Isolation of Pectin from Carrot Peel as Biosorbent of Pb(II) ion

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Abstract. Pectin is a promising bioadsorbents material for heavy metals' removal from aqueous solution. In this study, pectin was isolated from carrot peel by extraction method and evaluated as biosorbent for removal of toxic heavy metals (Pb(II)). The adsorption parameters for removal of Pb(II) were optimized, including pH, adsorbent mass, and contact time. The results shows that pectin can be isolated from carrot peel as was characterized by FT-IR spectra. The optimum condition for Pb(II) were at pH solution 6, Pb(II) with 44% removal capacity. The optimum adsorbent mass was 15 mg with 46% removal capacity, whereas the optimum contact time was 120 min with 38% removal capacity.

1. Introduction

Heavy metal contamination is considered to be one of the most ubiquitous environmental issues today. Accumulation of heavy metals in water is of particularly important because it can impact upon human health. In the metallic group, it is known that Arsenic, cadmium, lead, and mercury are listed among the ten chemicals of major public concern. Among them, lead (Pb) is one of the most significant health threats to children and pregnant women. A various adverse effects of Pb has been reported, including: inhibits enzyme activity involved in the formation of hemoglobin (Hb), increase levels of δ-aminolevulinic acid dehydratase (ALAD) and levels of protoporphin in red blood cells, shorten the life of red blood cells, red blood cells and reticulocytes, and increase Fe content in blood plasma.

Treatment processes for heavy metal removal from wastewater has been developed, where adsorption method is among the most effective technique for the removal of heavy metals. Adsorption is a surface phenomenon in which there is absorption or withdrawal of molecules on the surface of the adsorbent. In recent years, the interest in studying modification of pectin has increased. Pectin is an anionic plant cell wall polysaccharide based on α-(1→4) linked D-galacturonic acid [1]. Pectin is widely available in the middle lamella of plant cell walls. Pectin has many active groups, main functional groups contained in the pectin is hydroxyl, carboxyl, amide and methoxy [2]. Currently, pectin was widely used in pharmaceuticals and cosmetics, food industry, and as adsorbent [3,4]. Pectin contains a number of active groups, distributed along the backbone make pectin can be used as a biosorbent [2]. The main functional groups of pectin are hydroxyl, carboxyl, amide, and methoxyl. These functional groups can be used to bind heavy metals, especially hydroxyl groups [5].
Indonesia is a tropical country that has various types of fruits and vegetables which are potential sources of pectin. Isolation and identification of the pectin from pumpkin [6], cocolate peel [7], and durian rind and orange peel [8]. The order of adsorption effectiveness of pectin durian rind toward heavy metal ion are Cu> Pb> Ni> Cd> Zn [8]. Carboxyl groups of pectin has an ability to interact with heavy metal ions to form a complex [5]. The pectin reactivity of heavy metal ions is highly dependent on the degree of esterification. The modification process of durian rind pectin increases binding process of metal ions [8].

In this study, pectin from carrot peel will be isolated and applied as Pb (II) ion adsorbent. Pectin from carrot peel will be tested its absorption capacity, by optimizing the optimum condition in the adsorption process at first. The optimum conditions of pectin carrot peel adsorbent to adsorb Pb (II) ions include of pH optimization, contact time, and optimum mass.

2. Materials And Methodology

2.1. Material

Carrots (Daucus carota subsp. sativus) obtained from the local market of Surakarta, Indonesia. The materials used include hydrochloric acid, nitric acid, alcohol (96%), alcohol (70%), Pb(II) were analytical grade and purchased from Sigma-Aldrich.

2.2. Methodology

2.2.1. Isolation of pectin from carrot peel by extraction method

Carrot peel were washed carefully with tap water to remove dirt soil from the surface and dried under shade for 24 h, further dried at 30-40°C until constant weight was obtained. Dried fruit peel was cut into pieces and powdered. The dry powder was sieved using a stainless steel and the obtained powder was stored in the air-tight container until further use. Pectin was extracted from the carrot powder under reflux in a condensation system at 90°C for 60 min (solute/solvent 1:20), using water acidified with hydrochloric acid to pH 2.0. The obtained pectin was then dried and sieved using a stainless steel.

2.2.2. Precipitation and washing of pectin.

The acid pectin extract was precipitated with acidic alcohol solution (1 L of alcohol 96% was added with 2 mL of concentrated HCl) at a ratio 1:1 (v/v) for 24 h. The floating pectin precipitate was then filtered and separated from the filtrate. The pectin precipitate was washed with alcohol up to several times. The pectin was dried to constant weight at 40-50°C for approximately 6, cooled in a dessicator, and hard pectin cake was later grounded and sieved in order to obtain powdered pectin. The pectin yield was calculated on a dry weight basis (initial weight of sample).

2.2.3. Optimum condition of adsorption.

Study of the adsorption process was performed by analyzing several parameters: pH, adsorbent dose, and contact time. It was conducted in laboratory scale with variations in pH of solution (4, 5, 6, 7, and 8), adsorbent dose (5, 10, 15, and 20 mg), and contact time (30, 45, 60, 120, 240, and 360 min). Initial concentration of Pb(II) was 50 ppm by the volume of 10 mL. Analysis of the adsorbed Pb(II) ion was carried out with atomic absorption spectrophotometry (AAS). For those purposes, 20 mg pectin was immersed in 20 mL Pb(II) solution. Concentrations for each solution were 5, 10, 15 and 20 ppm. After being interrupted for 120 min, the contacting filtrate was filtered, and then tested with AAS.

3. Result and Discussion

In this study, pectin-based absorption material from carrot peel was isolated. Pectin has several active groups, which were confirmed by FTIR spectra. From Figure 1, the spectra of carot pectin (A)
shows a broad absorption band at 3404 cm$^{-1}$, indicates the range of the OH group vibrations. Absorption in the region of 1751 cm$^{-1}$ indicates the presence of an esterified carboxylic group and peak at 1636 cm$^{-1}$ of carboxylic groups. Furthermore, peak at 1636 cm$^{-1}$ and 1064 cm$^{-1}$ indicate the presence of –COOH group and the stretching vibration of the –CO, respectively. The FTIR spectra of carot pectin in general is comparable with those of commercial pectin (B).

Figure 1. FTIR spectra of A) carrot pectin and B) commercial pectin

3.1. The parameter of optimum condition of carrot peel pectin in adsorption of Pb(II)

3.1.1. Determination of optimum pH

Figure 2 illustrates the influence of pH on the removal of Pb(II). The pH of the solution is one of the important factors that determine the performance of the adsorbent in the adsorption process. If the pH value is too low or too high, the adsorption process cannot be maximized. From Figure 2, within the range tested shows that on pH 4 adsorption percentage of the adsorben is 17 % with adsorption capacity is 2.0 mg/g. Meanwhile, the percentage of adsorption tends to rise on pH 6. The pH 6 is found to be optimum condition, in which the percentage of Pb (II) absorbed is 44 % and the adsorption capacity is 6.0 mg/g. Furthermore at pH 7, the adsorption percentage decreased to 34 % and the adsorption capacity is 4.4 mg/g. At higher pH, the solution has more -OH ions in the solution. The existence of these ions causes Pb(II) ions are hydrolyzed and forms Pb(OH)$_3$. The adsorption process on pH 8 more decreasing with percentage of adsorption is 32% and the adsorption capacity is 4.2 mg/g.
3.1.2. Determination of optimum adsorbent dose

The amount of adsorbent significantly affected the adsorption rate of Pb (II). In this study 10 mL of Pb (II) ion solution at optimum pH (pH 6) was added with variation of adsorbent mass 5, 10, 15, 20 mg with contact time 120 min. From Figure 3, it can be seen that there is an increase in percentage of absorption due to increasing of adsorbent mass, but after passing the optimum point there is a decreasing in percentage of absorption toward Pb(II). It occurs because more amount of pectin used as an adsorbent, will provide more active sites that bind to Pb (II) ion, so the chances of binding of Pb ions are greater. However, on 20 mg there is a drastic decreasing, it may surface of an adsorbent have been saturated. The optimum mass adsorbent occurred at 15 mg. After the optimum condition is obtained, contacting the optimum condition is 10 mL of Pb(II) solution at pH 6 added with 15 mg carrot pectin and contacted for 120 min show absorption of pectin to Pb(II) is 6.13 mg/g and 46 % adsorbed.

![Figure 2. Effect of pH solution on adsorption capacity of Pb(II) on carrot pectin](image2)

![Figure 3. Effect of mass adsorbent on adsorption capacity of Pb(II) on carrot pectin](image3)

3.1.3. Determination of optimum contact time

The graph of the relationship between the contact time of Pb(II) ion with adsorption capacity of carrot pectin is show in Figure 4. Contact time is important to determine of the adsorption process, because it allows better mechanism the diffusion process and binding of adsorbate molecules. Variation contact time used was 30, 45,60, 120, 240, and 360 minutes. From Figure 4, it can be seen that within 30-360 min, the largest absorption occurs at 120 minutes. After reaching the optimum point there is a decrease in absorption capacity. This due to 120 of minute carrot peel pectin adsorb Pb(II) perfectly than 30, 60,
240 and 360 min. The optimum adsorption of Pb(II) by pectin carrot peel occurs on 120 minute with adsorption capacity 4.80 mg/g and 38 % Pb(II) adsorbed.

![Figure 4. Effect of contact time on adsorption capacity of Pb(II) on carrot pectin](image)

4. Conclusion
It can be concluded that pectin can be isolated from carrot peel proved by FT-IR that found peak at 3404 cm⁻¹ of –OH group, 1636 cm⁻¹ of -COOH group, and 1064 cm⁻¹ prove of the stretching vibration of the -CO. The optimum condition adsorption of pectin carrot peel to Pb(II) metal ion was at pH of solution 6 with contact time 120 min and the adsorbent dose 15 mg. Pectin carrot peel can be used to adsorb Pb(II) in solution.

5. References
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