Effective and Selective Adsorption of Zn^{2+} from Seawater on a Layered Silicate**

Yusuke Ide, Naonori Ochi, and Makoto Ogawa

Concentration of ions and molecular species from water on solid surfaces is a topic covering a wide range of scientific and practical applications for such purposes as the removal of toxic compounds and the collection of noble elements and molecules. The adsorption-based process is one of the most promising strategies; therefore, searching for and designing adsorbents for target ions and molecules have been actively conducted. Layered inorganic solids and their derivatives are promising adsorbents with the following advantages: a) large surface area derived from well-defined nanostructures composed of an ultrathin layer (a so-called "nanosheet"), b) chemical and thermal stabilities when compared with their organic counterparts, and c) material diversity.[1]

As for the ion-exchange selectivity on layered inorganic solids, it has been recognized that anions with higher charge and smaller size are preferred on layered double hydroxides.[2] Concentration of cationic species, especially heavy metals and radioactive ions, on ion-exchangeable layered materials, such as smectite clays,[3] synthetic micas,[4] layered metal phosphates,[5] and layered titanates,[6] has been studied so far. A wide variety of materials are available;[1,7] therefore, it is worth investigating the concentration of various cations on layered inorganic solids. To concentrate heavy-metal ions, the organic modification of layered[8] and mesoporous materials[9] has been conducted, and it was found that thiol groups attached on the solid surface played a role in the adsorption of Hg^{2+}. Because of the demands for the environmental purification and collection of noble-metal ions, there is a need for selective ion-exchange processes for a wide variety of target elements using environmentally friendly materials.[10]

Herein, we report the selective and effective adsorption of Zn^{2+} on a layered silicate, magadiite.[11] Zinc is an element essential for life; it exists in seawater (at the concentration of 0.4 ppb)[12] and has been shown to be harmful to human and aquatic animal health.[13,14] Magadiite is a naturally occurring layered alkali silicate[11d] that can be readily synthesized by a simple hydrothermal reaction between silica, sodium hydrox-

ide, and water.[11a,b] Therefore, the successful procedure reported herein opens up a new opportunity for collecting Zn^{2+} from seawater. In addition, we found that the concentration of Zn^{2+} can be achieved even in the presence of Cd^{2+}, which often competes and disturbs the concentration and detection of Zn^{2+}.[15,16]

The characteristics of magadiite and other adsorbents examined in this study (another kind of Na^+-type layered alkali silicate, octosilicate,[17] a naturally occurring Na^+-type smectite, and a commercially available ion-exchange resin) are summarized in Table 1. It should be mentioned that the

Table 1: Characteristics of adsorbents used in this study.

Adsorbent	Chemical formula	Cation-exchange capacity [mequiv g^{-1}][a]
octosilicate	$Na_2Si_8O_{17}$	2.84[b]
magadiite	$Na_2Si_{14}O_{29}$	2.00[b]
montmorillonite	$(Na_{0.53}Ca_{0.09})(Al_{3.28}Fe_{0.31}Mg_{0.43})$-$(Si_{7.65}Al_{0.35})O_{20}(OH)_4$	1.15
IRC748	–	1.01

[a] mequiv = milliequivalents. [b] Based on their chemical formulas.

cation-exchange capacity of layered alkali silicates is much larger than those of other adsorbents. Magadiite[11a] and octosilicate[17a] were synthesized as described previously. Sodium montmorillonite (Kunipia F) was obtained from Kunimine Industries Co., Japan. An ion-exchange resin with the iminodiacetic group (IRC748), which interacts with heavy-metal ions, was purchased from Organo Co.

Before the concentration of Zn^{2+} from a seawater-mimicking solution was examined, adsorption tests of Zn^{2+} from an aqueous NaCl solution were conducted to investigate the affinity of layered silicates with Zn^{2+} in the presence of Na^+. Figure 1a shows the adsorption isotherms of Zn^{2+} on montmorillonite and magadiite from an aqueous NaCl solution (10 000 ppm, pH 6.2). The adsorption isotherm of Zn^{2+} on magadiite exhibited the H type according to the Giles classification,[18] and showed strong interactions between magadiite and Zn^{2+}. On the other hand, Zn^{2+} hardly adsorbed on montmorillonite. Accordingly, we then examined the possible concentration of Zn^{2+} on magadiite from seawater. Table S1 in the Supporting Information shows the composition of the mixed electrolyte solution mimicking seawater (pH 6.9). Cd^{2+} was added to the aqueous mixture, since it is known that comparable amounts of Zn^{2+} and Cd^{2+} exist in

[*] Dr. Y. Ide,[+] N. Ochi, Prof. Dr. M. Ogawa
    Department of Earth Sciences, Waseda University
    1-6-1 Nishiwaseda Shinjyuku-ku, Tokyo 169-8050 (Japan)
    Fax: (+81) 3-3207-4950
    E-mail: makoto@waseda.jp

[+] Current address: Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University (Japan)

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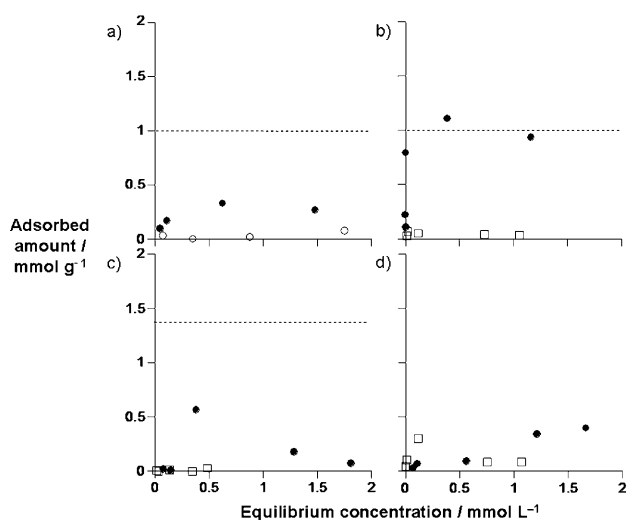
Figure 1. Adsorption isotherms of a) Zn^{2+} on (●) magadiite and (○) montmorillonite from an aqueous NaOH solution (pH 6.2) and b–d) (●) Zn^{2+} and (□) Cd^{2+} on b) magadiite, c) octosilicate, and d) ion-exchange resin from a seawater-mimicking solution containing Zn^{2+} and Cd^{2+} (pH 6.9). Horizontal lines denote the ion-exchange capacity for the dication of the corresponding silicates.

seawater,[19] and consequently it is interesting to separate the two cations for the development of adsorbents that efficiently concentrate Zn^{2+}.

Figure 1b depicts the adsorption isotherms of Zn^{2+} and Cd^{2+} on magadiite from the mixed electrolyte solution; the isotherm for Zn^{2+} was of the H type,[18] while Cd^{2+} hardly adsorbed. The amount of adsorbed Zn^{2+} was comparable to the cation-exchange capacity of the silicate (denoted as horizontal lines in Figure 1). The results indicate that the interlayer Na^+ of magadiite was almost quantitatively exchanged with Zn^{2+} in the mixed electrolyte solution containing Cd^{2+}, when taking into consideration the fact that almost all Zn in seawater exists as Zn^{2+}.[20] The replacement of the interlayer Na^+ with Zn^{2+} was also supported by the XRD patterns of magadiite before and after the reaction with the mixed electrolyte solution. The basal spacing of the products was slightly decreased depending on the amount of Zn^{2+} adsorbed (see Figure S1 in the Supporting Information), thus showing the change in the hydration of the interlayer space from the highly hydrophilic Na form to the Zn form.[21] The protonated form was not detected in the XRD patterns of the partially Zn-exchanged products, which indicated the direct exchange of Na^+ in magadiite with Zn^{2+}.[11g] The separation of Zn^{2+} from the aqueous Cd^{2+} mixture is worth mentioning since the electronic and binding properties of the two cations are similar, and the design of artificial receptors to sense Zn^{2+} in the presence of Cd^{2+} has been a topic of interest.[15,16] This result motivated us to design magadiite-based Zn^{2+} sensors, in which a functional dye is hybridized on the silicate (interlayer or particle surface) with the original interlayer structure maintained.[7]

The amount of Zn^{2+} adsorbed from the mixed electrolyte solution (pH 6.9) was larger than that from an aqueous NaCl solution (pH 6.2), which was explained as follows. The basal

spacing (1.64 nm) of magadiite in the mixed electrolyte solution was larger than that (1.59 nm) in an aqueous NaCl solution, so that Zn^{2+} was intercalated more efficiently into magadiite from the mixed electrolyte solution. Another explanation for the result is the competition between Zn^{2+} and H^+. The titration curve of magadiite with an aqueous HCl solution demonstrated that the replacement of the interlayer Na^+ with H^+ occurred below pH 6.5.[22] When magadiite was allowed to react with a Zn^{2+} aqueous solution at pH 6.2, competitive adsorption of H^+ suppressed the Zn^{2+} uptake.

Note that the effective concentration of Zn^{2+} from the mixed electrolyte solution was not achieved either by another layered alkali silicate, octosilicate, or by a commercially available ion-exchange resin (Figure 1c and d). At present, the reason for this result is not clear. The mechanism for the exclusion of cations other than Zn^{2+} by magadiite is also not understood at this stage. Komarneni and Roy have reported the selective adsorption of Cs^+ on α-zirconium phosphate from an aqueous mixture of Na^+ and Ca^{2+}.[5a] The mechanism was proposed that less hydrated Cs^+ is preferentially interca-lated in the narrow interlayer space (0.29 nm) of the phosphate than the more hydrated Na^+ and Ca^{2+}.[5a] Taking the size (Na^+ 0.19, K^+ 0.26, Mg^{2+} 0.13, Ca^{2+} 0.20, Zn^{2+} 0.15, Cd^{2+} 0.19 nm)[23] and hydration energy (Na^+ 114, K^+ 94, Mg^{2+} 490, Ca^{2+} 410, Zn^{2+} 528, Cd^{2+} 462 $kcal\,g^{-1}ion^{-1}$)[24] of the cations used here into consideration, the proposed mecha-nism is not applicable to the present case.

The ^{29}Si magic angle spinning NMR spectra of magadiite and materials exchanged with Zn^{2+}, Cd^{2+}, and K^+ were recorded. It was found that the intensities of the Q^3 and Q^4 peaks of the Cd^{2+}- and K^+-exchanged forms were much lower than those of the original Na form, whereas those of the Zn^{2+}-exchanged form were comparable to those of Na-type magadiite (see Figures S2 and S3 in the Supporting Informa-tion). These results imply that the intercalation of cations other than Zn^{2+} accompanies a substantial change of the layered structure of magadiite to suppress their uptake from the mixed electrolyte solution.

The adsorbed Zn^{2+} was replaced by Na^+ for possible Zn^{2+} collection. In other words, this shows that magadiite can be used repeatedly. The adsorbed Zn^{2+} on magadiite was quantitatively exchanged with H^+ and then replaced with Na^+ without any significant change of the layered structure by reaction with aqueous HCl and NaOH solutions sequentially (see Figure S1 in the Supporting Information). The amount of adsorbed Zn^{2+} on the recovered magadiite was almost equivalent to that on the pristine magadiite under identical conditions. The direct treatment of the used magadiite with an aqueous NaCl solution hardly replaced the adsorbed Zn^{2+} with Na^+, which indicated again that there were strong interactions between magadiite and Zn^{2+}. Magadiite exchanged with other cations, such as K^+ and Li^+, was also recovered by a similar procedure (Figure S2 in the Supporting Information), which supported the notion that the cation exchange of magadiite was reversible. Magadiite is naturally occurring[11d] and can be readily synthesized on a large scale by a simple hydrothermal technique;[11a,b] therefore, the present results show the potential of magadiite as a practically applicable adsorbent for Zn^{2+} in seawater.

In conclusion, we have reported the successful concentration of Zn^{2+} on a layered alkali silicate, magadiite, from a seawater-mimicking aqueous solution. Magadiite selectively and efficiently adsorbed Zn^{2+} from an aqueous mixture containing Cd^{2+} by ion exchange of the interlayer Na^+ with Zn^{2+}, which was not achieved on another kind of sodium-type layered alkali silicate, octosilicate. The separation was not attained on a commercially available ion-exchange resin. The ion-exchange process on magadiite is reversible so that the material can be reused for the concentration of Zn^{2+}.

Experimental Section

Preparation of mixed electrolyte solutions: Sample solutions were prepared using sodium, magnesium, and potassium chlorides, magnesium and calcium sulfates, and zinc and cadmium nitrates.

Adsorption test: Adsorbents (40 mg) were allowed to react with aqueous solutions (50 mL) for 1 day at room temperature. After the adsorbents were separated by filtration, the concentration of the remaining ions in the supernatants was determined by inductively coupled plasma–atomic emission spectroscopy.

Recovery of the adsorbent: $Zn_{0.26}Na_{1.5}Si_{14}O_{29}$ (15 mg) was allowed to react with an aqueous HCl solution (50 mL, 0.1 mol L^{-1}) and then an aqueous NaOH solution (molar ratio Na/H = 5.0, 50 mL) to quantitatively replace the adsorbed Zn^{2+} with Na^+. To directly exchange the adsorbed Zn^{2+} with Na^+, the same sample was reacted with an aqueous NaCl solution (molar ratio Na/Zn = 5.0, 50 mL).

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