The Role of Pectin in Pb Binding by Carrot Peel Biosorbents: Isoterm Adsorption Study

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Abstract. Cheaply and abundantly biosorption available materials such as carrot peels can be a cost-efficient method for removing heavy metals from wastewater. To investigate the role pectin plays in metal binding by carrot peels, commerce pectin was compared. FTIR spectra confirmed the presence of carboxyl and hydroxyl groups in commerce pectin and carrot pectin. Isoterm experiments showed that all materials could remove Pb (II) ion. All of materials binding Pb (II) follow Freundlich models adsorption. The commerce pectin binds Pb (II) by involving energy 16.6 KJ/mole whereas pectin from carrot peel involves energy 21.09 KJ/mole. It indicates that commerce pectin binds the Pb (II) by physics adsorption whereas pectin from carrot peel by physics and chemical adsorption.

1 Introduction

The availability of heavy metals in soil ecosystems and aquatic ecosystems due to anthropogenic activities such as mining, smelting and agriculture operations [1]. Metal species whose its existence in the aquatic environment exceeds the threshold will be a contaminant in the ecosystem [2]. Heavy metals are categorized as environmental pollutants such as Cd, Co, Cr, Pb, As and Ni. Heavy metals contamination in aquatic ecosystems is an important issue, as the impact of heavy metal toxicity and its accumulation in aquatic habitats [3]. One of the dangerous heavy metals is lead (Pb). Lead can cause damage to the central nervous system. Lead also can damage the kidneys, liver and reproductive system, basic cellular processes and brain function. Symptoms of poisoning are characterized by anemia, insomnia, headache, dizziness, irritability, muscle weakness, hallucinations and kidney damage [4].

Waste treatment technologies commonly used and are developing in waste treatment are filtration, precipitation, ion exchange and adsorption. Adsorption especially used when the products from other industries are used as biosorbents [5,6]. Compared with other methods, adsorption is one method of an efficient, low-cost alternative waste treatment. Adsorption is process of absorption of a substance (molecule or ion) on the surface of an adsorbent. One of potential biosorbent used as a heavy metal binder is pectin.

Pectin is an anionic plant cell wall polysaccharide based on α-(1–4) linked D-galacturonic acid[7]. Pectin widely available in the middle lamella of plant cell walls. Pectin has many active groups. The main functional groups contained in the pectin is hydroxyl, carboxyl, amide, and methoxy [8]. Lately, the pectin was widely used in pharmaceuticals and cosmetics, in the food industry and as adsorbent to remove heavy metal ions [9,10]. Pectin contains a lot of active groups, that can be used as
a source biosorbent [8]. 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 [11].

2 Methods

2.1 Materials and Method

Materials used: Carrots peels, universal indicator, hydrochloric acid, alcohol 96% and alcohol 70%, Pb (II), nitric acid, distilled water.

2.2 Research Method

2.2.1 Isolation of Pectin from Carrot by Extraction Method.

This dry carrot peel is crushed then and mixed, and the product is called carrot flour, and it is used as the raw material for all the assays made concerning pectin extraction and characterization. 1000 grams of carrot flour washed, dried initially at room temperature and then at 50-60°C for about 24 hours. Pectin was extracted 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, using carrot flour as raw material. Next, the flour was classified with metallic sieves (600 μm) in a shaker device.

2.2.2 Precipitation and Washing of Pectin.

The acid pectin extract is precipitated by alcohol acidic solution (1 liter of 96% alcohol solution added with 2 ml of concentrated HCl) at a ratio 1:1(v/v) for 24 hours. The floating pectin precipitate is filtered and be separated from the filtrate. Then the pectin precipitate is washed with alcohol up to several times. The pressed pectin is dried to constant weight at 40-50°C for approximately 6 hours. Cooled it in a desiccator and the yield calculated on a dry weight basis (initial weight of sample). The hard pectin cake was broken up, ground and sieved to obtain powdered pectin.

2.2.3 Isoterm Adsorption Determination.

Pectin 20 mg was immersed in a 20 ml Pb (II) metal solution. Concentrations of each solution were variations of 5, 10, 15 and 20 ppm. After being interrupted for 120 minutes, then filtered, the contacting filtrate was tested with AAS.

3 Results and Discussion

3.1 Characterization of the Adsorbent

The isolated pectin is tested with FT-IR spectroscopy to determine the esterification degree of carrot pectin and compare with commerce pectin spectra. According to Manrique & Lajolo [12], the esterification degree is determined by counting the number of active group of carboxylates (located in about 1730 cm⁻¹ area) divided by the total number of carboxylate groups (the areas ware between 1730 and 1600 cm⁻¹) then multiplied by 100.

From FT-IR spectra in Fig.1 can be shown that the spectra changes of carrots powder before extracting, pectin carrots and spectra from Commercial pectin. Pectin spectra has typical absorption of a strong band between 1760-1730 and 1630-1600 cm⁻¹ which is a carbonyl ester group and a stretching band of carboxylic ions.

In the carrot spectra before extracting there is no absorption in 1700 cm⁻¹ indicate the presence of an esterified carboxylic group. Whereas after extracting the absorption appeared in 1751cm⁻¹ indicate the presence of an esterified carboxylic group and the spectra in the 1636 cm⁻¹ indicate the presence of a carboxylic group.

Pectin has a fingerprint region of 1300-800 cm⁻¹ (there is a COO-stretching group). Other important absorption bands on pectin are C-H bending at 1380 cm⁻¹ and C=O stretching at 1300-1000 cm⁻¹. From
FT-IR spectra can be calculated the esterification degree of carrot is 56.82%, and commerce pectin is 59.32%. The esterification degree (DE) also called the methoxylatation degree is the proportion of galactic acid in the form of a methyl ester which is usually expressed by the percentage or percentage of the carboxyl group that was methylated with methanol. DE affects of a pectin properties. Other identification of pectin properties, i.e., moisture content and the moisture content of carrot pectin was 14%.

![FTIR Spectra of carrot powder, carrot pectin, and commerce pectin](image)

3.2 Isoterm Adsorption Determination

The adsorption isotherm saw the relationship between the amounts of adsorbed ions per weight of the adsorbent with the ion equilibrium concentration in the solution. By determination of the adsorption isotherm model, an adsorption mechanism of Pb (II) can be predicted on the adsorbent. The mechanism adsorption of pectin was studied using Langmuir and Freundlich isotherm adsorption models. The Langmuir isotherm adsorption model describes monolayer adsorption on a homogeneous surface with the same energy at all the active sites involved. The Freundlich isotherm adsorption model describes multilayer adsorption on heterogeneous surfaces. The determination of the adsorption isotherm model is shown in Table 1.

From Table 1 it appears that the Freundlich correlation coefficient is greater than the Langmuir correlation coefficient, so it can be assumed that both pectin adsorbents in adsorbing Pb (II) ions follow the Freundlich isotherms models in multilayer surface. It indicates that the reaction between the adsorbate pectin and Pb (II) metal ions occurs by physical mechanism, adsorption happens in a multilayer. The energy ($\Delta G$) of commerce pectin and carrot pectin was 16.60 and 21.09 kJ/mole respectively. The adsorption energy value under 20 kJ/mole indicates that adsorption process occurs by physical adsorption. The adsorption energy value between 20-80 kJ/mole indicates that adsorption process occurs by physical and chemical adsorption [13]. In this research, commerce pectin, to bind the Pb (II) occurring by physical adsorption, The carrot peel pectin, adsorp to Pb (II) by physical and
chemical adsorption Process. The Pectin and Chitosan adsorbent generate energy for 16.6 and 19.54 kJ/mol respectively.

| Adsorbent                 | Parameter | Langmuir | Freundlich |
|---------------------------|-----------|----------|------------|
|                           | b         | K        | R²         | ΔG        | n      | Kf      | R²    |
| Carrot pectin             | 1.08x10⁻⁴ | 4.698    | 0.3921     | 21.09     | 1.46   | 0.912   | 0.962 |
| Commerce pectin           | 4.167x10⁻³ | 0.187    | 0.15       | 16.60     | 1.04   | 0.936   | 0.866 |

4 Conclusion

From the research results can be concluded that: Pectin can be isolated from carrot peal that proved by FT-IR test results and test of water content on the adsorbent. The esterification degree of pectin from carrots is 56.82%, and commerce pectin is 59.32%. Carrots pectin can be used to adsorb lead metals. The adsorption isotherm pattern occurring in pectin commerce and carrot pectin to lead metal tends to follow Freundlich isotherm equation.

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