Lead Ion Removal in Water Using Low Methoxy Pectin-Guar Gum Beads Hybrid Adsorbent

Nadya Nursidah Pratiwi Subroto, Fadhil Muhammad Tarmidzi*, Ina Wati[1], Velia Mulya Armans

Chemical Engineering Department, Faculty of Industrial and Process Technology, Institut Teknologi Kalimantan, Jalan Soekarno Hatta KM 15, Balikpapan, Indonesia

Corresponding Author: fadhil.tarmidzi@lecturer.itk.ac.id

Received: February 2022
Received in revised: March 2022
Accepted: May 2022
Available online:

Abstract

A high level of lead in the sediment will cause contamination of aquatic biota. Lead pollutants in water may be treated by an easy and common adsorption process. A combination of both environmentally friendly and renewable materials, low methoxy pectin (LMP), and guar gum as adsorbents can reduce the need of activated carbon which requires high temperatures in its synthesis process. LMP was prepared from high methoxy pectin using a demethylation process under alkaline conditions. LMP and guar gum are diluted in 1 M calcium chloride as a crosslinking agent. The degree of esterification was carried out to determine the demethylation process. Adsorption of lead was carried out with a lead concentration of 165 ppm in acidic conditions for 24 hours. Lead concentration was measured using AAS. Results show that the optimal pH for demethylation was 12. The ratio of 1:2 pectin-guar gum produces the strong beads related to more O-H bonds in guar gum that can be developed. pectin-guar gum beads can adsorb 63% of lead at pH 6 due to the development of hydro-complex metal ions under more basic conditions.

Keywords: Lead, Beads adsorbent, Low methoxy pectin, Guar gum

INTRODUCTION

Pulp and paper are the biggest contributors of lead pollutants in water. A lead pollutant can be found in black liquor, especially in aerosol synthesize, along with a non-volatile sulfur compounds (Kevlich, Shofner, & Nair, 2017). The presence of non-biodegradable lead in waters causes damage to aquatic ecosystems so that waters that meet quality standards are not obtained that are safe for the environment (Tanheitafino, Zaharah, & Destiarti, 2016). Lead also has a bad influence on human health, both children and adults which can cause cancer, hypertension, coronary heart disease, and other. Lead levels in water also cause damage to mammalian organs (Male et al., 2017). Therefore, special attention is needed in the form of treatment of the waste to be discharged into the waters.

There are various methods to reduce metal levels in wastewater, including chemical precipitation filtration, ion exchange, adsorption, and membrane systems (Darjito, Purwonugroho, & Ningsih, 2014). The adsorption process is popular because of several advantages, including relatively high efficiency, does not have a bad impact on the environment, and is effective (Bijang, Tanasale, Kelrey, Mansur, & Azis, 2021). In addition, Adsorption has a simple process, can work with low concentrations, and can be recycled. Adsorption is a separation process that can be used for the removal of low concentration pollutants from large volumes of process, wastewater, and solution water. There are 3 types of adsorption systems, namely gas-liquid, liquid-liquid, solid-liquid, and solid gas (Nwodika & Onukwuli, 2017).

Pectin can be used as an adsorbent to absorb heavy metals where pectin content can be obtained, one of which is orange peel waste. Pectin is a polymer derived from D-galacturonic acid which can be found in plant cell walls linked by 1,4 glycosidic bonds and is commonly found in the middle lamellae of the wall (Latupeirissa, Fransina, Tanasale, & Batawi, 2019) (Rahayu, Harisma, Syamsuddin, Sofyana, & Mulyati, 2021). Pectin has the ability to form a good gel with the level of esterification of galacturonic acid residues as a parameter of the effect of solubility and gelling on pectin (Liu, Fishman, & Hicks, 2007). Pectin contains a carboxylate group which causes pectin to be used to absorb metals. The carboxylate group reacts with heavy metal ions to form complex compounds that can be excreted through feces and are insoluble in water. The reactivity of pectin on heavy metal ions depends on the value of the degree of esterification. As an adsorbent, the type of pectin used is pectin with many carboxyl groups (Tahir, Safitri, & Suhaenah, 2019).

Based on the degree of esterification, pectin is divided into two from the methoxy group. Low Methoxy Pectin (LMP) has less than 50% while High Methoxy Pectin (HMP) has more than 50% (Santos et al., 2020). HMP can be found in fruit peels and it needs modification through a demethylation step to convert to LMP. One of the modifications has been done by using the alkaline demethylation method to convert pectin into Low Methoxyl Pectin (Yapo & Koffi, 2014) (Sarandi, Alhusna, & Pandia, 2015).

This study focus on the synthesis of hybrid bead adsorption using LMP and guar gum. Guar-gum is a natural hydrocolloid as an interpenetrating agent that helps improve the mechanical strength of the gel formed (Sugita, Sjahriza, & Lestari, 2015). The addition of guar-gum is expected to increase the resistance of the beads so that they are not easily destroyed during the adsorption process.

METHODOLOGY

Materials and Instrumentals

This study was using HMP from citrus peel, guar, and gum as the main precursors. The demethylation process was done by using isopropanol alcohol, NaOH, and ethanol 96% from Merck. $CaCl_2$ was also added as a crosslinker in beads synthesis. The adsorption process was done by using HCl 37% and $Pb(NO_3)_2$ from Merck. Lead concentration in water was measured using Atomic Adsorption Spectrophotometer (AAS) in the Center for Standardization and Industrial Services, Samarinda.

Methods

The demethylation process was adapted and modified from Sarandi et al., (2015). The process begins with dissolved pectin in IPA with the concentration of 1.5% w/v. The base condition was adjusted and varied by using 3M NaOH solution to achieve a pH level of 10-12. The solution was incubated at 55 ^oC for 6 hours. Next, the solution was cooled to room temperature and then 3N HCl solution was added until the pH became 3. LMP was precipitated by adding ethanol 96% at 18 ^oC for 2 hours. The solid was filtered and washed with ethanol and dried using the oven at 50 ^oC. The degree of esterification was analyzed by dissolving 0.2 grams of LMP with distilled water and a phenolphthalein (PP) indicator was added.

The sample was titrated with 1 N NaOH and the titration results were recorded as initial conditions where the initial conditions indicated the number of carboxyl groups of beads. Then, 10 mL of 1 N NaOH solution was added to the sample and shaken vigorously until polygalacturonic acid was neutral and left for 2 hours at room temperature to de-esterify pectin.

Figure 1. LMP from the demethylation process

Then, 1 N HCl solution was added to the sample to neutralize the NaOH and shaken until the pink color in the sample disappeared. Then 3 drops of PP indicator were added and titrated with 1 N NaOH. Then the titration results were recorded as final conditions. To calculate the degree of esterification of pectin that has undergone a demethylation process, the following Equation 1 can be used.

$$DE = \frac{Final\ titration}{Initial + Final\ titration} \times 100\% \quad (1)$$

Synthesize hybrid bead adsorbent was adapted from (Jakóbik-Kolon, Milewski, Karoń, & Bok-Badura, 2016). Pectin and guar gum mixed with water with a ratio of LMP: guar gum are 1:0, 2:1, 1:1, and 1:2. The sample was stirred at 70°C for 4 hours and cooled to room temperature. Then the solution was dropped into a cold 1 M $CaCl_2$ solution to form beads. Beads were allowed to stand for 24 hours in a cold 1 M $CaCl_2$ solution at 12 ^oC for 24 hours. The chloride ions in the beads are removed by washing them with distilled water. Finally, the beads were filtered and dried at 35 °C for 24 hours.

To durability test of the beads was performed by adding 0.3 grams beads to 300 mL distilled water The stirring was done at 1000 rpm for 24 hours. The beads were observed to determine the beads resistance to shear stress. The adsorption step was carried out by making a solution of $Pb(NO_3)_2$ with a concentration of 165 ppm. HCl solution was added to vary its condition at pH level of 3-6. Adsorption of lead was done by adding 1% of beads into 300 mL of lead solution and stirring for 24 hours (Jakóbik-Kolon et al., 2016). Lead concentration in water was analyzed using AAS.

Figure 2. LMP - Guar Gum Hybrid Beads Pectin

RESULTS AND DISCUSSION

Effect of pH on LMP Degree of Esterification

The process used to decrease the degree of esterification is base demethylation caused by the reaction rate factor which when compared with all available methods, base demethylation is relatively faster (El-Nawawi & Heikal, 1995), the reaction that occurs in the process is irreversible, and the need for high temperatures in the process (Einhorn-Stoll et al., 2020). HMP from citrus peel was used for this process have a degree of esterification (DE) of 63%. After the demethylation process is carried out, then an analysis of the DE is carried out which has a function so that the number of carboxyl groups esterified by methyl to the total galacturonic acid in a number of pectin samples is known. The titration method was used to test the degree of esterification of pectin. From the pectin esterification degree test that has been carried out, the results are as shown in Figure 3.

Among all the variations in pH values that have been tested, pH 12 has the lowest esterification degree value which is in accordance with previous research conducted by (Kesuma, Widarta, & Permana, 2018). Lowering pH during the process that will bring the methoxy content higher by promoting the esterification of the carboxyl group. Higher pH means that there is more hydroxyl ion, which represents more ester groups will be demethylated to carboxylic acids and replace the ester groups in galacturonic acid in the pectin chain. The ratio of the number of galacturonic acid groups esterified by methyl to the total galacturonic acid in a number of pectin samples is called the degree of esterification. The number of demethylated ester groups from the galacturonic acid group of pectin affects the value of the esterification degree because the more galacturonic acid groups in the demethylated pectin chain, the smaller the value of the degree of esterification of pectin will be. This pectin can be referred to as LMP. Therefore, pH 12 is the optimal condition for demethylating under alkaline conditions because it produces the lowest esterification degree value is 20%.

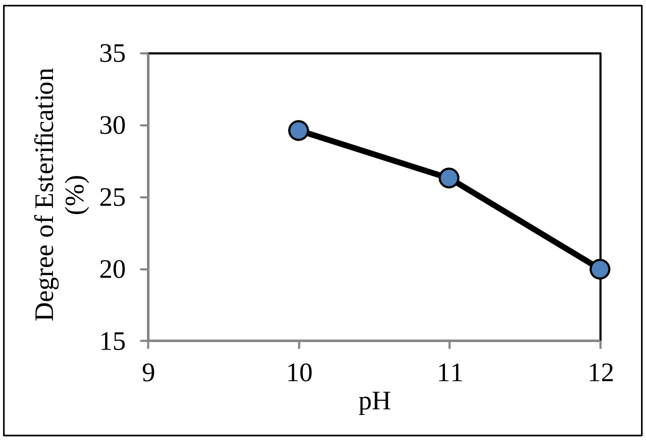

Figure 3. Effect of pH toward Degree of Esterification

Beads Resistance from Shear Stress

To increase the resistance of the beads from shear stress during the adsorption process, LMP was mixed with guar gum to develop a strong bead (Figure 4). because the molecular weight of pectin is greater than guar gum, when pectin is mixed with guar gum, the amount of guar gum must be 40% more so that it can be completely mixed (Satyamaiah, Prasad, Chandrasekhar, Suhasini, & Suryanaraya, 2014).

Figure 5 shows that the beads with a ratio of 1:2 (D) have the best shear stress resistance ability at 1000 rpm for 24 hours. With a ratio of 1:2 (D) the amount of guar gum used has met the requirements so that pectin and guar gum can be mixed perfectly so that the beads formed have better resistance characteristics in stirring.

Effect of pH to Lead Adsorption using Hybrid Beads Adsorbent

The initial lead concentration in the water was 165 ppm. The adsorption was carried out for 24 hours in acidic conditions by varying from pH level of 3-6 (Figure 6). It is shown that the value of pH is inversely proportional to the value of the concentration of the lead solution that is removed through the adsorption process. The higher the pH variable, the lower the concentration of the Pb solution that has been adsorbed. The efficiency of the adsorption of beads is directly proportional to the pH value, where the greater the pH value, the greater the adsorption efficiency (Yantyana, Amalia, & Fitriyani, 2018).

Figure 4. Hybrid Beads Adsorbent after Shear Stress Test

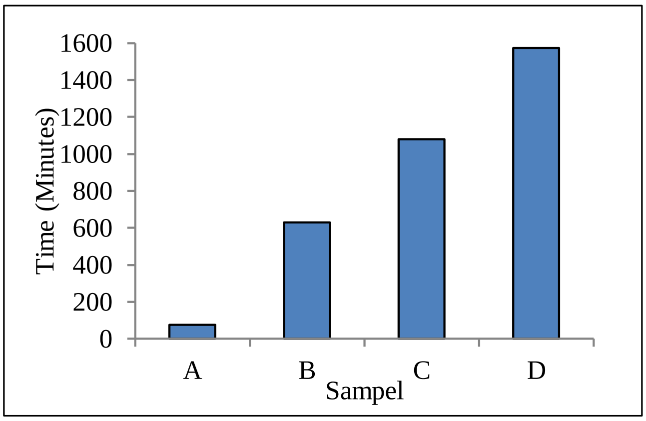

Figure 5. Shear Stress Resistance of Beads at 1000 rpm with Ratio LMP: Guar Gum A. 1:0, B. 2:1, C. 1:1. And D. 1:2.

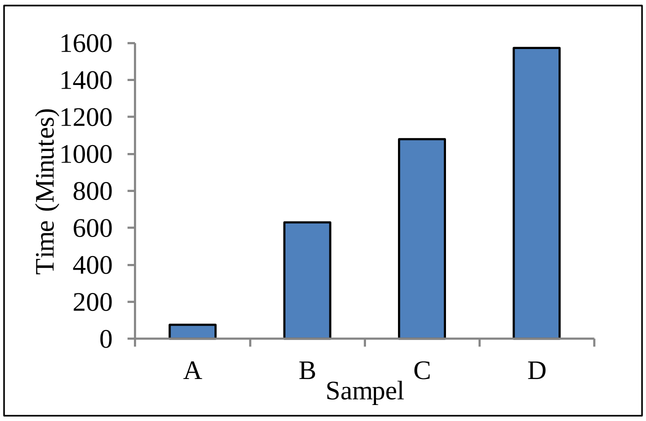

Figure 6. Final Lead Concentration at Various pH from Initial Lead Concentration 165 ppm

Based on Figure 7, it is known that the percentage of decrease in lead concentration was highest at pH 6, which was 63%. This is because the active site on the adsorbent can absorb more lead metal ions because the number of H^+ ions has decreased at this condition. Otherwise, a low pH value will result in low absorption of metal ions because the surface of the adsorbent is surrounded by H^+ ions, and the surface of the adsorbent will be positively charged which will cause the adsorbent's repulsion with metal ions (Yantyana et al., 2018). The metal ions of hydro-complexes do not dissociate in solution and have a large size making it difficult to bind to the active groups present in the beads. Therefore, it can be concluded that pH 6 is the optimal condition for adsorption.

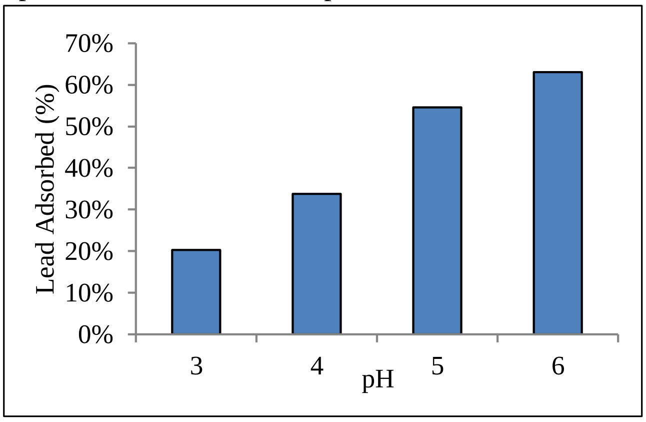

Figure 7. Percentage of Lead Removal in Water after 24 Hours of Adsorption

CONCLUSION

This study shows that the demethylation process can be done in base conditions with the optimum DE 10% was achieved at pH 12 because more ester groups will be demethylated to carboxylic acids and replace the ester groups in galacturonic acid in the pectin chain. Hybrid beads adsorbent from LMP and guar gum have successfully developed. The ratio of 1:2 pectin-guar gum produces the best characteristics with stirring resistance at 1000 rpm for 24 hours. The bond that occurs between LMP and guar gum increases the mechanical strength and increases the resistance of the beads to temperature and solvent. As well as pectin-guar gum beads can adsorb Pb metal well. The largest Pb adsorption capacity was obtained when the Pb solution was at pH 6 which was the optimal condition for adsorption. This happens because at pH 6 the carboxyl group is not protonated and metal ions do not become hydro-complex ions. Under these conditions, the pectin-guar gum beads can adsorb as much as 104.08 mg/L of Pb or the concentration of the Pb solution decreased by 63%. The metal ions of hydro-complexes do not dissociate in solution and have a large size making it difficult to bind to the active groups present in the beads. Therefore, it can be concluded that pH 6 is the optimal condition for adsorption.

REFERENCES

Bijang, C. M., Tanasale, M. F. J. D. P., Kelrey, A. G., Mansur, I. U., & Azis, T. (2021). Preparation of Natural Ouw Clay-Chitosan Composite and Its Application as Lead and Cadmium Metal Adsorbent. *Indonesian Journal of Chemical Research*, *9*(1), 15–20.

Darjito, D., Purwonugroho, D., & Ningsih, R. (2014). The Adsorption of Cr (VI) Ions Using Chitosan-Alumina Adsorbent. *Journal of Pure and Applied Chemistry Research*, *3*(June), 53–61.

Einhorn-Stoll, U., Kastner, H., Fatouros, A., Krähmer, A., Kroh, L. W., & Drusch, S. (2020). Thermal Degradation of Citrus Pectin in Low-Moisture Environment–Investigation of Backbone Depolymerisation. *Food Hydrocolloids*, *107*, 104–115.

El-Nawawi, S. A., & Heikal, Y. A. (1995). Production of a Low Ester Pectin by De–Esterification of High Ester Citrus Pectin. *Carbohydrate Polymers*, *27*, 191–195.

Jakóbik-Kolon, A., Milewski, A. K., Karoń, K., & Bok-Badura, J. (2016). New, Hybrid Pectin-Based Biosorbents. *Separation Science and Technology (Philadelphia)*, *51*(15–16), 2604–2611.

Kesuma, N. K. Y., Widarta, I. W. R., & Permana, I. D. G. M. (2018). Effect of Acid Type and Ph Solution on Characteristics Of Pectin From Lemon Peel (citrus limon). *Jurnal Ilmu Dan Teknologi Pangan (ITEPA)*, *7*(4), 192.

Kevlich, N. S., Shofner, M. L., & Nair, S. (2017). Membranes for Kraft Black Liquor Concentration and Chemical Recovery: Current Progress, Challenges, and Opportunities. *Separation Science and Technology*, *52*(6), 1070–1094.

Latupeirissa, J., Fransina, E. G., Tanasale, M. F. J. D. P., & Batawi, C. Y. (2019). Extraction And Characterization of Pectin from The Oranges Peel of Kisar (*Citrus sp.*). *J. Chem. Res*, *7*(1), 61–68.

Liu, L. S., Fishman, M. L., & Hicks, K. B. (2007). Pectin in Controlled Drug Delivery-A Review. *Cellulose*, *14*(1), 15–24.

Male, Y. T., Malle, D., Bijang, C. M., Fransina, E. G., Seumahu, C. A., Dolaitery, L. M., Gaspersz, N. (2017). Analysis of Cadmium (Cd) and Lead (Pb) metal content in sediments in Inner Ambon Bay. *Indonesian Journal of Chemical Research*, *5*(1), 22–31.

Nwodika, C., & Onukwuli, O. D. (2017). Adsorption Study of Kinetics And Equilibrium of Basic Dye on Kola Nut Pod Carbon. *Gazi University Journal of Science*, *30*(4), 86–102.

Rahayu, W. P., Harisma, I. W., Syamsuddin, Y., Sofyana, S., & Mulyati, S. (2021). Extraction Of Pectin from Orange Peel and Banana Peel as Biosorbent in Heavy Metal Fe Adsorption. *Jurnal Serambi Engineering*, *6*(2), 1899–1907.

Santos, E. E., Amaro, R. C., Bustamante, C. C. C., Guerra, M. H. A., Soares, L. C., & Froes, R. E. S. (2020). Extraction of Pectin From Agroindustrial Residue with an Ecofriendly Solvent: Use of FTIR And Chemometrics To Differentiate Pectins According to Degree of Methyl Esterification. *Food Hydrocolloids*, *107*, 105921.

Sarandi, R. R., Alhusna, Y., & Pandia, S. (2015). Production of Pectin From Yellow Passion Fruit (*Passiflora edulis*). *Jurnal Teknik Kimia*, *4*(4), 71–76.

Satyamaiah, G., Prasad, M., Chandrasekhar, M., Suhasini, D.M., Suryanaraya, C., Subha, M.C.S. and Chowdoji Rao, K. 2014. Miscibility Studies on Guargum/Pectin Blends. *Indian Journal of Advances in Chemical Science*, 2(2): 116-123.

Sugita, P., Sjahriza, A., & Lestari, S. (2015). Synthesis and Optimization of Chitosan-Guar Gum Gel, *Jurnal Natur Indonesia*, *9*(1), 32–36.

Tahir, M., Safitri, I., & Suhaenah, A. (2019). Analysis of Pamelo Citrus Albedo Pectin as Adsorbent for Heavy Metals Lead (Pb), Cadmium (Cd) and Copper (Cu). *Jurnal Farmasi Galenika*, *5*(2), 158–165.

Tanheitafino, S., Zaharah, T., & Destiarti, L. (2016). Chitosan Modification with Kaolin and Its Application as Lead(II) Adsorbent, *Jurnal JKK*, *5*(2), 33–42.

Yantyana, I., Amalia, V., & Fitriyani, R. (2018). Lead(II) Metal Ion Adsorption Using Ca-Alginate Microcapsules. *Al-Kimiya*, *5*(1), 17–26.

Yapo, B. M., & Koffi, K. L. (2014). Extraction and Characterization of Highly Gelling Low Methoxy Pectin from Cashew Apple Pomace. *Foods*, *3*(1), 1–12.