



Determining the selectivity of divalent metal cations for the carboxyl group of alginate hydrogel beads during competitive sorption



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HIGHLIGHTS

- The shape of the hydrogel bead was determined by the alginate concentration.
- Divalent metal stoichiometrically interacted with the carboxyl group of alginate.
- The sorption of Pb²⁺ was unaffected by pH.
- Selectivity followed the sequence of Pb²⁺ » Cu²⁺ » Ni²⁺ > Ca²⁺ > H⁺.
- HCl is an effective regenerant without the loss of the alginate polymer.

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ABSTRACT

To investigate the competitive sorption of divalent metal ions such as Ca²⁺, Cu²⁺, Ni²⁺, and Pb²⁺ on alginate hydrogel beads, batch and column tests were conducted. The concentration of carboxyl group was found to be limited in the preparation of spherical hydrogel beads. From kinetic test results, 80% of sorption was observed within 4 h, and equilibrium was attained in 48 h. According to the comparison of the total uptake and release, divalent metal ions were found to stoichiometrically interact with the carboxyl group in the alginate polymer chain. From the Langmuir equation, the maximum capacities of Pb²⁺, Cu²⁺, and Ni²⁺ were calculated to be 1.1, 0.48, and 0.13 mmol/g, respectively. The separation factor (α) values for $\alpha_{\text{Pb/Cu}}$, $\alpha_{\text{Pb/Ni}}$, and $\alpha_{\text{Cu/Ni}}$ were 14.0, 98.9, and 7.1, respectively. The sorption capacity of Pb²⁺ was not affected by the solution pH; however, the sorption capacities of Cu²⁺ and Ni²⁺ decreased with increasing solution pH, caused by competition with hydrogen. According to the result from the fixed column test, Pb²⁺ exhibited the highest affinity, followed by Cu²⁺ and Ni²⁺, which is in exact agreement with those of kinetic and isotherm tests. The sorbent could be regenerated using 4% HCl, and the regenerated sorbent exhibited 90% capacity upto 9 cycles.

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1. Introduction

Many industries such as ceramic, glass, and mining release large amounts of heavy metal into waste water; these heavy metals can accumulate in living organisms. Owing to the rapid development of these industries, the treatment of industrial wastewater has attracted considerable attention [1].

According to toxicology studies, most heavy metals are toxic or carcinogenic [2]. For instance, lead exposure causes the rapid deterioration of the brain and nervous system, kidney failure, and Alzheimer's disease [3]. Meanwhile, although copper is essential for human health, when present in excess, via accumulation and biomagnification in the food chain, it causes damage to the liver and kidneys as well as causes nausea, vomiting, and stomach cramps [4–6]. Electroplating, electronics, and metal cleaning industries probably discharge high amounts of nickel into wastewater [7], which can cause lung and kidney problems, gastrointestinal distress, and skin dermatitis [7,8].

For removing heavy metals from wastewater, various technologies such as chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation or flocculation, and flotation have

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been employed and investigated to determine the optimal operating conditions [9]. Among the abovementioned technologies, ion exchange (IX) is typically used because of advantages of simple operation and high removal efficiency [1]. Despite the effectiveness and widespread use of commercial chelating resins, they suffer from limitations such as high cost and non-biodegradability [10]. Considering these factors, the use of natural organic matter based on polysaccharides is especially attractive as it is an economical and eco-friendly medium for water treatment, for examples, alginate [11,12], cellulose [13,14], chitin [15,16], chitosan [17,18], and starch [19,20]. However, the use of cellulose, chitin, and starch showed lower metal sorption capacity and they need to be functionalized by chemical synthesis. In this regard, alginate is the suggested alternative with excellent metal sorption capacity, and high physical and chemical stability without any additional treatment [11,12]. Alginate, a linear copolymer of L-guluronate (G) and D-mannuronate (M), can be obtained from marine brown algae [21]. Owing to the presence of many carboxylate groups ($\text{COOH} \rightarrow \text{COO}^- + \text{H}^+$) in alginate, alginate has been typically used for the removal of heavy metals such as Pb^{2+} [10], Cu^{2+} [22], Ni^{2+} [8], Cd^{2+} [23], and Cr^{3+} [24] from solution in the form of bead, which can be typically explained by the egg box model [25]. Previous studies have shown that alginate can be easily prepared as granules called hydrogel beads, which serve as feasible sorbents with an effective removal efficiency. As a commercial cation exchanger, alginate beads consist of a matrix (D-mannuronic acid and L-guluronic acid), functional group containing a fixed ion (carboxyl group), and an exchangeable counter ion (typically Ca^{2+}).

Most studies have investigated the sorption capacity and mechanism between alginate and a single target contaminant. However, it is quite unusual for only one heavy metal to be present in natural water and wastewater [26,27]. In multi-component systems, each heavy metal will influence the sorption efficiency and behavior of the other as competing ions. Herein, Pb^{2+} , Cu^{2+} , and Ni^{2+} are selected as transition metals, and Ca^{2+} as the exchanging metal ion from alginate, and the sequence of selectivity is essential for understanding the sorption of metals for practical utility.

The overall objective of the present study aims to investigate the sorption behavior of Pb^{2+} , Cu^{2+} , Ni^{2+} , and Ca^{2+} in a multi-component solution using alginate hydrogel beads (ABs) prepared in the laboratory. The specific studies are to (1) characterize the physical properties, (2) determine the individual and multi-sorption capacity, (3) test the effect of solution pH, (4) investigate the breakthrough behavior of the cations in a multi-component system, and (5) test the reusability of multi-metal saturated ABs.

2. Materials and methods

2.1. Chemicals

Sodium alginate powder (average molecular weight of 155,000) was purchased from Sigma–Aldrich (USA). Reagent or analytical grade $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{N}_2\text{O}_9\text{Pb}$, and CaCl_2 were used to prepare single or multi-metal solutions without further purification. HCl and NaOH were obtained from SHOWA (Japan). All

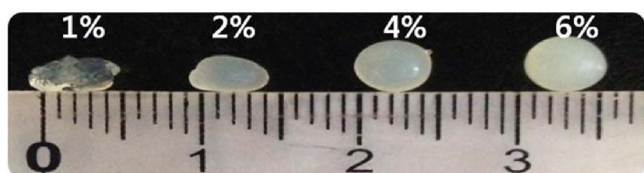


Fig. 1. Photograph of AB-Ca prepared with different initial concentrations of alginate solution.

solutions were prepared using ultrapure, deionized (DI, 18.2 M Ω) water.

2.2. Preparation of alginate hydrogel beads

First, 1%, 2%, 4%, and 6% (w/w) alginate solutions were prepared by dissolving a desired amount (g) of sodium alginate powder in 200 mg DI water and stirring at 100 rpm for 12 h at room temperature (21 °C); the alginate solutions turn translucent when the alginate is completely dissolved. By visual inspection, the viscosity of the solution was found to increase with increasing sodium alginate concentration. The dissolved alginate solution was added dropwise using a burette into 200 mL of a 4% (w/w) CaCl_2 solution, which was stirred at 150 rpm. Next, the prepared alginate hydrogel beads standing for AB-Ca was stirred for an additional 5 h to reach equilibrium between the carboxyl groups and Ca^{2+} . Finally, the AB-Ca was washed several times using DI. After AB-Ca was treated using HCl, it was referred to AB-Ca-H.

2.3. Kinetic test

To determine the sorption rates for the four different metals, we conducted batch kinetic tests using AB-Ca and AB-Ca-H. First, ~ 0.1 g of AB-Ca or AB-Ca-H was added into a glass bottle containing 200 mL of a 0.3 mM or 30 mg/L of a mixed metal solution of Cu^{2+} , Pb^{2+} , Ni^{2+} , and Ca^{2+} at an initial fixed pH of 5.0 ± 0.3 . Note that all alginate weight was obtained after dry oven after individual experiment. Next, the mixture was shaken at 150 rpm using a platform shaker (JSSI-100C). Finally, 2 mL of the sample was withdrawn at a

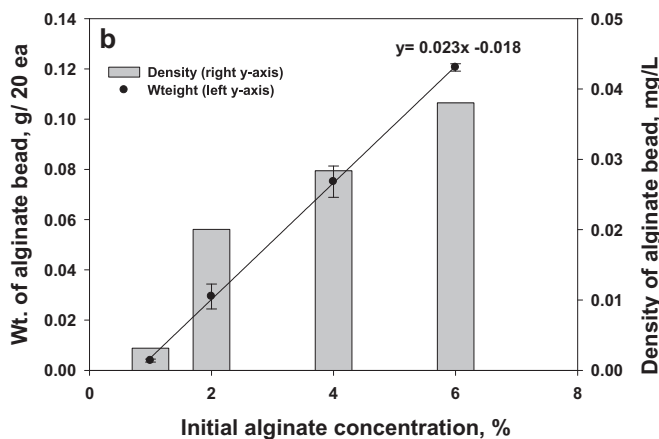
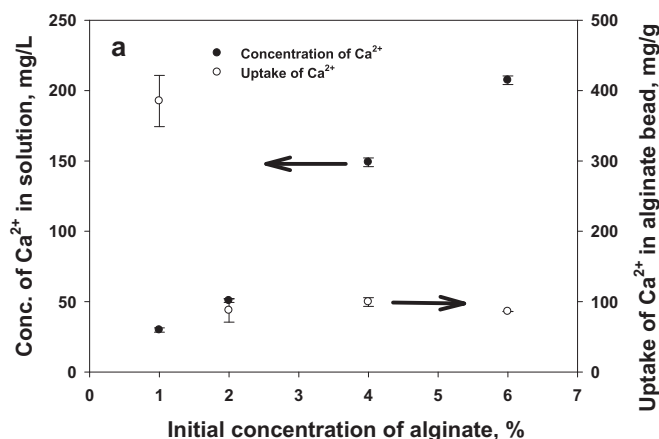


Fig. 2. Comparison of the chemical properties of AB-Ca on Ca^{2+} uptake, weight of alginate polymer, and density in terms of the initial alginate concentration.

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