Heavy metal adsorptivity of calcium-alginate-modified diethylenetriamine-silica gel and its application to a flow analytical system using flame atomic absorption spectrometry☆

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H I G H L I G H T S

- Calcium-alginate-modified dien-silica gel adsorbed multivalent metal ions.
- Metal ions adsorbed on CaAD were eluted using low acidic concentrations.
- Flow system with CaAD-packed column enriched metal concentrations up to 50-fold.

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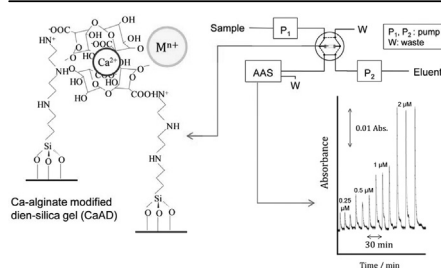
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This study aimed to evaluate the heavy metal adsorptivity of calcium-alginate-modified diethylenetriamine-silica gel (CaAD) and incorporate this biosorbent into a flow analytical system for heavy metal ions using flame atomic absorption spectrometry (FAAS). The biosorbent was synthesized by electrostatically coating calcium alginate onto diethylenetriamine (dien)-silica gel. Copper ion adsorption tests by a batch method showed that CaAD exhibited a higher adsorption rate compared with other biosorbents despite its low maximum adsorption capacity. Next, CaAD was packed into a 1 mL microcolumn, which was connected to a flow analytical system equipped with an FAAS instrument. The flow system quantitatively adsorbed heavy metals and enriched their concentrations. This quantitative adsorption was achieved for pH 3–4 solutions containing 1.0×10^{-6} M of heavy metal ions at a flow rate of 5.0 mL min^{-1}. Furthermore, the metal ions were successfully desorbed from CaAD at low nitric acid concentrations (0.05–0.15 M) than from the polyaminecarboxylic acid chelating resin (Chelex 100). Therefore, CaAD may be considered as a biosorbent that quickly adsorbs and easily desorbs analyte metal ions. In addition, the flow system enhanced the concentrations of heavy metals such as Cu^{2+}, Zn^{2+}, and Pb^{2+} by 50-fold. This new enrichment system successfully performed the separation and determination of Cu^{2+} (5.0×10^{-8} M) and Zn^{2+} (5.7×10^{-8} M) in a river water sample and Pb^{2+} (3.8×10^{-9} M) in a ground water sample.

1. Introduction

Calcium alginate is a water-insoluble, gelatinous, cream-colored substance obtained by the addition of aqueous calcium chloride to aqueous sodium alginate. It is mainly used to produce insoluble artificial seeds for plant tissue culture, to immobilize

enzymes by entrapment, and to generate edible substances. In addition, it forms a stable egg-box structure [1–3], in which the alginate biopolymer binds to calcium ions; it is applied as a biosorbent for heavy metal ions such as Cu^{2+}, Cd^{2+}, and Pb^{2+} [4–8]. The heavy metals are expected to interact with the deprotonated carboxyl and/or polar hydroxyl and ether functional groups. Many reports of heavy metal adsorption and desorption on calcium alginate have addressed the removal of these metals from water solutions. Very recently, An et al. reported that a fixed-bed column containing alginate beads in calcium from with the hydrogen from effectively removed copper ions from aqueous mixtures and exhibited reusability after 10 regeneration cycles [8].

In this study, calcium alginate was fixed on silica gel that was previously modified with aminopropyltrimethoxysilane-like N-[3 (trimethoxysilyl)propyl]diethylenetriamine (dien) to ensure its stable immobilization and reusability (Fig. 1), providing a calcium-alginate-modified dien-silica gel (CaAD). In preliminary tests, the adsorption kinetics and maximum adsorption capacity of CaAD were investigated using Cu^{2+} as a typical analyte heavy metal ion.

Next, CaAD was packed into a 1 mL microcolumn connected to a flow analytical system. This flow system, which consisted of the pump, sample injector, and detector, was used for the adsorption and desorption of heavy metal ions and for the concentration of trace metal ions in water samples. Flame atomic absorption spectrometry (FAAS) was employed for detection. Although FAAS exhibits much lower sensitivities for heavy metal ions than graphite furnace AAS or inductively coupled plasma mass spectrometry (ICP-MS), it benefits from the ease of use, very fast analytical time, and low capital and running costs.

To enhance detection levels, precipitation [9–11], liquid–liquid extraction [12–15], and solid-phase extraction (SPE) [16–19] have commonly been applied to analyte–matrix separation and metal ion concentration. In particular, SPE has proven effective because of its reusability and easy connection with the detector. Several online systems using precolumns packed with ion-exchange or chelating resins have also been reported [20–25]. Therefore, this study evaluated the performance of CaAD as a flow-type SPE column, along with its ability to adsorb and desorb heavy metal ions. Furthermore, the ability of CaAD-packed microcolumn to preconcentrate trace heavy metals in water solutions was determined, and its potential use for real water specimens such as ground water and river water samples, was assessed.
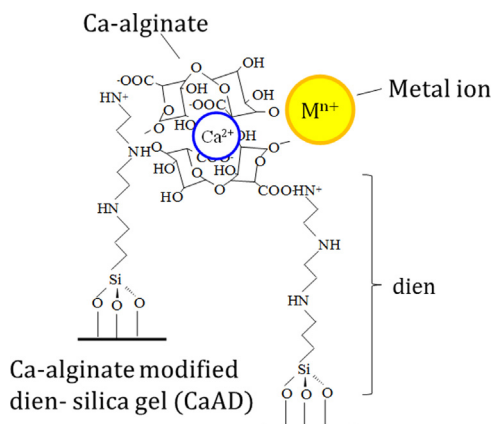

Fig. 1. Chemical structure showing the interactions between CaAD and a metal ion (M^{n+}).

2. Methods and materials

2.1. Reagents

All reagents were of analytical grade and were purchased from Wako Pure Chemical Industries, Ltd., (Osaka, Japan) unless mentioned otherwise. Dien was purchased from Gelest, Inc., (95%). Water used for reagent dissolution and sample dilution was obtained from an ASK-2DS ultrapure water system (Iwaki). Stock solutions of metal ions (0.1 M) were prepared by diluting the corresponding aqueous 1% HNO_3 AAS standard solutions (1000 mg L^{-1}) with an appropriate amount of water. Buffer solutions containing metal ions were prepared using 0.1 M HCl/NH_4Cl (pH 1–2.5) and 0.1 M CH_3COOH/CH_3COONH_4 (pH 3–5) in water.

2.2. Apparatus

pH measurements of test solutions were performed using pH meter electrodes (Horiba F-22). Metal ion analyte concentrations were determined using a Z-5300 flame atomic absorbance spectrophotometer (Hitachi). Functional groups in CaAD and its silica gel and dien–silica precursors were identified by Fourier transform infrared spectroscopy (FTIR, Nicolet Magna 560/Continuum). Nitrogen atoms in dien-silica and CaAD were identified by X-ray photoelectron spectroscopy (XPS) using a Shimadzu AXIS-NOVA instrument equipped with an Al Kα source operating at 15 kV and 10 mA. Sample surface morphologies were analyzed by scanning electron microscopy (SEM, Hitachi S-3000 N). Brunauer–Emmett–Teller (BET) surface areas of modified and unmodified silica particles were obtained using a NOVA® Surface Area Analyzer 2200e (Quantachrome Instruments, US). ICP-MS (PerkinElmer ICP-MS ELAN 600) was used to identify the metal concentrations obtained by this method. Devices used in the studied flow system are described in Section 2.6.

2.3. Synthesis of CaAD

The three-step synthesis of CaAD consisted of (1) dien modification of silica gel, (2) electrostatic binding of sodium alginate to the resulting dien-silica gel, and (3) calcium alginate formation on the modified silica gel by $CaCl_2$ addition (Fig. S1).

First, 200-mesh silica gel (Wakogel® C-200, 50 g) was stirred into a mixture of dien (22 mL) and 17 M CH_3COOH (10 mL), and water (100 mL) was added to the dispersion. The silica gel mixture was transferred into a 300 mL pear-shaped flask and heated to reflux for 24 h at 80 °C using a REN-1 series rotary evaporator (Asahi Techno Glass Co., Ltd., Japan). The dien-silica gel was collected on a 0.45 μm MF™ membrane filter (Merck Milipore, Ltd.) by suction filtration and dried for 24 h at 80 °C in a constant-temperature DN410I drying oven (Yamato Scientific Co., Ltd., Japan).

Second, dien-silica gel (12.5 g) was added to a 2% sodium alginate solution (125 mL). The mixture was transferred into a 300 mL pear-shaped flask and heated to 40 °C for 12 h using the rotary evaporator. The gel collected on membrane filter by suction filtration was dried for 24 h at 75 °C in a constant-temperature drying oven.

Third, alginate-dien-silica (12.5 g) was added to 200 mL of a 20% $CaCl_2$ solution, and the mixture was stirred for 1 h at room temperature. The obtained particles were washed using 1 M HNO_3 (50 mL) for 1 h at room temperature and were dried for 24 h at 75 °C.

2.4. Calcium alginate modification of silica gel

To evaluate effect of dien spacer coated on silica gel, calcium-alginate-modified silica gel (CaA) was obtained by direct coating without dien. Silica gel (12.5 g) was mixed into a 2% sodium