Removal of Mn(VII) from Industrial Wastewater by using Alginate-Poly(vinyl) alcohol as Absorbent

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Abstract. An alternative heavy metal treatment method using a low cost absorbent for aqueous medium was studied. Calcium alginate was used as the absorbent together with Poly(vinyl)alcohol for manganese, Mn(VII) extraction from industrial wastewater. The prepared Alginate and Alginate/PVA beads were characterized and the performance of Mn(VII) extraction process by the beads was evaluated in terms of the Mn(VII) extraction efficiency. The adsorption experiments indicate that the amount of adsorbed Mn(VII) improved in addition of PVA with percentages removal up to 65% from the industrial wastewater. As a result, the extraction process proposed was suggested to be simple, safe, and environment-friendly for treating an industrial wastewater. However, further study need to be carried out to gain the concrete information and evidence.

1. Introduction
The industrial effluents from varies manufacturing industries may contributes to the water pollution in the world. Unlike organic contaminates, heavy metals are not biodegradable and known to be toxic or carcinogenic [1]. Manganese (Mn) and its compounds caused a problem in taste and odour of water and toxicity to aquatic lives. Biosorption and accumulation of Mn induced parkinsonism to human [2]. In Malaysia, the contamination of Mn rivers exceeding standard limits and become the main problem to drinking water treatment plants [3]. The main intention for the water treatment is to eliminate any potential threat to our biodiversity system.

To prevent the adverse effect of the heavy metals in wastewater, exploring innovative need to be widely open for a betterment of our global freshwater resources. Several techniques have been applied to remove the heavy metal elements including ion-exchange and water softening, adsorption by natural low-
cost adsorbents, ionic liquid extraction, and so forth [4–9]. Among all approaches proposed, bio-sorption is one of the most popular methods and is currently considered as an effective and efficient method, especially for waste water treatment. Bio-sorption in metal removal study can be defined as the ability of biological materials to accumulate the heavy metals from waste water through metabolically mediated or physico-chemical pathways of uptake [10]. Bio-sorption can be an option to remove metal in aqueous solution by introducing varies solid support materials. The modified sorbents such as solvent impregnated resins, polymeric/compound microcapsules, chitosan beads, activated carbon, silica gel, and polymeric sorbents and the magnetic nanoparticles among the most sorbent materials which have received much attention for various types of metal extraction [11–14]. Most of the methods are based on the modification of physisorption and chemisorption mechanism. However, chemical methods provide high stability and reusability [14].

It is known that sodium alginates of algal cell walls play an important role in metal binding [15]. Sodium alginate is a linear polysaccharide composed of β-D-mannuronic (M) and α-L-guluronic acid (G) residues arranged in a nonregular and blockwise sequence along the chain, obtained from brown algae or seaweeds [16]. Sodium alginate use for metal removal by following the principal of bio-sorption and has been found to be superior choice than other commercial techniques [17]. However, the physicochemical properties of alginate need to be improved for example by polymer blends method. Poly(vinyl alcohol) (PVA) is a synthetic, nontoxic, high strength polymer for enzyme and cell immobilization, and possess better mechanical properties [18]. PVA-Alginate blends are physically stronger and more durable than the alginate ones, although both gels possess water contents extremely higher than their polymer contents [19].

The present work reported on the fabrication and characterization of PVA-Alginate beads in mixed solution of acid boric-calcium chloride. Then the performance of Mn(VII) extraction from industrial wastewater was evaluate in terms of Mn(VII) removal efficiency, the effect of contact time, water transport by the equilibrium degree of swelling and adsorption capacity of the beads (PVA-Alginate).

2. Materials and Methods

2.1. Materials
Commercially available alginic acid sodium salt (99%) and PVA were purchased from Sigma-Aldrich. Double deionized water (Milli-Q Millipore 18.2 MΩ cm⁻¹ conductivity) was used for all dilution. Wastewater from one of the manufacturer factory was collected and used as working solution. All other chemicals used in this works were analytical grade.

2.2. Preparation of PVA-Alginate beads
The PVA-Alginate-acid boric acid immobilization method was reported [20] and used in this work. An amount of sodium alginate (0.675 g) and PVA (4 g) were dissolved in 50 mL of Millipore water with boiled oil bath for 1 h with stirring at 240 rpm. A homogenous beads were obtaining by the intrusion from a syringe with needle aperture 1 mm in 3% of acid boric-calcium chloride solution. The mixed solution of acid boric-calcium chloride was constantly stirring at 150 rpm to keep the beads suspended. The PVA-Alginate beads formed were allowed to be harden overnight before introducing to the wastewater for the adsorption experiments.
2.3. Beads characterization
After obtaining the beads in the crosslinked agent, the beads were dried on the filter paper for a few minutes, before they were taken for analyzed by Scanning electron microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). The beads were coated by gold (Au) coating to enable and improve the image of beads prior to the SEM analysis. FTIR spectra were recorded by ATR method at room temperature in the range of 400 - 4000 cm⁻¹.

2.4. Batch sorption procedure
1000 dilution factor (DF) of wastewater was prepared by dissolving in 100 mL of Millipore water. 0.3 g of the PVA/alginate/ILs hydrogels were shaken in 3 mL of wastewater at 400 rpm for 5 h by orbital shaker. All experiment were performed in duplicates and the result were given as average. The percentages removal of Mn(VII) efficiency are calculated using the following equations respectively.

\[ \text{Mn(VII) ions removal (\%) } = \frac{C_i - C_f}{C_i} \times 100 \]  

(1)

Where \( C_i \) and \( C_f \) are the initial and final concentration of Mn (VII) in mg L⁻¹. Spectrophotometric method is simple and easy to perform, which is used to obtain the concentration of Mn(VII) in this study. Spectrophotometer (UV 1200, Shimadzu). It is known that the main element in the wastewater is manganese. Therefore, varies concentration of Potassium permanganate (KMnO₄) was used in this work for the construction of calibration curve. The detection wavelength for the maximum absorbance is found at 525.5 nm.

3. Analysis and Discussion

3.1 Alginate/PVA beads
The image of calcium alginate beads formed is shows in the following figure after crosslinking with 2% CaCl₂ (for Alginate) and 3% CaCl₂-acid boric (for Alginate/PVA). According to the image by digital microscope (DinoCapture), the beads were almost clear and relatively spherical with the size of diameter about 2.48 mm. No apparent difference of the beads in addition of PVA in the alginate formulation. Furthermore, no agglomeration problem appears during the formation of beads in 3% acid boric-calcium chloride mixture for Alginate/PVA beads. The Alginate/PVA beads prepared is as hydrophilic as alginate, while the former has neither adsorption affinity for the metal ions [19].
3.2 Scanning Electron Microscope, SEM
SEM is one of the most widely used of surface morphology diagnostic tools. The beads were stocked over a holder and sprayed with gold. Fig. 1 (c) and (d) shows the SEM micrographs of the Alginate and Alginate/PVA beads respectively. Alginate beads formed almost smooth surface with a small number of bumps and dimples. On the other hand, the Alginate/PVA beads has rough surface irregular pores and ‘crack’ of various dimension, at the same time increase in the surface area. In the absence of PVA, the surface of Alginate was no pore or hollow was found. In fact, after adsorption experiment were carried out, there was no visible change in their shape was observed.

3.3 Fourier Transform Infrared Spectroscopy, FTIR
The FTIR spectra of adsorbents used in this study were recorded before exposure to wastewater. The FTIR spectrum of all spectrum in Fig. 3 shows the strongest absorption peaks at about 3256 cm\(^{-1}\) corresponded to the –OH stretching of hydroxyls group. The spectrum at about 1086 and 1415 cm\(^{-1}\) belong to –C-O group is shows in Fig. 2(b) and (c). Peaks of Alginate in Fig. 2(c) at 3440, 1610, and 1089 cm\(^{-1}\) were attributed to hydroxyl, C-O-O-, and C-O-groups, respectively. It is clear from the FTIR spectra that there were no peaks in the spectrum of the blend other than peaks corresponding to its individual components, and so FTIR shows no evidence of a strong chemical interaction changing the nature of the functional groups in the Alginate/PVA formulation.
3.4 Mn(VII) Adsorption

3.4.1 Effect of contact time

The effect of contact time on the adsorption capacity of the beads give a very successful results and is shown in Figure 3. It was observed that initial adsorption of Mn(VII) was rapid on the Alginate beads before the adsorption equilibrium was obtained within 3 hrs. After 3 hrs, the removal efficiency of Mn(VII) by Alginate was 40% and there was no considerable increase after that. This may be due to the lack of available sites which fully utilize at the first 3 hrs of contact time.

The effect of contact time on the adsorption capacity of Alginate/PVA is different compared to Alginate beads. In this case, as the contact time increased, the percentages removal also were slowly increased from 57% to 62%. There is no equilibrium points found for Alginate/PVA within 5 hrs contact time. However, in overall the percentage removal was higher than Alginate beads. This suggest for more efficient adsorbent at a long time operation.
The percentages removal of Mn(VII) ions from wastewater for both adsorbents gives slightly different results. However, they shared a same trends within the experimental contact time. The adsorption of metal ions generally occurs in two phases. The first phase occurs on the cell surface and consist of fast inactive biosorption, which is completely independent of cellular metabolism while the second phase consists of active sorption is dependent on cell metabolism [21]. In this case, the metal ions has been attributed to the presence of carboxyl as binding groups on the alginate cell and is enhanced by the presence of PVA.

3.4.2 Effect of beads dosage
Figure 4 illustrates the effect of beads dosage that is added into the industrial wastewater. It is observed that the percentages removal of Mn(VII) ions increases from 45% to 79% on the increasing the mass of beads dosage from 0.3g to 1.2g for Alginate beads after 5 hrs of contact time. Generally, increasing adsorbent dosage at constant Mn(VII) concentration provided more available adsorption sites of the beads thus increased the of dye removal [22]. Unfortunately, the percentages removal of Mn(VII) ions for sage Alginate/PVA were declined on the usage of adsorbent dosage more than 0.9g. The maximum adsorptive removal was found for 0.9 g of beads dosage with 74%. The decreased may be attributed to the saturation of active sites of the beads with Mn(VII).
4. Conclusion
This study has demonstrated the capability of sodium alginate blend together with PVA in the forms of beads adsorbent for Mn(VII) ions removal from industrial wastewater. The operating parameters, contact time and adsorbent dosage were effective on the adsorption of Mn(VII). This study established a higher percentages removal up to 62% within 4 hrs contact time in the presence of PVA in the formulation. The observed contact time are promising for Alginate/PVA and the beads dosage may influence the percentages removal as well.

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References
[1] F. Fu, Q. Wang, Removal of Heavy Metal Ions from Wastewaters: A Review, J. Environ. Manage. 92 (2011) 407–418.
[2] T.R. Guilarte, K.K. Gonzales, Manganese-induced Parkinsonism is Not Idiopathic Parkinson’s Disease: Environmental and Genetic Evidence, Toxicol. Sci. 146 (2015) 204–212.
[3] H.A. Hasan, S.R.S. Abdullah, S.K. Kamarudin, N.T. Kofli, Problems of Ammonia and Manganese in Malaysian Drinking Water Treatments, World Appl. Sci. J. 12 (2011) 1890–1896.
[4] O.E. Abdel Salam, N.A. Reiad, M.M. ElShafei, A Study of the Removal Characteristics of Heavy Metals from Wastewater by Low-cost Adsorbents, J. Adv. Res. 2 (2011) 297–303.
[5] G. Annadural, R.S. Juang, D.J. Lee, Adsorption of Heavy Metals from Water using Banana and Orange Peels, Water Sci. Technol. 47 (2002) 185–190.
[6] T.B. Budak, Removal of Heavy Metals From Wastewater Using Synthetic Ion Exchange Resin, Asian J. Chem. 25 (2013) 4207–4210.
[7] A.E. Visser, R.P. Swatloski, W.M. Reichert, J.H. Davis Jr., R.D. Rogers, R. Mayton, S. Sheff, A. Wierzbicki, *Task-specific Ionic Liquids for the Extraction of Metal Ions from Aqueous Solutions*, Chem. Commun. (2001) 135–136.

[8] G.-T. Wei, Z. Yang, C.-J. Chen, *Room Temperature Ionic Liquid as A Novel Medium for Liquid/Liquid Extraction of Metal Ions*, Anal. Chim. Acta. 488 (2003) 183–192.

[9] D.L. Xiaoqi Sun, Bo Peng, Yang Ji, Ji Chen, *Chitosan(Chitin)/Cellulose Composite Biosorbents Prepared Using Ionic Liquid for Heavy Metal Ions Adsorption*, An Off. Publ. Am. Instutute Chem. Eng. 55 (2009) 2062–2069.

[10] N. Ahalya, T.V. Ramachandra, R.D. Kanamadi, *Biosorption of Heavy Metals*, Res. J. Chem. Environ. 7 (2003) 71–79.

[11] C. Araneda, C. Fonseca, J. Sapag, C. Basualto, M. Yazdani-Pedram, K. Kondo, E. Kamio, F. Valenzuela, *Removal of Metal Ions from Aqueous Solutions by Sorption onto Microcapsules Prepared by Copolymerization of Ethylene Glycol dimethacrylate with Styrene*, Sep. Purif. Technol. 63 (2008) 517–523.

[12] E.S. Dragan, D.F. Apopei Loghin, A.I. Cocarta, *Efficient sorption of Cu$^{2+}$ by Composite Chelating Sorbents Based on Potato Starch- Graft-Polyamidoxime Embedded in Chitosan Beads*, ACS Appl. Mater. Interfaces. 6 (2014) 16577–16592.

[13] M. Zougagh, J.M. Cano Pavón, A. Garcia De Torres, *Chelating Sorbents Based on Silica Gel and Their Application in Atomic Spectrometry*, Anal. Bioanal. Chem. 381 (2005) 1103–1113.

[14] P. Pant, R. Bansal, S. Gulati, S. Kumar, R. Kodwani, Porous and Chelated Nanostructured Multifunctional Materials: Recoverable and Reusable Sorbents for Extraction of Metal Ions and Catalysts for Diverse Organic Reactions, J. Nanostructure Chem. 6 (2016) 145–157.

[15] H.G. Park, M.Y. Chae, *Novel Type of Alginate Gel-based Adsorbents for Heavy Metal Removal*, J. Chem. Technol. Biotechnol. 79 (2004) 1080–1083.

[16] S. Peretz, D.F. Anghel, E. Vasiliscu, M. Florea-Spiroiu, C. Stoian, G. Zgherea, *Synthesis, Characterization and Adsorption Properties of Alginate Porous Beads*, Polym. Bull. 72 (2015) 3169–3182.

[17] A. Soni, A. Tiwari, A. K. Bajpai, *Adsorption of O-nitrophenol onto Nano Iron Oxide and Alginate Microspheres : Batch and Column Studies*, African J. Pure Appl. Chem. 6 (2012) 161–173.

[18] Á.A.A. De Queiroz, E.D. Passes, S. De Brito Alves, G.S. Silva, O.Z. Higa, M. Vitolo, *Alginate-poly(vinyl alcohol) Core-shell Microspheres for Lipase Immobilization*, J. Appl. Polym. Sci. 102 (2006) 1553–1560.

[19] T. Kobayashi, M. Yoshimoto, K. Nakao, *Preparation and Characterization of Immobilized Chelate Extractant in PVA Gel Beads for an Efficient Recovery of Copper ( II ) in Aqueous Solution*, Ind. Eng. Chem. Res. 49 (2010) 11652–11660.

[20] Y. Zhang, D. Kogelnig, C. Morgenbesser, A. Stojanovic, F. Jirsa, I. Lichtscheidl-Schultz, R. Krachler, Y. Li, B.K. Kepppler, *Preparation and Characterization of Immobilized $[A336/MTBA]$ in PVA-Alginate Gel Beads as Novel Solid-phase Extractants for an Efficient Recovery of Hg (II) from Aqueous Solutions*, J. Hazard. Mater. 196 (2011) 201–209.

[21] A.K. Zeraatkar, H. Ahmadzadeh, A.F. Talebi, N.R. Moheimani, M.P. McHenry, *Potential use of Algae for Heavy Metal Bioremediation, A Critical Review*, J. Environ. Manage. 181 (2016) 817–831.

[22] M. El-Latif, *Alginate/Polyvinyl Alcohol-Kaolin Composite for Removal of Methylene Blue from Aqueous Solution in a Batch Stirred Tank Reactor*, J. Am. 6 (2010).