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Sorption of Pb(II), Cd(II), and Ni(II) Toxic Metal Ions by Alginate-Bentonite

Teoh Wah Tzu, Takuma Tsuritani, Kazunori Sato

Department of Environmental Engineering, Nagaoka University of Technology, Nagaoka, Japan.
Email: teoh@vos.nagaokaut.ac.jp

ABSTRACT

The sorption of Pb(II), Cd(II), and Ni(II) toxic metal ions from aqueous solution by composite alginate-bentonite and alginate was investigated. The affinity and sorption capacity of the toxic metal ions for both type of samples were evaluated. The Langmuir maximum sorption capacity for each toxic metal ion increased for alginate-bentonite as compared to alginate. However, affinity for toxic metal ion remained unchanged for both alginate-bentonite and alginate in the order of Pb(II) > Cd(II) > Ni(II). Alginate-bentonite also shortens the duration required for complete sorption. Elementary mapping analysis depicts the gradient diffusion of toxic metal ions into the centre of alginate-bentonite beads indicated that sorption was contributed by surface adsorption and diffusion.

Keywords: Toxic Metals; Alginate; Bentonite; Wastewater

1. Introduction

The presence of toxic metal ions such as Pb(II), Cd(II), and Ni(II) in the aquatic environment is posing serious health threats to all livings. These toxic metals have long half-life and the toxicity is cumulated in human bodies for long duration. Industrialization and the growth of population is the main contributor in the release of these toxic pollutants. Since toxic metal ions in aquatic environment are of high mobility and able to spread to large area in short time, the removal of these toxic metal ions from aquatic environment is one of the challenges in science. Efforts to develop effective and efficient sorbent that fulfill both the cost as well as the performance are in great demand.

Mineral clay such as bentonite, has been found to be capable of removing toxic metal ions in wastewater through sorption process [1]. The abundance of this naturally occurred low cost bentonite makes it a strong candidate for toxic metal ions removal application. However, the use of powder sorbent such as bentonite introduces practicality problems since separation of solid and wastewater is difficult and costly [2]. This problem can be overcome by powder immobilization technique which retained the bentonite in suitable polymer support. Utilizing renewable bioresources such as alginate natural polysaccharide polymer to immobilize bentonite powder contribute to feasibility of developing low cost sorbent. Apart from the cost and availability, alginate is also known to have good affinity to adsorb divalent toxic metal ions [3-4] since it is rich in negatively charge functional group such as carboxylate group.

Studies of the alginate-bentonite were more focused on the application for drug delivery system and only very limited research focusing on toxic metal ions removal. In this study, the Pb(II), Cd(II), and Ni(II) sorption capacity as well as sorption rate of alginate bead and alginate-bentonite beads was evaluated using data which best-fitted with Langmuir isotherm model. The sorbents were characterized to understand the sorption mechanism.

2. Materials and Method

2.1. Materials

Sodium alginate (EP grade) and bentonite powder (EP grade) were used without any further purification process. 0.2 M calcium chloride ($CaCl_2$) solution was prepared from calcium chloride salt (GR grade). Pb(II), Cd(II) and Ni(II) solutions for sorption experiments were prepared from lead nitrate (purity over 99%), cadmium nitrate tetrahydrate (purity over 99%), and nickel nitrate hexahydrate (purity over 99%). The toxic metal ions concentration was determined by Inductively Coupled Plasma Atomic Emission Spectroscopy/ICP-AES (Shimadzu, ICP-7510), standard calibration was carried out using 100 mg/L Pb(II), 100 mg/L Cd(II), and 100 mg/L Ni(II) standard solutions that diluted to produce 1 mg/L, 10 mg/L and 100 mg/L solution. All the above mentioned chemicals were supplied by Nacalai Tesque.

2.2. Alginate-Bentonite Beads Preparation and Characterization

Alginate-bentonite beads were prepared by adding 4.0 g of bentonite into 100 ml of distilled water, the mixture was stirred for 0.5 hour and 1.5 g of sodium alginate was slowly added. The solution was stirred until a uniform creamy color alginate-bentonite solution was formed. To form alginate-bentonite beads with consistent diameter, the solution was dispensed into 0.2 M $CaCl_2$ solution from a syringe (1.2 mm in diameter) using an automated dispensing pump (As One, SPE-1) at fixed height. The beads were immersed in the $CaCl_2$ solution for 3 hours to enhance the polymerization process and subsequently rinsed with distilled water. The gel beads were dried at ambient atmosphere until constant weight was obtained. To prepare of alginate beads, the procedure is similar except bentonite was excluded in the preparation.

The morphology of the dried alginate and alginate-bentonite beads before and after sorption experiments were analyze using scanning electron microscope/SEM (Shimadzu, EPMA-2000). To investigate the diffusion of toxic metal ions into the alginate-bentonite beads, elemental mapping analysis was carried out on a cross-sectioned of post-sorption alginate-bentonite bead. All the samples were sputtered with gold prior to the SEM observation and elemental mapping analysis.

2.3. Sorption Experiment

Batch isotherm sorption experiments were conducted by placing 0.02 g of sorbent, *i.e.* alginate beads or alginate-bentonite bead in respective 50 ml glass bottle containing 30 ml of various concentration of Pb(II), Cd(II), and Ni(II) solution. The toxic metal ions concentration used in this experiment was 0.2 mM, 0.4 mM, 0.6 mM, 0.8 mM, 1.0 mM, 1.5 mM. The bottles were agitated at 100 rpm using a waterbath shaker (BT100, Yamato Scientific) for 24 hours; the temperature of the waterbath was set at 303 K. Final concentration of toxic metals ion after the sorption process was determined by ICP-AES.

To study the sorption against time, the samples were placed in 100 ml of 1 mM Pb(II), Cd(II), and Ni(II) solution respectively; 3 ml of the toxic metal ions solution was sampled at the specified interval, namely 0.5 hour (h), 1 h, 2 h, 3 h, 6 h, 12 h, and 24 h. The concentration of Pb(II), Cd(II), and Ni(II) at interval time was determined by ICP-AES.

3. Discussions

3.1. Characterization of the Beads

SEM was employed to determine the surface properties of the samples before and after the toxic metal ions sorption. The surface morphology of alginate and algi-

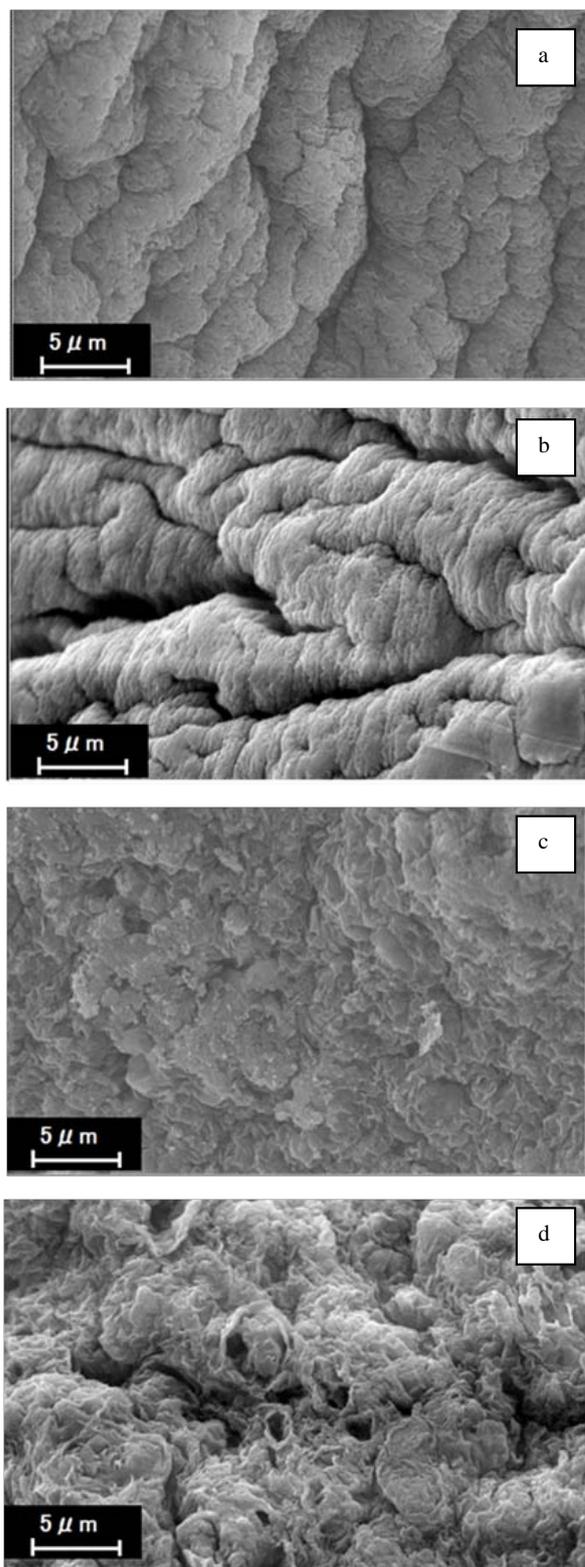nate-bentonite bead was given in **Figure 1**. SEM analysis

Figure 1. Surface morphology for: (a) alginate before sorption, (b) alginate beads after sorption, (c) alginate-bentonite before sorption, and (d) alginate-bentonite after sorption.

revealed that compact ridge-like structure was observed at the surface of alginate beads showed in **Figure 1a** which related to the high degree of dehydration during the drying process. After the toxic metal ions sorption process; the morphology of the alginate bead was not significantly change as showed in **Figure 1b**. The ridge-like folded structure may attributed by the repeating of swelling followed by the shrinking during the drying process. **Figure 1c** revealed that inclusion of bentonite in alginate changed the surface morphology of alginate. The ridge-like structure of alginate was not detected in alginate-bentonite. This morphology changes after bentonite inclusion can be explained by the cross-linking process of alginate. Alginate consists of linear monomers from mannuronic acid (M) and guluronic acid (G). These monomers formed different sequence of monomer blocks such as M blocks, G blocks and MG blocks. G monomers are responsible for the reaction with divalent metal cation cross-linker such as Ca(II) and subsequently bind the G blocks from M and GM blocks closely [5]. Bentonite which is uniformly suspended in alginate gel solution disrupted the sectional alginate chain formation during the cross-linking process and thus altered surface properties of alginate beads.

An examination of the SEM analysis on alginate- bentonite bead after sorption process showed in **Figure 1d**, indicated the presence of pores on the surface of alginate-bentonite bead. Bentonite is an expandable clay mineral consist mainly montmorillonite in a 3 layers structures. The basic structural unit is composed of 2 tetrahedrally coordinated sheets of silicon ion layer sandwiched the octahedrally coordinated sheet of aluminum ion layer as illustrated in **Figure 2**. The inter-layer spacing expands when it adsorbed water or metal ions [6]. During the absorption process, the alginate-bentonite beads swell and allowed the toxic metals ions to penetrate into the inner part of the beads. The Pb(II) and Cd(II) which had larger ionic radii compared to Ca(II) were bonded within
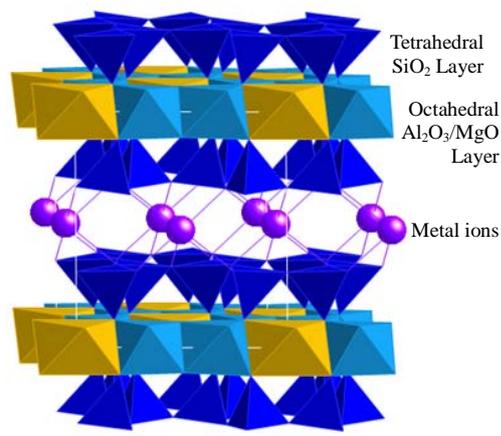
the inter layer spacing causing irreversible expansion of the inter-layers spacing. The pores observed can be attribute to the irreversible expansion of inter layer spacing of bentonite due to toxic metal ions sorption as well as structural changes due to drying process.

3.2. Sorption Isotherm

Isotherm data were fitted with the Langmuir and Freundlich model, the Langmuir model gives the best representation. The linear mathematical expression of Langmuir model is given as Equation (1):

$$C_e/q_e = (C_e/q_{max}) + [(1/b)*(1/q_{max})] \qquad (1)$$

where q_e (mmol/m^2) is the toxic metal sorption at the equilibrium state, C_e (mM) is the final concentration of toxic metal at equilibrium, b is the Langmuir constant that measure the affinity of the sorbent-sorbate, and q_{max} (mmol/m^2) is the theoretical maximal sorption capacity of the monolayer.

The data of isotherm sorption by alginate beads and alginate-bentonite beads were fitted with Langmuir model and tabulated in **Table 1** and **Table 2** respectively. According to the Langmuir affinity constant, b, the affinity of the toxic metals for alginate beads is as followed: Pb(II) > Cd(II) > Ni(II). Inclusion of bentonite in alginate beads did not change the preferential state. This outcome is consistent with the findings from other researchers, the alginate affinity for toxic metal ions was found to follow the order of: Pb(II)) > Cd(II) > Cu(II) [7]; while affinity of bentonite for toxic metals was followed the order of: Pb(II) > Cd(II) > Cu(II) [2], both of the samples were found to have similar affinity and therefore inclusion of bentonite did not alter the affinity order.

Figure 2 Basic structure of montmorillonite.

Tetrahedral SiO$_2$ Layer

Octahedral Al$_2$O$_3$/MgO Layer

Metal ions

Table 1. Coefficients of Langmuir Isotherm for Alginate.

Metal ion	Alginate		
	$qmax$	b	R^2
Pb(II)	2.5	38.4	0.9933
Cd(II)	1.6	10.0	0.9981
Ni(II)	1.2	3.3	0.9979

Table 2. Coefficients of Langmuir Isotherm for Alginate-bentonite.

Metal ion	Alginate-bentonite		
	$qmax$	b	R^2
Pb(II)	5.8	46.4	0.9913
Cd(II)	4.2	14.2	0.9970
Ni(II)	3.4	5.5	0.9995

Inclusion of bentonite in alginate beads significantly improved the sorption capacity (q_{max}) for each toxic metal. The calculated maximum sorption capacity of alginate-bentonite beads for Pb(II), Cd(II), and Ni(II) is 5.8 mmol/m^2, 4.2 mmol/m^2, and 3.4 mmol/m^2 respectively; this values are consistently higher compared to alginate beads, namely 2.5 mmol/m^2, 1.6 mmol/m^2, and 1.2 mmol/m^2. Alginate-bentonite beads are consistently showing better sorption performance regardless of the type of toxic metals.

Both alginate and bentonite are hydrophilic materials with negatively charge functional groups that attract the cationic metals species leading to sorption. For bentonite, other than having the cation exchange capacity at the outer surface and edges of its octahedral and tetrahedral sheet, it also possessed excellent sorption properties which is available within its interlayer space. This contributed to higher sorption capacity for the alginate-bentonite beads.

3.3. Toxic Metal Sorption Against Time

Figure 3 showed the sorption amount (q_t) of Ni(II), Cd(II) and Pb(II) up to 24 hours. The sorption process was rapid for the first 3 hours for both alginate and alginate-bentonite. However, alginate-bentonite consistently showing higher sorption amount for Ni(II), Cd(II), and Pb(II). Furthermore, alginate-bentonite is able to reach sorption equilibrium in shorter duration particularly for Pb(II). It is obvious that alginate-bentonite is both effective and efficient in toxic metals sorption when compared to alginate.

Figure 3c showed that Pb(II) sorption by alginate-bentonite reached saturation at 12 hours whereas Pb(II) sorption by alginate showing no sign of saturation as yet at 24 hours. For alginate-bentonite, the first sharpest increased in Pb(II) sorption (0.5 hour to 3 hours) was attributed to the sorption of Pb(II) on the surface of alginate-bentonite beads. The second portion of the plot (3 hours to 12 hours) indicating gradual sorption stage, where diffusion is rate limiting. The last portion (12 hour onward) attributed to the final equilibrium stage. In the case of alginate beads, the second stage which attributed by diffusion process was much longer (3 hours onward without showing saturation at 24 hours) compared to alginate-bentonite.

The shorter duration time required by alginate-bentonite to achieve sorption saturation is attributed by the inclusion of bentonite that is easily swelled when contact with liquid, this expansion of inter-layer spacing within the cross-linked alginate polymer chain makes the beads swell faster and to a larger extent. Hence the average opening between the alginate chains will be greater. The Pb(II) will exhibit a greater intra-gel diffusivity if the openings between the chains are greater [5].

To elucidate the occurrence of Pb(II) diffusion into the alginate-bentonite beads, element mapping analysis was performed on a cross-sectioned alginate-bentonite bead shown in **Figure 4**. The mapping analysis showed that Pb(II) was detected as far as 200 μm from the edge of the bead, the intensity of Pb(II) distribution was gradually decreased toward the centre of the beads indicating diffusion of Pb(II) into the alginate-bentonite bead.

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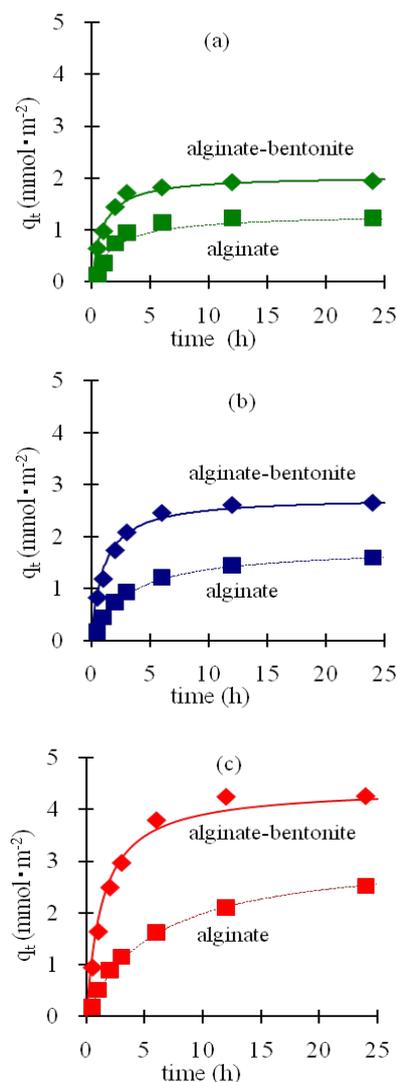

Figure 3. Sorption of alginate-bentonite beads and alginate beads: (a) Ni(II), (b) Cd(II), and (c) Pb(II).
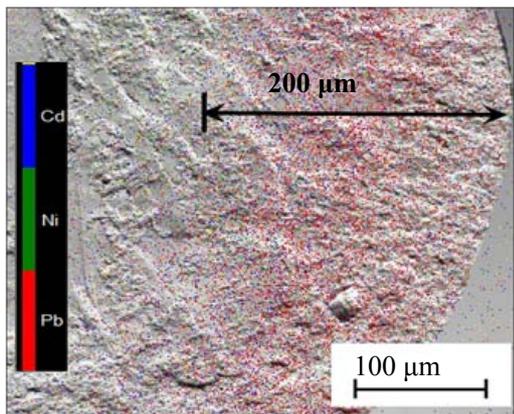
Figure 4. Elemental mapping analysis at the cross-sectioned of post-sorption alginate-bentonite bead.

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4. Conclusion

Alginate-bentonite beads had evidently shown effectiveness and efficiency for the sorption of Pb(II), Cd(II) and Ni(II) toxic metals compared to alginate. The toxic metals affinity is in the order of Pb(II) > Cd(II) > Ni(II). Langmuir sorption capacity coefficient shows that inclusion of bentonite in alginate increased the surface active sites for toxic metals sorption. Mapping analysis confirmed the diffusion of Pb(II) into the beads, attributed by the expandable inter-layer spacing of bentonite that enlarged the openings between the chains of alginate polymer. Combination of this low cost bentonite and alginate sorbents had proven to show synergy effects in the sorption of toxic metals from aquatic environment.

5. Acknowledgements

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