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Utilization Palm Shell Bioelastomeric as Composite Foams for the Removal Hg^{2+} in Liquid Waste

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Abstract. Efforts to deal with waste using the adsorption method showed effective results. However, it was discussed of the sorbent after the remediation process is cumbersome. An alternative to overcome this problem can be done by fixing the adsorbent into a solid form consisting of a porous polymer without changing its chemical affinity with metal ions. In this study, the adsorbent used was bioelastomeric containing activated charcoal from palm shell waste and elastomeric, which would then be contacted with Hg^{2+} metal ions. The process variable in this study was the composition of heavy metal Hg^{2+} 8, 12, 16, 20, and 24 mg/L with the contact time until it reached equilibrium. Based on the calculation, the palm shell bioelastomeric used three adsorption isotherm models, Freundlich isotherm ($R^2 = 0.991$), Langmuir isotherm ($R^2 = 0.967$) and Dubinin-Radushkevich isotherm ($R^2 = 0.871$). The results showed that the efficiency of adsorption of heavy metal Hg^{2+} with bioelastomeric palm shell was almost close to 100%. In conclusion, palm shell bioelastomeric can be a potential adsorbent with a high heavy metal removal ability.

1. Introduction

Individual activities, as well as the rapid development of industry, cause many environmental problems, one of which is water pollution. Water pollution can occur because of waste from various industrial process activities. In Aceh, there are many industries that operate in the food processing industry and the mining industry. One of them is the gold mining industry in Krueng Sabee, Aceh Jaya, which becomes a highly discussed topic because it uses the amalgamation method. Gold mining activities that contaminate the environment have resulted in adverse impacts on the community and the surrounding environment marked by contamination in soil, aquatic ecosystems, and so forth [1].

Contamination caused by liquid waste can be overcome by various methods, one of which is the adsorption method. An adsorption process is an event that occurs on the surface of the stationary phase, where material from the free period is adsorbed. This process is generally used to reduce heavy metals, ions, and compounds that are harmful to humans and the environment [2]. Research into the use of palm shell's activated charcoal as an adsorbent in the adsorption process showed efficient results for the removal of heavy metals from liquid waste. However, after the procurement process that enhances complicated processes, activated charcoal requires methods such as centrifugation and load screening [3, 4].

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An alternative to overcome this problem was by configuring activated palm oil into a solid form (in the form of porous polymer composites) without changing its chemical affinity using metal ions. It became an attractive solution for increasing the use of more specific activated charcoal applications. Based on research that had been done on the utilization of spent coffee ground as elastomeric composite foams, it was found that spent coffee ground successfully removed heavy metal ions from water. Besides, research on the utilization of elastomeric nanocomposite foams in water contaminated with Pb^{2+} or Hg^{2+} succeeded in removing Pb^{2+} ions exceeding 98% and Hg^{2+} ions approaching nearly 100%. Utilization of biomass waste into bio-based polymer products derived from agricultural raw materials and renewable biomass became more important because this environmentally friendly and sustainable product reduced greenhouse gas emissions [3, 4, 5].

Indonesia is one of the biggest oil palm producers in the world. The area of oil palm plantations in Indonesian is 14,677,560 ha in 2019. Sumatra has 8,762,135 ha of oil palm plantations in 2019, which is the largest oil palm producing area in Indonesia. Aceh is one of the provinces that has extensive oil palm plantations in Sumatra. The area of oil palm plantations in Aceh is 566,378 ha in 2019. Besides that, palm shell waste from palm oil production, which is gradually increasing so far, has been used mainly as fuel. Therefore, palm shell can be used as an adsorbent in the form of polymer composites to add value to it, as it is easily handled and environmentally friendly [6, 7]. It can be used as a source of sorbent due to its organic components, such as cellulose, hemicellulose, and lignin [8].

2. Materials and Methods

2.1 Materials, The palm shell waste was obtained from the palm oil industry in Aceh, Indonesia, and used as the material for making activated charcoal, Acetoxy-Polydimethylsiloxane (PDMS), Poly (ethylene oxide) -b-PDMS, Hexane and Sanding Sugar used as the material for bioelastomeric manufacturing. The other supporting materials were $HgCl_2$ as an artificial contaminant sample and distilled water were also used in this work.

2.2 Preparation of Activated Carbon Sorbent from Palm Shells, The palm shell was dried under sunlight and then carbonized at 350°C for 120 minutes using a muffle furnace until the carbon was formed. The resulting carbon was crushed using ball mill then sifted using a +100/-200 mesh sieve. Then the physics activation process will be carried out by heating using a muffle furnace at a temperature of 800°C for 120 minutes. After the activation process is complete, the carbon is allowed to cool, stored in a desiccator.

2.3 Bioelastomeric Fabrication Process, The foam was made using a sugar leaching technique [9,4], 16 g elastomer (acetoxy-PDMS) and 0.16 g poly surfactant additive (ethylene oxide) -b-PDMS (wt. Ratio 10.0: 0.1) mixed in 12 ml hexane. Furthermore, 0.4 gram of activated charcoal is slowly added to the polymer solution under constant stirring for 1 hour. Then, 12 g of sugar is added to the solution slowly. The mixture is then poured in a Petri dish and placed in a fume hood for 24 hours at room temperature to allow the evaporation of solvents and the formation of polymers. Composites that have been formed are then placed in hot water under an ultrasonic for 2 hours to dissolve sugar, and bioelastomer foam will form.

2.4 Adsorption Test on Artificial $HgCl_2$ Wastewater, Artificial $HgCl_2$ wastewater solution was prepared with varying initial concentrations of 8, 12, 16, 20 and 24 mg/L. A total of 250 ml sample was contacted with 0.8 gram sorbent with the contact time until it reached equilibrium, the process was carried out with a stirring speed of 250 rpm. The concentration of $HgCl_2$ in feed solution and after adsorption was measured Hg using Atomic absorption spectrometer (AAS).

3. Results and Discussion

3.1 Effect of contact time and concentration variation on the adsorption capacity of Hg^{2+} ions

Contact time and concentration variation were factors affecting the adsorption process. Determination of the optimum contact time for adsorption aimed to determine the time needed by the bioelastomeric palm shell sorbents to adsorb the maximum Hg^{2+} ion. The relationship between contact time and concentration variation on the adsorption capacity of Hg^{2+} ions can be seen in Figure 1.

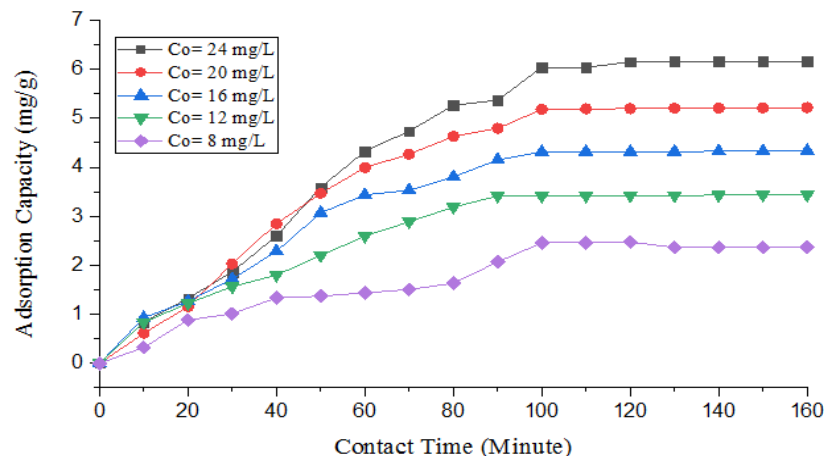


Figure 1. Effect of contact time and concentration variation on the adsorption capacity of Hg^{2+} ions

Based on Figure 1, it can be seen that the adsorption capacity increased along with the increasing adsorbate concentration and the longer contact time. At a high concentration of 24 mg/L, an absorption capacity of 6,171 mg/g was obtained. Meanwhile, at a lower concentration of 8 mg/L, an absorption capacity of 2,371 mg/g was obtained. The higher the concentration of adsorbate, the greater the amount of substance that is collected on the surface of the adsorbent. It happened since there were more dissolved substances dispersed in the solvent, so that the likelihood of contact between the adsorbate and the adsorbent was greater [10]. The maximum adsorption capacity for each variation an average concentration were in 100 minutes, then in the 110 minutes to the 160 minutes the value of the adsorption capacity starts to reach equilibrium ie it has no significant changes. At the contact time of 10 to 100 minutes, the pores on the active surface were large so that the adsorption ability was also high, but starting from the 100th minute, the adsorbent started to saturate. This was indicated by the constant value of absorption capacity and the equilibrium between the concentration of metal ions in activated carbon and metal ions in solution. Thus, the adsorption capacity at contact time above 100 minutes became constant [11].

3.2 Effect of contact time and concentration variation on the adsorption efficiency of Hg^{2+} ions

Adsorption efficiency was the percentage of adsorbate absorption on the surface of the adsorbent. The relationship between contact time and concentration variation on the adsorption efficiency of Hg^{2+} ions can be seen in Figure 2.

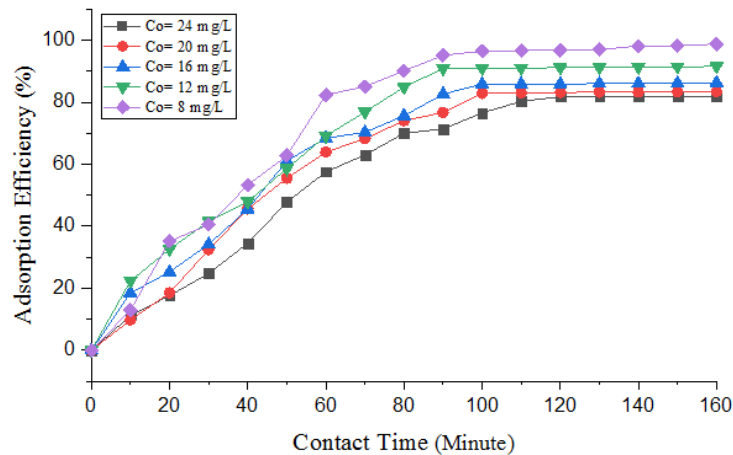


Figure 2. Effect of contact time and concentration variation on the adsorption Efficiency of Hg^{2+} ions

Based on Figure 2, adsorption efficiency was increasing gradually from the contact time of 10 minutes to 100 minutes. The longer the contact time, the greater the ability to bind to the adsorbent and adsorbate. Therefore, more adsorbates were bound to the surface of the adsorbent [12]. The efficiency value from time to time was increasing gradually, but after some time, i.e. above 100 minutes, it showed a constant value that indicated the achievement of equilibrium. At a concentration of 24 mg/L with a contact time of 160 minutes, an absorption efficiency of 81.94% was obtained. Meanwhile, at a concentration of 8 mg/L with the same contact time, an adsorption efficiency value of 94.61% was obtained. This showed that adsorbate concentration that was too high caused a decrease in absorption efficiency. The decrease occurred due to the higher concentration, the amount of metal ions in solution was not proportional to the amount of available adsorbent. Thus, the surface of the adsorbent reached saturation point and absorption efficiency did not increase significantly [10, 11].

3.3 Adsorption isotherm

Adsorption isotherm was used to describe the relationship between the adsorbent and the adsorbed substance in equilibrium [4, 13, 14]. This research tested three adsorption isotherm models, namely Langmuir isotherm, Freundlich isotherm and Dubinin-Radushkevich isotherm. The Langmuir Hg^{2+} adsorption isotherm was obtained by making a comparison curve between the equilibrium of the liquid phase (C_e) against the equilibrium of the solid phase (C_e/q_e). The comparison graph of Langmuir isotherm can be seen in Figure 3.

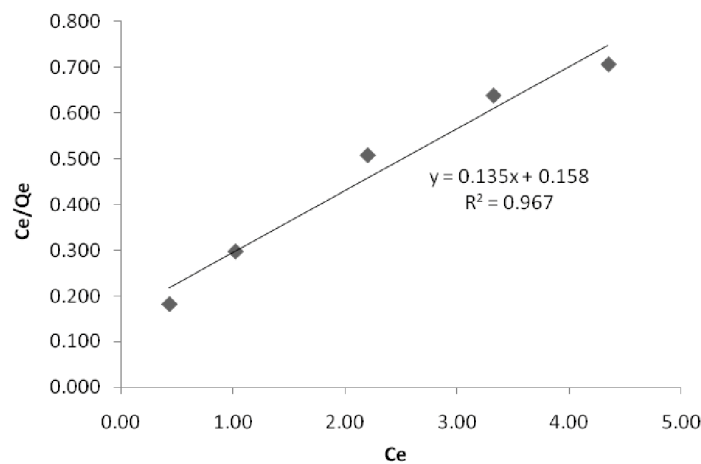


Figure 3. Langmuir isotherm model on the adsorption of Hg^{2+} ions

Freundlich adsorption isotherm was obtained by determining the relationship between $\log C_e$ and $\log q_e$. The Freundlich isotherm graph can be seen in Figure 4.

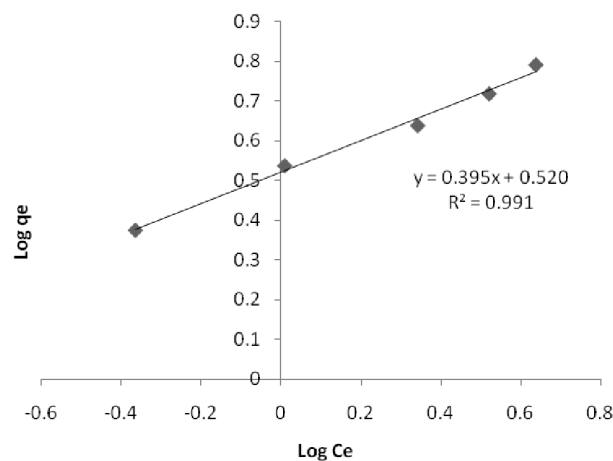


Figure 4. Freundlich isotherm model on the adsorption of Hg^{2+} ions

Dubinin-Radushkevich adsorption isotherm was obtained by determining the relationship between ϵ^2 and $\ln q_e$. The Dubinin-Radushkevich isotherm graph can be seen in Figure 5.

Based on Figure 3, Figure 4, and Figure 5, it can be seen that the adsorption of Hg^{2+} ions using palm shell bioelastomeric foam followed the Freundlich isotherm model. This can be seen from the value of the determinant coefficient (R^2) of the Freundlich isotherm model, which was equal to 0.991. It was higher than the determinant of the Langmuir and Dubinin –Radushkevich isotherm model, which was value to 0.967 and 0.871. The Freundlich isotherm assumed that the surface of the adsorbent was heterogeneous; the adsorption formed many layers. This allowed the adsorbate to move freely until the adsorption process physically occurred in those layers [14].

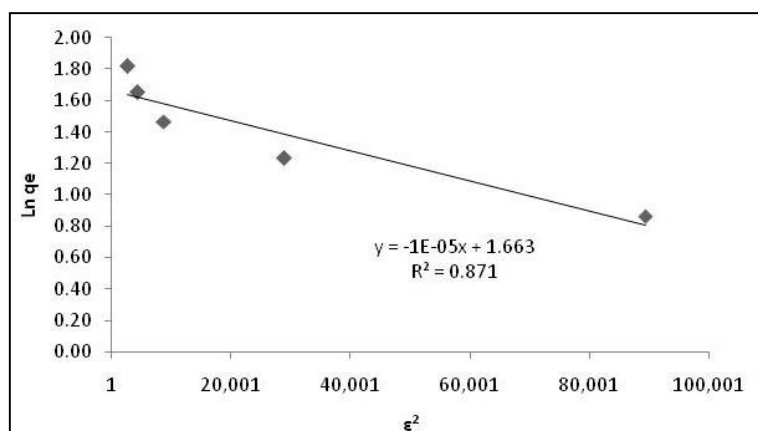


Figure 5. Dubinin-Radushkevich isotherm model on the absorption of Hg^{2+} ions

Dubinin-Radushkevich isotherm model described the adsorption relationship using the Gaussian energy distribution on the heterogeneous surface of the adsorbent [14]. From Figure 5, it can be determined that the free energy was $E = 0.7 \text{ kJ/mol}$, which showed the physisorption process. Based on the three isotherm models analyzed, the value of the adsorption capacity and its constant in each isotherm model can be seen in Table 1

Table 1 The results of the calculation of adsorption isotherm

Langmuir Isotherm			Freundlich Isotherm			Dubinin-Radushkevich isotherm		
q_m	K_L	R^2	n	K_F	R^2	q_m	K_{ad}	R^2
7,4074	0,854	0,967	2,5316	3,3113	0,991	1,508	1×10^{-5}	0,871

4. Conclusion

In conclusion, the present study demonstrates that the utilization of bioelastomeric palm shell waste as an adsorbent for the adsorption of heavy metal Hg^{2+} produces good adsorption efficiency. The adsorption efficiency of Hg^{2+} increases with increasing contact periods and the lower concentration of the solution. At a concentration of 24 mg/L with a contact time of 160 minutes an absorption capacity of 6.171 mg/g was obtained and an absorption efficiency of 81.94% while at a concentration of 8 mg/L with the same contact time an absorption capacity of 2.337 mg/g was obtained and an efficiency value adsorption of 94.61% was almost close to 100% . The adsorption process is more likely to follow the Freundlich isotherm model with a determinant value of R^2 of 0.991 .

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