2012 International Congress on Informatics, Environment, Energy and Applications-IEEA 2012
IPCSIT vol.38 (2012) © (2012) IACSIT Press, Singapore

Lead Ion Uptake By Sodium Alginate And Calcium Alginate Film: A Comparison Study

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Abstract. Lead ion (Pb(II)) uptake from aqueous solution by two different alginate compounds was investigated. Sodium alginate (Na-Alg) and calcium alginate (Ca-Alg) films were successfully fabricated from the commercially available sodium alginate powder. The Pb(II) uptake performance by Na-Alg and Ca-Alg films was evaluated against time in a 10 mM Pb(II) solution's batch sorption system. Ca-Alg film was consistently showing a better Pb(II) uptake performance as compared to Na-Alg film within the investigated duration. Further evaluation on Ca-Alg film was carried out at lower Pb(II) concentrations, i.e. 1 mM and 0.1 mM, the Ca-Alg film showed the best performance in 0.1 mM Pb(II) solution at a uptake rate higher than 98%. The Pb(II) uptake performance of Ca-Alg film was also compared with that of the conventionally fabricated Ca-Alg beads. This result indicates that with the same amount of Ca-Alg used, the film shows approximately three time better Pb(II) uptake performance compared to the beads. The results reported herein indicates that Ca-Alg compound is an effective and efficient biosorbent, furthermore the Pb(II) uptake performance is influenced by the sample fabrication method as well, i.e. film versus bead, which contributed to the overall surface area.

Keywords: alginate; films; lead uptake; sorption

1. Introduction

Heavy metal ions are well-known toxic and carcinogenic agents, these metal residues in the environment pose threats not only to human health, but also to the environment due to the bio persistence which lead to serious poisoning effects for aquatic ecosystem[1]. Heavy metals are widely used in electroplating, painting, surface treatment, printed circuit board manufacture, etc. Several methods have been suggested for the removal of toxic metals from aqueous solution, such as chemical precipitation, evaporation, ion-exchange, adsorption, cementation, electrolysis and reverse osmosis. Due to the specific nature of industrial effluents (low pH, variety of cations and anions, oil emulsions, particles, etc.) the effectiveness of removal has proven to be a very difficult and costly process[2]. Although adsorption is the most effective and widely used method[3], commercial chelating resins, one of the mostly utilized sorbents, are still an expensive material and most are non-biodegradable. Hence, research is focused on the preparation of novel, cheap and more effective sorbents. One of the promising materials that offer such advantages is alginate, a natural anionic polymer.

Na-Alg is a linear copolymer of guluronate (G) and mannuronate (M), which constitutes 10–40% of the dry weight of all species of brown algae [4-6]. The capability of this copolymer to form stable biodegradable gels in the presence of divalent cations has been known and studied extensively [7, 8]. These gelation properties can be attributed to the simultaneous binding of the divalent cations such as Ca(II) to different chains of guluronate blocks (G-blocks). As a result of their configuration, these chains form electronegative

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cavities, capable of holding the cations via ionic interactions, resulting in cross-linking of the chains into a structure resembling an “egg box” [7]. Conventionally, Ca-Alg is widely prepared in beads form, the heavy metal ions uptake mechanism is by ion-exchange between Ca(II) of the beads and the heavy metal ions in the aqueous solution.

In this studies, the Pb(II) uptake performance was compared between Na-Alg and Ca-Alg, the formal is the commercially available starting materials, the later is produced by cross-linking Ca(II) to the Na-Alg. It is worth noted that, the commercial Na-Alg is in powder form and soluble in water, thus this study developed a method to form Na-Alg into bulk films which are more practical for heavy metal ions removal application. Investigation on Pb(II) uptake performance between Ca-Alg film and conventionally produces Ca-Alg beads was also conducted.

2. Materials and methods

2.1. Samples preparation

Extra pure reagent sodium alginate powder (Nacalai Tesque) is used for this study. To prepare a 2%w/w Na-Alg solution, 2 g of Na-Alg was dissolved in 100ml of water under vigorous agitation. To fabricate Na-Alg films, 8 ml of the above solution was spread into a frame of 8.5 cm X 5.5 cm, and dry the film for 24 hours at 50ºC, the dried films is approximately 0.2 g. For Ca-Alg films, the sodium films were soaked in a 0.2M calcium chloride (Nacalai Tesque) solution for 3 hours. The films were rinsed with ion exchange water to remove any excess calcium chloride on the film and dried for 12 hours at 50º C. To produce Ca-Alg beads, 8 ml of the 2%w/w alginate solution was measured with a syringe and slowly drops into a 0.2M calcium chloride solution under vigorous agitation for 3 hours. The beads were rinsed with ion exchange water and dried the beads for 12 hours at 50º C.

2.2. Pb(II) uptake experimental procedures.

Pb(II) solutions (10mM, 1mM, 0.1mM) was prepared using analytical reagent grade $Pb(NO_3)_2$ (Nacalai Tesque). Batch sorption experiment were conducted by placing either the Na-Alg film, Ca-Alg film, or Ca-Alg beads into a wide mouth beaker which contained 100 ml of Pb(II) solution. The samples were left for at least 6 hours. Concentrations of Pb(II) were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (Shimadzu, ICP-7510). Each experiment was at least duplicated under identical conditions.

3. Results and Discussion.

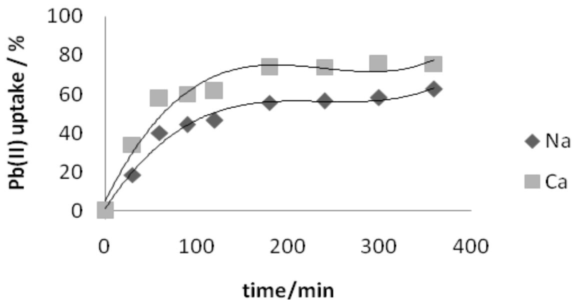

Figure 1 Lead uptake percentage against time in minutes.

The concentration of alginate of 2%w/w used in this study was chosen among three different concentrations, i.e. 1%w/w, 2%w/w and 2.5 %w/w, due to the relatively easy processing. Figure 1 showed the Pb(II) uptake performance between Na-Alg film and Ca-Alg film. This experiment was carried out for 6 hours in a 10mM Pb(II) solution. Ca-Alg film was showing better Pb(II) uptake performance consistently within the investigation duration as compared to Na-Alg film. The uptake of Pb(II) for both samples reached plateau after 3 hours.

The better Pb(II) uptake performance shown by Ca-Alg film might be explained by the formation of “egg-box” which described in the earlier section. For Ca-Alg film, the “egg-box” structure was established by the cross-linking process using Ca(II) solution, the schematic structure of Ca-Alg is shown in Figure 2.

Therefore, Ca(II) which are located at the cavity of the "egg-box" are readily substituted with Pb(II) which have higher affinity towards alginate [9-11]. As for Na-Alg film, it is purely consist of random alginate monomers without any established structure, hence Pb(II) which has the largest ionic radii compared to Ca(II) and Na(I) cannot easily bonded with the alginate monomers.

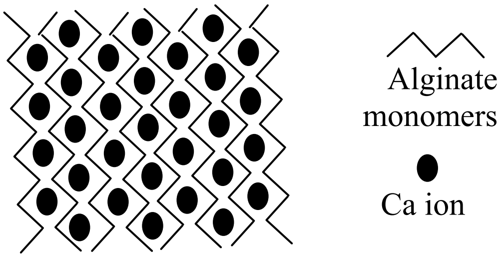

Figure 2 Schematic diagram of Ca-Alg structure

Figure 3 showed the results of Pb(II) uptake performance by Ca-Alg film in different Pb(II) concentration solutions. Due to the high concentration of Pb(II) in 10 mM solution, the initial Pb(II) uptake performance, i.e. before 100 min, was the highest. However, in the overall Pb(II) uptake performance, Cal-Alg film showed the best result in 0.1 mM Pb(II) solution. The Pb(II) uptake performance in 1 mM and 10 mM Pb(II) solution are relatively similar. The result indicated that Ca-Alg film has good uptake capability in low concentration Pb(II) solution, in this study, it is capable of removing more than 98% of the Pb(II) from 0.1 mM Pb(II) solution.

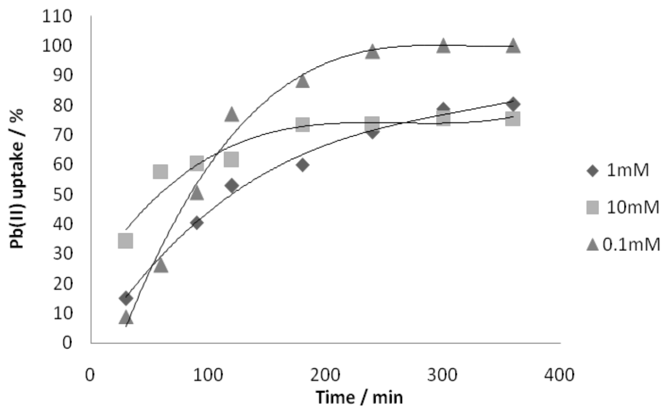

Figure 3 Lead uptake against time for Ca-Alg films in Pb(II) solutions with different concentration

Figure 4 showed Pb(II) uptake comparison between Ca-Alg film and Ca-Alg beads, which is the conventional method of Ca-Alg preparation. The study was carried out in 10 mM Pb(II) solution. The result indicated that film-type Ca-Alg showed higher Pb(II) uptake percentage, it is about three times higher that the Ca-Alg bead. This is contributed by the bulk surface area of film sample, which is much larger than the beads sample at the same weight used in this experiment, therefore providing abundance of active sites to bind with Pb(II).

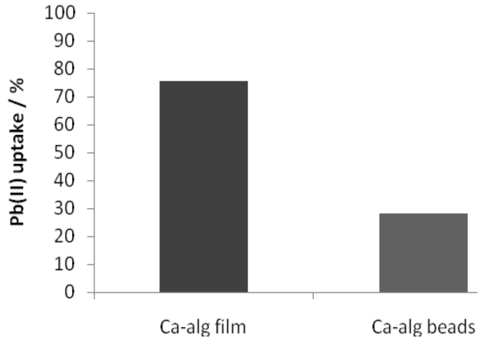

Figure 4. Lead uptake percentage for calcium alginate films and beads after 360 minutes

4. Conclusions

The present study established that both Ca-Alg film and Na-Alg film are capable of Pb(II) uptake with Ca-Alg film showing better Pb(II) uptake performance. The Pb(II) uptake performance between Ca-alg film and Ca-Alg beads indicated that effective surface area which exposed to the Pb(II) solution are essential to enhance the Pb(II) uptake performance.

5. Acknowledgements

This work was supported by the JASSO program of the government of Japan and CONACYT from the government of México.

6. References

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