Evaluation of Pb (II) Removal from Water Using Sodium Alginate/Hydroxypropyl Cellulose Beads

Rodel Guerrero*, Catherine Acibar, Christine Marie Alarde, Jane Maslog and Christine Joy Pacilan

Department of Chemical Engineering and Technology, MSU-Iligan Institute of Technology, Iligan City, Philippines

Abstract. This study examined the removal of Pb^{2+} ions from aqueous solution with two different lead concentrations using a hydrogel-forming polymer based on hydroxypropyl cellulose (HPC) and sodium alginate (SA). The feasibility of the adsorption behavior of SA/HPC beads has been investigated with three varying ratios of 50:50, 75:25 and 100:0 under a stir condition. The adsorption experiments were done to determine the effects of contact time, lead concentration and SA-HPC ratio to the adsorption capacity of SA-HPC hydrogel beads. The results showed that the ratio 75:25 showed higher adsorption capacity compared to 100:0 and 50:50. It showcased 47.72 mg/g adsorption capacity and 95.45% adsorption percentage after three hours of contact time. The adsorption kinetic model indicated that the adsorption of Pb^{2+} ions onto the beads followed a pseudo-second order kinetic equation. This means that the adsorption mechanism shows a chemisorption process and its sole rate-limiting step is intraparticle diffusion.

Introduction

Landfill leachate is a dangerous liquid, because this black liquid consists of organic and inorganic compounds which can be very toxic to the environment and health because they can also contain notable amounts of heavy metals. In any case, the long-term impacts of landfill are predictably critical. Leachate pollutes the groundwater, and this represents health risks since groundwater is one of the sources of water for human consumption [1].

In connection to the arising problem, many researches and innovative processes have been introduced for the removal and reduction of lead in water. In general, simplicity and cost-effectiveness are the key factors in selecting the most suitable treatment for contaminated water [2]. As such, biosorption is a method in the remediation of contaminated water. It is a process that is commonly used in water purification, since it is effective, comparatively easier for the removal of heavy metals from water, and non-toxic, which is easy to design and implement [3]. Some sorbent materials used in this technique are activated carbon, silica gel, activated alumina, ion exchange fibers and molecular sieves zeolites. However, these sorbents have disadvantages, such as low speed of desorption and poor regeneration performance [4].

Compared to conventional sorbent materials mentioned, hydrogel-based sorbents have been discovered to exhibit very high sorption capacities for removing heavy metals such as lead from water. Hydrogels, which are a class of non-toxic natural polymeric materials and by nature, are highly swollen solids having three-dimensional network

structure and cross-linking characteristics. Chemical and physical cross-linking of hydrophilic polymers are typical approaches to form hydrogels. Alginate, for example, is typically used in the synthesis of these hydrogels. This is a family of linear, non-branched copolymers containing blocks of (1,4)-linked β -D-mannuronate (M) and α -L-guluronate (G) residues. This hydrophilic polysaccharide is renewable, biodegradable and nontoxic. The guluronic acid of sodium alginate can be cross-linked with divalent cations (such as Ca^{2+}) to obtain an egg-box structure, forming a gel [5]. This type of hydrogel has been previously used in the removal of metal ions in water [6]. A study by Pandey et. al. last 2007 made use of calcium alginate for the adsorption of Cr(VI), Pb(II), and Cu(II). Using this alginate as adsorbent, Cr(VI) was removed 86% from the solution, while Pb(II) and Cu(II) removal efficiencies were around 57% and 64%, respectively. This reduction maybe due to the limitations in the binding and movement of metal ions or either affinity of sites for metal or binding sites on relevant biopolymer.

Because of this, with an aim to improve the properties of the sorbents for practical applications, cellulose derivatives may also be used. They exhibit properties for the required application since it is the most abundant type of biopolymer [7]. When combined, alginate and cellulose derivatives' functional groups will likely increase the adsorption sites and metal adsorption selectivity. Various studies have already dwell on the use of mixed or composite materials for adsorption of heavy metals [8]. Romera et.al and Wan Maznah et. al. further suggested that the functional groups that are effective at attracting heavy metal ions are mainly carboxyl, hydroxyl, sulphate, phosphate, amino, amido and phenolic groups. However,

* Corresponding author: rodel.guerrero@g.msuiit.edu.ph

the use of alginate and a cellulose derivative, specifically hydroxypropyl cellulose, has never been done for this adsorption process. These materials containing primarily of carboxyl and hydroxyl groups suggest that they are highly qualified in the adsorption of heavy metals from aqueous solutions.

Thus, it is the aim of this study to make use of hydrogel beads based on sodium alginate (SA) blended with a cellulose derivative, particularly hydroxypropyl cellulose (HPC) for the removal of a heavy metal ion, specifically lead ions, from an aqueous solution. Effect of contact time and initial metal ion concentration were studied. Finally, kinetics of the adsorption process are carried out to explain this particular adsorption process.

Materials and Methods

Materials

The materials used include sodium alginate, hydroxypropyl cellulose, calcium chloride, and lead chloride. All other reagents used were of analytical grade.

Preparation of SA/HPC Hydrogel Beads

Different solutions of 2 wt% of the SA/HPC were prepared by dissolving SA to HPC ratios of 100:0, 75:25, and 50:50 in distilled water. These solutions were stirred at 25°C for 10-20 minutes until solution is homogenous. Through ionotropic gelation, SA/HPC solutions were then extruded through a syringe wherein droplets were cured into a 5 wt% CaCl₂ solution for 10-15 minutes. After this process, the beads were washed and filtered. Then the samples were dried in an oven at 45°C within 5 hours.

Removal of lead (II) ions from water

The adsorbent material, SA/HPC beads, (0.1 g) were placed into a volumetric flask containing 25 mL lead chloride solution of concentrations 100 and 200 ppm, shown in Table 1. The beads and the lead chloride solution were stirred with a magnetic stirring bar at a rate of 150 rpm. The amount of Pb²⁺ left in the solution after each contact time was measured to determine the adsorption capacity of the SA/HPC hydrogel beads with the use of Atomic Absorption Spectroscopy (AAS). Adsorption capacity (mg/g), *q*, was then calculated using:

$$q = [(C_0 - C_e)/m] \times V \quad (1)$$

where: *C*₀ and *C*_e are the concentration of Pb²⁺ before and after the adsorption process; *m* is the mass of hydrogel; and *V* represents the volume of the solution in liters

Table 1. Experimental Design.

Concent ration of Lead (mg/L)	Different Ratios of SA-HPC		
	60 mins.	120 mins.	180 mins.
100	100:0	100:0	100:0
	75:25	75:25	75:25
	50:50	50:50	50:50
200	100:0	100:0	100:0
	75:25	75:25	75:25
	50:50	50:50	50:50

Results and Discussion

Adsorption Capacity

The adsorption capacities of the beads with varying ratios at a given time were measured with the data based on the amount of lead concentration left in the solution after the adsorption.

a)

b)

Fig. 1. Adsorption capacities of varying ratios of SA/HPC hydrogel beads with respect to increasing contact time for Pb²⁺ initial concentration of a) 100 ppm and b) 200 ppm.

As observed, the adsorption capacities of all ratios in both concentrations increase as time increases. The adsorbent beads were dosed in the lead solution at a longer time, thus it has the capacity to adsorb greater amount of lead ions. This reflects the ability of HPC in adsorbing lead ions in addition to the functional groups of the SA in the hydrogel, as well as increase in the adsorption capacity of hydrogel as a whole. However, this property still depends on the ratio between the two materials used.

Based on Fig. 1, the beads containing 100% SA has an adsorptive capacity smaller than that of 75:25, because SA has lesser active sites compared to the combination of SA and HPC. In addition, according to the results calculated in adsorption capacity of each ratio, it showed that the adsorptive capacity at ratio 75:25 is larger compared to 100:0 and 50:50. This is primarily because of the presence of HPC, which therefore increased the number of binding sites compared to what a pure SA can offer. However, when HPC is increased to 50:50 ratio, the hydrogel becomes more complex, which increases the likeliness or possibility of competition between the binding of metal ions to the material's surface and the hydrogen bonding happening between SA and HPC.

Shown in Table 2 are the percentage removal of Pb^{2+} ions from aqueous solutions with variation in SA/HPC ratio.

Table 2. Percent Pb^{2+} removal of the SA/HPC beads for 100 and 200 ppm initial concentrations.

Lead Concentration mg/L	Ratio	Contact time, min	Pb^{2+} Removal, %
100	100:0	60	61.3
		120	82.6
		180	89.0
	75:25	60	73.0
		120	83.9
		180	92.1
	50:50	60	68.2
		120	84.1
		180	89.2
200	100:0	60	62.6
		120	72.8
		180	86.4
	75:25	60	70.8
		120	82.5
		180	95.5
	50:50	60	66.1
		120	78.0
		180	87.3

Adsorption Kinetics

Fitting the experimental data into different kinetic models enables to study the adsorption rate, model the process and predict information about adsorbent/adsorbate interaction (physisorption or chemisorption) [10]. In this study, three different models were used such as the first-order, pseudo-second order and intraparticle diffusion.

First Order and Pseudo-Second Order Equations

First order (FO) reaction of kinetic is the reaction that proceeds at a rate that is dependent linearly on one reactant concentration while pseudo-second order (PSO) of reaction is the kind of adsorption process wherein the chemical reaction seems significant in the rate-controlling step and it best describes and provides the best correlation of the experimental data and if the adsorption mechanism is chemically rate controlling. With respect to this study, Table 4 shows the values of r^2 for varying ratios of SA and HPC.

Table 4. r^2 Values of FO and PSO Reaction Kinetic Models for 100:0, 75:25, and 50:50 SA/HPC beads for 100 and 200ppm initial concentrations.

SA-HPC Ratio	100 ppm		200 ppm	
	FO	PSO	FO	PSO
100:0	0.763	0.953	0.892	0.989
75:25	0.728	0.997	0.990	0.997
50:50	0.841	0.982	0.926	0.988

As calculated, the r^2 is higher for all variations both in 100 ppm and 200 ppm under the PSO reaction model. This implies that the kinetic model of the study inclines to that of chemisorption mechanism, which plays an important role in the adsorption of the lead ions to the beads. This represents the binding of the lead ions to the surface of the SA/HPC bead. The mechanism involved in the adsorption of lead ions may be a result of the ion exchange and complexation.

Intraparticle Diffusion

The intraparticle diffusion model describes the adsorption process in which the rate of adsorption depends on the speed of how the adsorbate diffuses towards the adsorbent.

Table 5. r^2 value of Intraparticle Diffusion for varying ratio of SA and HPC

Intraparticle Diffusion SA/HPC Ratio	100 ppm			200 ppm		
	r^2	K_{id}	Intercept	r^2	K_{id}	Intercept
100:0	0.84	0.83	11.0	0.95	1.47	24.3
75:25	0.94	0.95	10.5	0.98	2.87	8.54
50:50	0.91	0.81	12.0	0.86	1.74	18.8

As shown in the table above, IPD model shows high values of intercepts for all SA/HPC variations and both lead ions concentrations used. This means that the adsorption process showcased fast intraparticle diffusion or intraparticle mass transfer of the adsorbate to the adsorbent. Furthermore, from the data above, the intraparticle diffusion is the major rate-limiting step in controlling the rate of lead ions removal from the aqueous solution.

Therefore, the mechanism of heavy metal adsorption process in this study can be described as follows: the lead ions are transferred from the solution to the adsorbent surface, which contains the various functional groups that act as active binding sites. This is where chemisorption happens as described by the PSO kinetic model. Also, this first step is mostly affected by metal ion concentration. Next, the second step includes transport, i.e. diffusion of metal ions into pores of adsorbent. Finally, the last stage is related to the diffusion of the metal ions on the internal surface of the material and is considered to be a rate-limiting step as presented by the intraparticle diffusion result [11].

Conclusions

In conclusion, the research done was successful in removing lead ions in a simulation of a contaminated water by synthesizing SA and HPC into hydrogel beads with varying ratios of, 50:50, 75:25 and 100:0. Varying the concentrations of SA and HPC greatly influences the adsorption capacity of the produced beads. As observed in the results of this study, the ratio 75:25 resulted to higher adsorption capacity compared to 100:0 and 50:50. Adsorption of lead ions onto the beads showed that the adsorption mechanism is a pseudo-second order kinetic model, which means that the process follows chemisorption. Also, it was found out that the sole rate-controlling step of the process is the intraparticle diffusion.

References

1. Z. Youca, Pollution Control Technology for Leachate from Municipal Waste. **1-30**, (2018)
2. M.A. Barakat, Arabian Journal of Chemistry, **4(4)** (2011)
3. S. Qaiser, A.R. Saleemi, M. Umar, Journal of Hazard Matter, **166(2-3)** (2009)
4. K.Y. Zhao, Y.J. Zhao, Y. Li, L. Liu, X. Zhang, J. Li, X. Wang, Sci. China Tech. Sci, **60** (2017)
5. Y. Wu, H. Qi, C. Shi, R. Ma, S. Liu, Z. Huang, The Royal Society of Chemistry, **7** (2017)
6. S. Kwiatkowska-Marks, M. Wojcik, Separation Science and Technology, **49(14)** (2014)
7. L.A. Casalmé, P.J. Nalzaró, R.J. Osabel, *thesis* (2016)
8. V. Gopalakannan, N. Viswanathan, Ind. Eng. Chem. Res., **54** (2015)
9. K.Y. Lee, D.J. Mooney, Prog. Polymer Science, **37(1)** (2012)
10. T. Alslaibi, I. Abustan, M. Azmier, A. Foul, Desalination and Water Treatment, **52(40-42)** (2013)
11. A. Petrovic, M. Simonic, Int. J. Environ. Sci. Technol. **13(1761-1780)** (2016)
12. A. Pandey, D. Bera, A. Shukla, L. Ray, Chemical Speciation and Bioavailability. **19(17-24)** (2007)
13. E. Romera, F. Gonzalez, A. Ballester, ML. Blásquez, JA. Muñoz. Bioresour. Technol. **98(3334-3353)** (2006)
14. W. Wan Maznah, A. Al-Fawwaz, M. Surif. J. Environ. Sci. **24(1386-1393)** (2012)