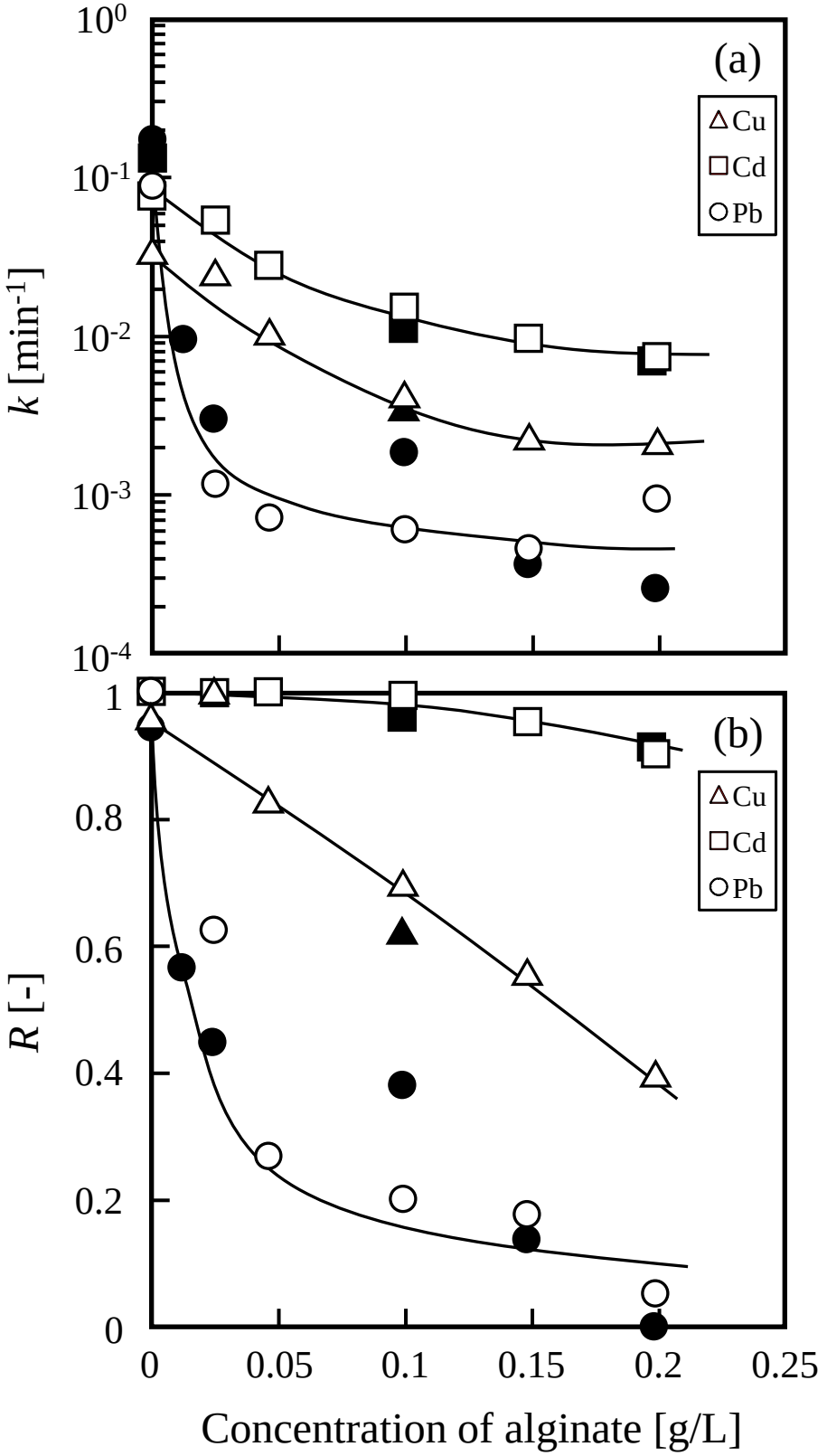

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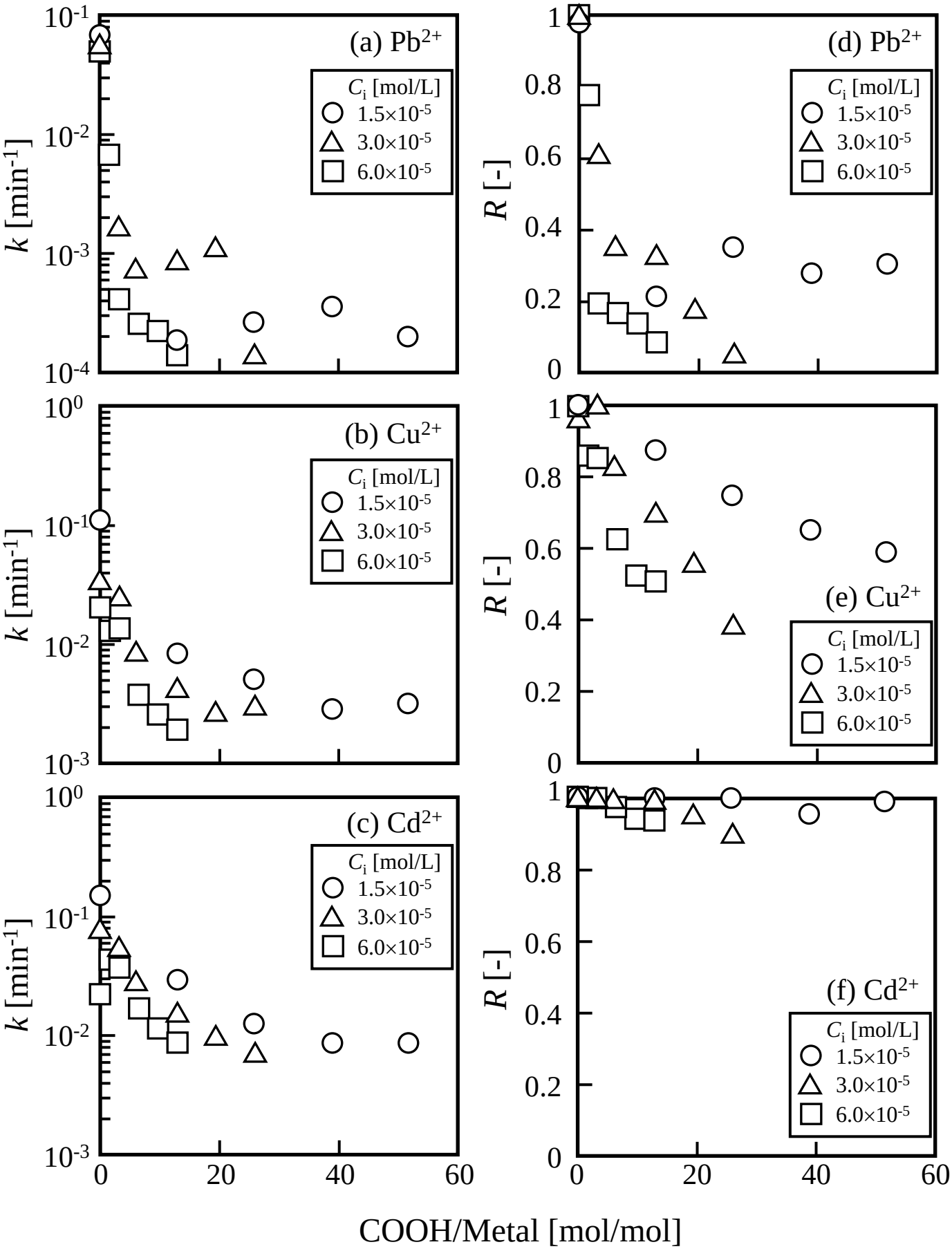

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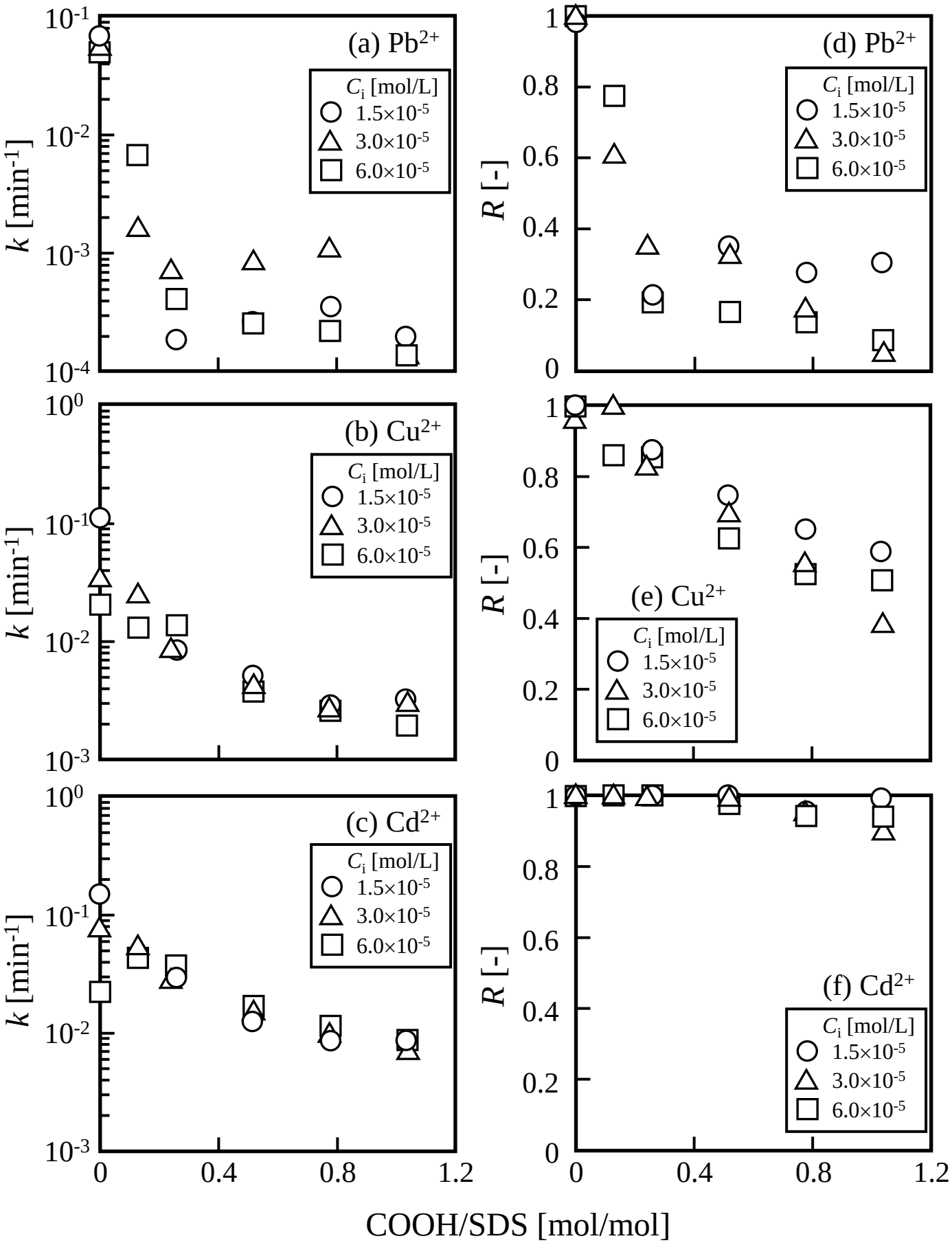

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