Adsorption of Mercury from Aqueous Solution on Durian (Durio zibethinus) Seed Immobilized Alginate

Intan Lestari1*, Silfia Devi Eka Putri1, Martina Asti Rahayu1, Diah Riski Gusti1

1Program Study of Chemistry, Faculty of Science and Technology, Universitas Jambi, Indonesia

Abstract. The increasing pollution of toxic heavy metals in the environment is an important issue worldwide. Heavy metal ions such as mercury have attracted special attention because of their high toxicity and long half-life which increase the potential to accumulate in the food chain and cause serious damage to the environment. The potential of an adsorbent durian (Durio zibethinus) seed immobilized alginate bead was carried out and used for the adsorption of Mercury in an aqueous solution. Adsorbents were characterized by FTIR, SEM, and XRF. FTIR analysis shows the functional groups of alcohol, amine, and carboxylic acid. Scanning Electron Microscopy shows that the surface morphology of durian seed powder of granules and durian seed immobilized in Ca-alginate of like as tissue eggs in an egg box shape. XRF analysis durian seed immobilized showed that Hg(II) ion adsorbed as much as 37%. The adsorption parameter of Hg(II) ion are pH at 6 with an adsorption capacity was 1.553 mg/g, contact time at 150 minutes with adsorption capacity was 2.880 mg/g, mass 0.1 g with adsorption capacity of 2.274 mg/g, and concentration 250 mg/g with adsorption capacity of 62.067 mg/g.

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Keywords: Adsorption, Mercury, Immobilized, Alginate, Durian (Durio zibethinus) Seed

1. Introduction
Along with today's technological progress and industrial development, this has caused a lot of problems in the surrounding natural environment, such as environmental pollution problems. The increasing pollution of toxic heavy metals in the environment is an important issue worldwide.
Heavy metal ions such as mercury have attracted special attention because of their high toxicity and long half-life which increase the potential to accumulate in the food chain and cause serious damage to the environment [1][2][3]. The mercury ion is one of the heavy metals of concern because it has been used in power plants and is found in waste originating from oil refineries, the alkaline chlorine, plastic, metallurgical, electronic, and metal coating operations industry [4]. The mercury ion is in the form of oxide namely Hg(I) and Hg(II) [5]. Mercury ions can be absorbed into the human body through the skin, lungs, and digestive tract which can result in several acute and chronic disorders such as emphysema, hypertension, damage to the nervous system, cancer, and testicular atrophy [6][7].

Several studies have been developed to remove Hg(II) ions from aqueous solutions such as oxidation or chemical reduction methods [8], ion exchange, coagulation, electrochemistry, membrane adsorption [9][10][11][12], chemical coagulation[13], membrane filtration [14], and adsorption [4]. The adsorption method is one of the environmentally friendly methods and is relatively inexpensive. The adsorption is effective for removing water pollutants at low concentration, simple, high efficiency, and flexibility in large-scale applications [15][16][17].

Many natural materials can be used as an adsorbent, it has a functional group where the metal ions can binding by physically interacting with electrostatic interactions or Van Der Waals forces or chemically such as displacement of bonding metal cation (ion exchange), formation of chelation complexes, precipitation, reduction [18]. Adsorbent from agricultural waste contains several active functional groups like as amine, amide, imidazole, thioether, sulfonate, carboxyl, sulfohydryl, carboxyl, phosphor diester, phenolic, imine, and phosphate groups which plays a role in the adsorption of metal ions. They are key factors controlling and characterizing these mechanisms in adsorption process. Many agricultural wastes that can be used as adsorption of heavy metal waste include Arenga pinnata shell, durian seeds (Durio zibethinus), langsat seeds (Lansium domesticum), melon seed, palm shell. Durian seed consisted of holocellulose (73.5%), α-cellulose (60.5%), and hemicellulose (13.1%), it has used potential as adsorbents for heavy metal ions [19].

An industrial operation, the use of non-living cells in powder form has several problems such as difficulties in separation after adsorption, mass loss during separation, low mechanical strength, and small particle size, which makes it difficult to use in batch and sustainable systems [20][21]. These problems can be overcome by immobilizing cells using natural or synthetic polymers. Several immobilization media such as alginate, carrageenan, chitosan, chitin, and cellulose derivatives have been used to immobilize biomaterials. Alginate is one of the polymers that are more often used because of its superiority in biocompatibility and cost-effectiveness. Immobilization can increase adsorption capacity and offer opportunities for the retention of biomass in the working environment due to the easy separation of products from cells and relatively high local cell density.

Alginate, a linear polysaccharide composed of -D-mannuronate (M) and -L-guluronate (G), is another natural polymer extracted from brown algae, which naturally contains carboxyl groups in each residual constituent. In addition, acid-base properties or solubility properties have been used to make the encapsulation of active substances in the form of hydrogels and adsorbents with microparticle size. Alginate has been applied in various industries such as textiles, pharmaceutical food and is used as a coagulant and adsorbent for the absorption of heavy metal ions. The function of the carboxylic group of polysaccharides can be considered as a place of absorption of divalent metal ion cations such as Cu(II), Cd II) and Pb(II) [19]. This research aims to study of adsorption Hg (II) ions on durian seed powder immobilized Ca-alginate beads.
2. Experimental Section

2.1 Materials and Equipment
Material: Durian seed was obtained from Ma. Jambi District Province of Jambi, Indonesia. Na-alginate (Sigma Aldrich), vgAll other chemicals used were of analytical grade and distilled water. The equipment in this research were Whatman 42 filter paper, analytical balance (FA 1004G, shaker, and oven. Instrumentation used is X-ray Diffractometer (Shimadzu model XRD-6000), Fourier Transform Infra-Red, hot plate-stirrer, and Atomic Absorption Spectrophotometer (AAS, Perkin Elmer 3110).

3. Methods
The method in this study can be seen in the Figure 1.

![Methods](Figure 1. Series of Methods Used)

3.1 Preparation of Sample
Durian seed washed with distilled water, cut and dried in an oven at 100°C, and grounded with grinder. The durian seed powder shifted with a particle size of 100 µm and dried in an oven at 80°C. Durian seed powder is soaked in 0.1 M HNO₃ for 1 hour while stirring and neutralized with distilled water until pH 7. Durian peel powder has been activated is filtered and dried in an oven at 70°C and particle size was homogenized using a 100 µm sieve.

3.2 Immobilization of Durian Seed
The immobilization of durian seed via entrapment was carryout as follow: Na–alginate as much as 2.0 g dissolved in distilled water and then mixed with durian seed suspension in a ratio of 1: 1. The mixture was put into a solution containing 0.20 M CaCl₂ with a syringe and the solution was stirred to prevent aggregation of Ca-alginate beads trapped in the durian seed suspension. The beads
trapped in the durian seeds were left in the CaCl2 solution for 2 hours and then washed several times with distilled water. The beads with immobilized durian seeds were then removed and dried at room temperature. The immobilized Ca alginate durian seed bead is stored in a bottle [19].

3.3 Preparation of Stock Solution Hg(II)
The stock solution of 1000 mg/L Hg(II) ion was prepared by dissolving Hg(NO3)2.5H2O pro analyze in a 1000 mL volumetric flask. Standard solutions are made with range standard concentrations of 10, 25, 50.75, and 100 mg/L.

3.4 Adsorption Procedure
The adsorption of Hg(II) metal ions in an aqueous solution were done in a batch reactor. An amount of 25 mL of Hg(II) 10 mg/L solution was put into a 50 mL Erlenmeyer. The pH of the solution is adjusted at pH 2-7 by adding 0.1 M HNO3 solution or 0.1 M NaOH. The amount of 0.1g adsorbent was put into Hg(II) solution and shaker at 100 rpm and 15 minutes. At the equilibrium state, the mixture is filtered and the concentration of Hg(II) metal ions in the filtrate were analyzed by AAS. The amount of absorbed Hg(II) metal ions is calculated using the following equation:

\[ Q_e = \frac{C_o - C_e}{v} \times w \]

Where \( Q_e \) is equilibrium uptake capacity (mg/g) of durian seed immobilized alginate bead adsorbent, \( C_o \) is the initial concentration (mg/L) of Hg(II), \( C_e \) is equilibrium concentration (mg/L) of Hg(II), \( v \) is the volume solution of Hg(II) and \( w \) is the mass of adsorbent.

4. Result and Discussion
Alginate is a natural polymer and can be easily converted to hydrogel via crosslinking with Calcium ions. Immobilized cell in alginate bead has the advantage of strong mechanical properties, are hydrophobic, biodegradable, and has many functional groups on the surface of the adsorbent because alginate is rich in carboxyl and hydroxyl groups, it can increase the adsorption capacity. The durian peel immobilized alginate beads have been done by mixing durian peel and Na-alginate in ration 1:1 and dropping mixture into the CaCl2 solution using a syringe and then droplet of the mixture form beads in CaCl2. The durian seed immobilized alginate bead can be seen in Figure 2.

![Figure 2. Gel (a) and (b) Durian Seed Immobilized Alginate Beads](image-url)
4.1 Characterization of Durian Seed Immobilized Ca-alginate Adsorbent

The durian seed immobilized alginate beads adsorbent was characterized by FTIR and shown in Figure 2. The peak at wave number 3269.33 cm\(^{-1}\) and 3850.78 cm\(^{-1}\) indicated stretching -O-H vibration, peak at wave number 2933.31 cm\(^{-1}\) indicated of -CH\(_3\), -CH\(_2\), -CH and -OH stretching vibration, the peak at wave number 2933.31 cm\(^{-1}\) indicated stretching -C=O vibration and absorption band at wave number 2933.31 cm\(^{-1}\) indicated the existence of C-O stretching vibration. The presence of carboxyl and hydroxyl groups in durian seed immobilized alginate bead was confirmed by FT-IR spectra.

Durian seeds are a discarded waste material and due to some of their properties may have various applications in removing heavy metal ions. Durian seeds contain cellulose is high so that it shows a high metal adsorption capacity. The content of agricultural wastes such as proteins, lipids, lignin, hemicellulose, starch, hydrocarbons, and functional groups facilitates metal complexation which helps in the removal of heavy metals. Several types of functional groups are generally involved in the adsorption process, namely hydroxyl, amino and carboxyl groups [22]. These groups play an influential role in the metal adsorption process. Heavy metals are more efficiently absorbed by phenolic, lactonic, and oxygen functional groups compared to other groups.

![Figure 3. FT-IR Spectra of Durian Seed Immobilized in Ca-alginate Bead](http://www.eksakta.ppj.unp.ac.id/index.php/eksakta)
which they are replaced by absorbed metal ions so that the pores are closed again like as the egg process in the egg box. The XRF analysis of elemental composition before and after adsorption can be seen in Tables 1 and 2.

According to data in Table 1, it can be seen the composition element contained before adsorption Hg(II) on durian seed adsorbent. There are several elements in durian seed in macro and micro quantities and there are no Hg(II) ions in the adsorbent. In Table 2, it can be seen element of Hg(II) was 37%. This has shown durian seed immobilized Ca-alginate can adsorb of Hg(II) ion. This is following previous research on durian seed immobilized Ca-alginate for adsorption Zn(II)[19].

**Figure 4.** SEM of Durian Seed Powder (A), Durian Seed Immobilized Ca-alginate before Adsorption (B) and After Adsorption Hg(II) (C)

**Table 1.** Composition of Durian Seed Immobilized Alginate Bead before Adsorption Hg²⁺

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (%)</th>
<th>Compound</th>
<th>Concentration (%)</th>
<th>Compound</th>
<th>Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>0.955</td>
<td>SiO₂</td>
<td>1.750</td>
<td>SiO₂</td>
<td>1.748</td>
</tr>
<tr>
<td>P</td>
<td>2.963</td>
<td>P₂O₅</td>
<td>5.716</td>
<td>P₂O₅</td>
<td>5.712</td>
</tr>
<tr>
<td>S</td>
<td>1.829</td>
<td>SO₃</td>
<td>3.760</td>
<td>SO₃</td>
<td>3.757</td>
</tr>
<tr>
<td>Cl</td>
<td>2.893</td>
<td>Cl</td>
<td>2.257</td>
<td>K₂O</td>
<td>18.348</td>
</tr>
<tr>
<td>K</td>
<td>20.549</td>
<td>K₂O</td>
<td>18.373</td>
<td>CaO</td>
<td>66.129</td>
</tr>
<tr>
<td>Ca</td>
<td>68.310</td>
<td>CaO</td>
<td>66.228</td>
<td>TiO₂</td>
<td>0.066</td>
</tr>
<tr>
<td>Mn</td>
<td>0.022</td>
<td>Mn</td>
<td>0.014</td>
<td>MnO</td>
<td>0.018</td>
</tr>
<tr>
<td>Fe</td>
<td>0.890</td>
<td>Fe₂O₃</td>
<td>0.826</td>
<td>Fe₂O₃</td>
<td>2.177</td>
</tr>
<tr>
<td>Ag</td>
<td>0.519</td>
<td>Ag</td>
<td>0.388</td>
<td>Ag₂O</td>
<td>0.368</td>
</tr>
</tbody>
</table>

**Table 2.** Composition of Durian Seed Immobilized Alginate Bead after Adsorption Hg²⁺

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (%)</th>
<th>Compound</th>
<th>Concentration (%)</th>
<th>Compound</th>
<th>Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.522</td>
<td>Al₂O₃</td>
<td>0.892</td>
<td>Al₂O₃</td>
<td>0.882</td>
</tr>
<tr>
<td>Si</td>
<td>0.318</td>
<td>SiO₂</td>
<td>0.606</td>
<td>SiO₂</td>
<td>0.598</td>
</tr>
<tr>
<td>P</td>
<td>1.943</td>
<td>P₂O₅</td>
<td>3.875</td>
<td>P₂O₅</td>
<td>3.817</td>
</tr>
<tr>
<td>Cl</td>
<td>1.189</td>
<td>Cl</td>
<td>0.976</td>
<td>K₂O</td>
<td>4.619</td>
</tr>
</tbody>
</table>
4.2 Study Adsorption of Hg(II) Ions
4.2.1 The Effect of pH on Adsorption Capacity
pH is one of the important parameters to determine the adsorption capacity of ion metals from an aqueous solution. This is directly related to the ability of hydrogen ions to compete with active sites on the surface of the adsorbent. pH can affect the surface charge of the adsorbent and the degree of ionization on the surface of the adsorbent [23]. The adsorption mechanism is related to physicochemical interactions of heavy metals in solution and functional groups in the adsorbent. In this study, the effect of pH on adsorption capacity has been conducted by interacting 10 mg/L Hg(II) with adsorbent at different pH 3-7 and results can be seen in Figure 4.

![Graph showing the effect of pH on adsorption capacity of Hg(II) on Durian Seed Immobilized Ca-alginate](image)

In Figure 4, it can be seen that the Hg(II) ion adsorbed on the adsorbent increases with increasing pH of the metal ion solution and after reaching the maximum value, the amount of Hg(II) adsorbed will decrease. When the pH increases from 4 to 7, an increase in metal ion adsorption occurs, but after pH 7 is saturated at lower pH, the adsorption capacity of metal ions is smaller. This trend may be explained as follow, at low pH, the concentration of H+ ion in the solution is high, resulting in the active groups on the surface of the adsorbent being protonated and producing a partially positive charge on the functional groups/active site of adsorbent. This condition is not favorable for the occurrence of the interaction between the positively charged Hg(II) and the protonated active groups on the surface of the adsorbent, due to electrostatic repulsion this is due to the metal ions Hg^{2+} competing with H^+ ions to interact with the active site of the surface of durian.

http://www.eksakta.ppj.unp.ac.id/index.php/eksakta
seed immobilized in Ca-Alginate, the only a small portion of metal ions are absorbed. In the process of adsorption, maximum adsorption of heavy metal ions occurs when the pH is between 4 and 7.

The adsorbate molecule would undergo lateral expansion or lateral repulsion at this pH value, thereby reducing the adsorption capacity [23]. At pH below 4 high proton concentrations minimize metal adsorption and above pH 7 metal precipitation will occur. The adsorption of Hg(II) in the bead occurs at pH 6 with an adsorption capacity of 1.786 mg/g. After pH 6 the adsorption capacity of Hg (II) metal ions decreases to 0.411 mg/g. This is in agreement with that reported by the adsorption of Hg(I) occurs at pH 6. At pH 6-7, it is expected that the protonated H⁺ on the surface of the adsorbent is released, so that the active group on the surface of the adsorbent becomes negatively charged. On the other hand, the Hg(II) ion in solution is still in the form of a positive ion, so these are good adsorption conditions that allow for the interaction between Hg(II) and the active groups on the adsorbent surface. The optimum adsorptive capacity of Hg(II) ion at pH 6 due to functional groups undergoing deprotonation and electronegative charge so that interaction between Hg(II) ion and active side groups can occuroptimally [24]. The same optimum pH of 4-6 has been reported by [23] for the adsorption of Hg(II) on activated carbon, while optimum pH of 7 has also been reported for removal toxic Hg from liquid effluents [25]. However, further increasing of pH results in the decrease of the amount of adsorbed Hg(II). This may be attributed to the deposition of Hg(II) as Hg(OH)₂ (K_{sp} Hg(OH)₂ = 3.13x10⁻²⁶). Also, the functional groups on the adsorbent will undergo de-protonation at higher pH, resulting in a partially negative charged active site. Similarly, the Hg(II) ion at higher pH also tends to form a negatively charged complex in the excess of OH⁻ ions. Therefore, electrostatic repulsion of negatively charged species occurs in the solution, as the result, the metal ions are becoming very difficult to interact with the active groups of the adsorbent, leading to the decline in the number of adsorbed metal ions.

4.2.2 Effect of Contact Time on Adsorption Capacity
The rate of adsorption is important for designing batch adsorption experiments. Therefore the effect of contact time on Hg(II) adsorption was studied. Contact time is carried out to determine the optimum time needed for adsorbent to adsorption metal ions maximally. The results measurement of the effect of contact time of adsorbent bead immobilized durian peel can be seen in Figure 5. Adsorption occurs rapidly in the early stages and gradually decreases over time until equilibrium is reached [(26)]. The higher adsorption rate in the initial period may be due to the lack of availability of free active sites on the adsorbent. Equilibrium time was reached at 150 minutes. Over time, the adsorption rate decreases because the active site of the adsorbent can be occupied so that copper ions are difficult to find binding sites. Lack of sufficient active sites to accommodate Hg(II) in solution.

Adsorption capacity Hg(II) increased rapidly from 15 minutes until the contact time reached 150 min. This is possible because the contact time is not enough for the active sides of the adsorbent to interact with the metal in the solution, meaning that not many active groups have the role of adsorbing Hg(II). Based on the research results the optimum time is 150 minutes with an adsorption capacity of Qe is 2.88 mg/g. Further increase in contact time did not increase the adsorption capacity and therefore 150 minutes was chosen as the contact time for further experiments. Figure 5 was showed that adsorption capacity reaches equilibrium state at a contact time of 150 min.

The mechanism of the heavy metal adsorption process can be explained as follows: first, metal ions are transferred from solution to the surface of the adsorbent, which contains various functional groups that act as binding sites, and depending on the pH, cationic or anionic sites are available for adsorption, wherein physical adsorption, chemisorption, or ion-exchange occurs rapidly. Functional groups that have previously been reported to be effective in attracting heavy metal ions are mainly carboxyl, hydroxyl, sulfate, phosphate, amino, amido, and phenolic groups. The first step is mostly
influenced by metal concentration, agitation period and velocity. The second stage involves transport, which is the diffusion of metal ions into the pores of the adsorbent, while the last stage deals with the diffusion of metal ions on the internal surface of the material and is considered a rate limiting step [27].

4.2.3 The Effect of The Adsorbent Mass
The biomass dose is an important parameter because it is related to the adsorption capacity at the initial concentration of the solution. The adsorption capacity Hg(II) ion is as a function of biomass dosage was investigated and the result can be seen in Figure 6. The increased adsorbent dosage caused a decrease in the adsorption capacity of the Hg(II) ion. However, the adsorption capacity becomes nearly constant above this dosage. Therefore, the optimum mass dosage was taken as 0.1 g for further experiments. This result can be explained by the fact that adsorption sites remain unsaturated during the adsorption reaction while the number of sites available for biosorption sites increased by increasing of adsorbent mass. Moreover, the maximum adsorption, 0.1 g for Hg(II) ions was obtained at a biomass dose. The higher mass adsorbent caused the adsorption capacity decreases.

![Figure 6. The Effect of Contact Time on Adsorption Capacity Hg(II) Ion](http://www.eksakta.ppj.unp.ac.id/index.php/eksakta)
4.2.4 The Effect of Concentration on Adsorption of Hg(II) Ion

The effect of the initial concentration of the metal ion solution on adsorption capacity Hg(II) was carried out at a concentration of 10-300 mg/L. The effect of initial concentration is important because there is a difference concentration of metal ions in wastewater [28]. Figure 4 shows the effect of initial concentration on Hg(II) adsorption using alginate immobilized durian seeds. The adsorption capacity increases as the initial concentration of Hg(II) increases. The initial increase in concentration produces a concentration gradient as the driving force to overcome the mass transfer resistance of Hg(II) between aqueous and solid phases during the adsorption process [29], the interaction of Hg(II) with the durian seed immobilized alginate surface increases at high concentration of Hg(II). In this condition, the ratio of available active sites to the initial adsorbate concentration is high but at higher adsorbate concentrations the ratio becomes lower because the active sites are already saturated with adsorbate. Adsorption capacities increased with increasing metal ions. The effect of concentration can be seen in Figure 7. With the greater concentration of metal ions, adsorption capacity will increase because more metal ions will bind to the active groups in the adsorbent. The adsorption of Hg(II) metal ion increasing concentration 300 mg/L with an adsorption capacity is 74.121 mg/g.

Figure 7. Effect of Dosage on Adsorption Capacity Hg(II) by Bead
5. Conclusion
The durian seed immobilized Ca-alginate bead has potential as an adsorbent Hg(II) ion from an aqueous solution. Durian seeds are a discarded waste material and due to some of their properties may have various applications in removing heavy metal ions. Durian seeds contain cellulose is high so that it shows a high metal adsorption capacity. The content of agricultural wastes such as proteins, lipids, lignin, hemicellulose, starch, hydrocarbons, and functional groups facilitates metal complex which helps in the removal of heavy metals. In the adsorption process, optimal conditions were obtained at pH 6, contact time of 30 minutes, the mass of adsorbent 0.1 g, and concentration of 300 mg/L with adsorption capacity 74.121 mg/g. The characterization of FTIR adsorbent durian peel immobilized Ca-alginate bead showed the presence of functional groups such as alcohols, amines, carboxylic acids. The XRF can be seen contained components in bead after adsorption of Hg (II) are 37%. This shows that durian peel has the potential to use as a heavy metal adsorbent.

Reference

http://www.eksakta.ppj.unp.ac.id/index.php/eksakta
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