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Composite of Hydroxyapatite (HAp) from *Meretrix meretrix* Shells and Biochar from Cassava Peel (*Manihot esculenta*) as Green Adsorbent for Cadmium Removal

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This study aimed to determine the characteristics of hydroxyapatite (HAp)-biochar adsorbent from *Meretrix meretrix* shells and cassava (*Manihot esculenta*) peel biochar using Fourier Transform Infra-Red (FTIR), and Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX) analysis, efficiency of Cd (II) adsorption based on pH variation and Cd (II) concentration. The results obtained showed that optimum pH of adsorption was 7, optimum Cd (II) concentration was 50 mg/L. The results of FTIR analysis showed the presence of CO_3^{2-}; C≡C; C=C; C-H; PO_4^{3-} in the composite of hydroxyapatite and biochar. SEM-EDX results obtained showed the morphology of hydroxyapatite-biochar adsorbents of *Meretrix meretrix* shells and cassava peel (*Manihot esculenta*) biochar, favoured to Cd (II) removal.

1. Introduction

Since the industrial revolution, the use of chemicals in products has increased in number and type. This has led to an increase in the volume of waste generated, which has become one of the causes of environmental pollution. Water pollution is a major global problem that requires evaluation and revision of water resources policies at any levels. Water pollution can occur anywhere at a very fast rate and an increasingly heavy pollution load due to industrial waste from various chemicals including heavy metals (Azis et al., 2023).

Heavy metal waste produced by an industry is considered as one type of environmental pollutant that is very dangerous because it is non-biodegradable, toxic, and able to bioaccumulate in the food chain so that it is included in the hazardous waste group. Cadmium (Cd) waste from industrial activity can menace the environment (Charkiewicz et al., 2023). The disposal of waste containing heavy metals into aquatic system is regulated to meet the quality standards of aquatic system (e.g. river water). The regulation is important as implementation of environmental protection and management. It limits the amount of cadmium waste that can be found in the environment. The presence of cadmium in water or wastewater with concentrations exceeding the threshold can have a negative impact on the environment. Therefore, efforts are needed to reduce environmental pollution by cadmium.

Several techniques, such as ion exchange, sedimentation, adsorption, and biological treatment have been successfully used to remove heavy metal contaminants from aqueous solutions (Fei and Hu, 2023). Among these techniques, adsorption has drawn increasing interest because of its benefits for heavy metals treatment, including its high efficiency, affordability, ease of application, and selectivity ().

Hydroxyapatite (HAp) has been utilized as an adsorbent to reduce contaminants such as heavy metals, dyes, hydrocarbons, as well as other pollutants in wastewater. This is because HAp has characteristics that support adsorption such as functional groups, surface charge and porosity (Fatimah et al., 2018). Several reports show the ability of HAp in removing heavy metals such as Pb (Iconaru et al, 2018; Le et al. 2019). The mixture of HAp and biochar is interesting. There was report on the utilization of HAp and biochar to remove heavy metals. The HAp used was made from $Ca(OH)_2$ and biochar from rice husk (Fu et al. 2018).

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Meretrix meretrix (a kind of clam) are easily available in Southeast Asia and its shells have not been optimally utilized, cassava (*Manihot esculenta*) peels are also found in abundance. Both materials have the potential to be used as adsorbent. This research contributes to the adsorption of cadmium using a composite of HAp from *Meretrix meretrix* shells-biochar from cassava peel waste as a green adsorbent.

2. Materials and methods

2.1 Preparation of *Meretrix meretrix* Shells Powder

Meretrix meretrix shells as raw material for hydroxypatite (HAp) were washed and the shells were separated from the remaining meat that was still attached to the clam shells. The clam shells were washed by running water and rinsing until getting clean. The clam shells that had been washed were then dried under sun light for at least 3 days. Dried *Meretrix meretrix* shells were then pulverize. *Meretrix meretrix* shells were kept in the oven at 120 ºC for approximately 24 hours until the mass of the shells became constant (no mass change). It was then sieved using a sieve to get *Meretrix meretrix* shells in powder form. It was then calcined in a furnace at 900 ºC for 4 hours then the clam shells powder was ready for use.

2.2 Preparation of Cassava (*Manihot esculenta*) Peel Biochar

Cassava peels were washed by running in water and rinsing again to get clean condition. Cassava peels that had been washed clean were then cut into small pieces and dried under sun light for several days. The dried cassava peels were pyrolyzed by a pyrolyzer for approximately 2 hours at 350 ºC. After becoming biochar, biochar was pulverized until it became powder. Furthermore, sieved with a sieve to get cassava biochar (*Manihot esculenta*) in powder form.

2.3 Adsorbent preparations

Composite hydroxyapatite (HAp)-biochar from *Meretrix meretrix* shells and cassava (*Manihot esculenta*) peel biochar were prepared by wet chemical precipitation method (Fu et al., 2018). To prepare the adsorbent, CaO from *Meretrix meretrix,* cassava biochar, H_3PO_4 solution were used. The CaO, cassava biochar and H_3PO_4 solution was stirred until homogeneous. The treatment was made at 40 °C with a pH of 10. The mixture was stirred using a magnetic stirrer for 24 hours at 40 °C. The composite of hydroxyapatite (HAp)-biochar that had been treated for 24 hours is then washed 3 times using demineralized water and dried at 40 °C for 3 days. The final product is said to be hydroxyapatite when the Ca/P ratio = 1.67. Comparison of the two elements obtained from SEM-EDX analysis results.

2.4 Adsorbent characterization

Characterization test of composite hydroxyapatite (HAp)-biochar fom *Meretrix meretrix* shells and cassava (*Manihot esculenta*) peel biochar using FTIR (Fourier Transform Infra-Red) and SEM (Scanning Electron Microscope) and EDX (Energy Dispersive X-Ray) analysis. The samples containing the hydroxyapatite (HAp)-biochar composite were put into an airtight container to be analyzed using the FTIR method (Thermo Scientific Nicolet iS10). The FTIR test was conducted using a wavelength of 400-4000 cm^{-1}. In addition to FTIR, SEM-EDX (Hitachi Flexsem 100) analysis was also conducted to determine the morphology of the adsorbent and its content.

2.5 Adsorption experiment

To study the effect of pH, this study used variations in pH levels of 2, 3, 4, 5, 6, 7, and 8. Adjustment of the pH was done using 1 M HCl and 1 M NaOH solutions. Synthetic Cd (II) solution of 50 mg/L (100 mL) was adjusted according to the pH variation used. The synthetic Cd(II) solution was then put into a 100 mL glass bottle and then 0.4 g adsorbent of hydroxyapatite (HAp)-biochar. The solution was then stirred using a shaker with a speed of 160 rpm for 90 minutes. The solution was then allowed to stand for 1 minute to ensure that the precipitate had settled completely. Then, it was filtered. The filtered sample was transferred into sample bottle for further analysis using the Atomic Adsorption Spectrophotometry (Shimadzu AA-700) method. The study the effect of adsorbate concentration was carried out in the same way as the study of pH. the adsorbate concentration variations used were 5, 10, 15, 25, 50, 75, 100, 125, and 150 mg/L.

3. Results and discussions

3.1 Characterization of adsorbent

The results of FTIR analysis of the hydroxyapatite (HAp)-biochar from *Meretrix meretrix* shells and cassava (*Manihot esculenta*) peel biochar before and after adsorption can be seen in Figure 1.

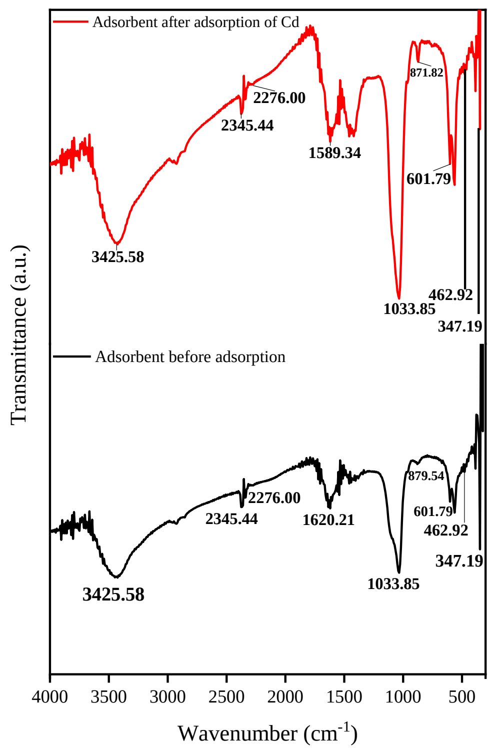

Figure 1: Result of FTIR analysis

Table 1: Fourier Transform Infra-Red (FTIR) analysis results

Wave Number (cm^{-1})		**Wave Number Range (cm^{-1})**	**Functional Groups**
Before Adsorption	**After Adsorption**		
3425.58	3425.58	3800 – 2600	OH^-
2345.44	2345.44	1900 – 2400	CO_3^{2-}
2276	2276	2250 – 2400	C≡C
1620.21	1589.34	1580 – 1660	C=C
1033.85	1033.85	1030 – 1100	PO_4^{3-}
879.54	871.82	829.39 – 879.54	C–H
601.79	601.79	550 – 600	PO_4^{3-}

FTIR graphs have points that indicate peak conditions. Peak conditions are defined as conditions when the graph has a significant decrease, indicating the presence of certain functional groups in the adsorbent. FTIR analysis was performed using wave numbers 4000-300 cm^{-1}. The graph of FTIR test results above shows that there are vibrational adsorption bands of functional groups present in the adsorbent. At wave number 3425.58 cm^{-1} there is OH- functional group. At wave number 2345.44 cm^{-1} there is CO_3^{2-} functional group, while at wave number 2276 cm^{-1} there is C=C functional group. At wave numbers 1033.85 cm^{-1} and 601.79 cm^{-1} there are PO_4^{3-} functional groups. The main peak observed at around 1620.21 cm^{-1} has a C=C functional group. This peak shifts from 1620.21 to 1589.34 cm^{-1} and thus reveals the possible involvement of C=C groups in the adsorption of Cd. It also occurs at a wave number around 879.54 cm^{-1} which shifts to 871.82 cm^{-1} which indicates the presence of hydrocarbon derivatives, namely C-H. Functional groups that have a high affinity such as OH- and C=C on the adsorbent have high potential to adsorb metals (Yang et al., 2019). Compilation related to the functional groups contained in the composite adsorbent of hydroxyapatite (HAp)-biochar from *Meretrix meretrix* shells and cassava (*Manihot esculenta*) peel biochar can be seen in Table 1. The peaks change indicates interaction between adsorbate and adsorbent (Fatimah et al., 2018).

SEM analysis in this study was conducted before and after adsorption of Cd(II). Based on Figure 2., the results of SEM analysis before and after adsorption, they have surface morphology results that are not much different. Based on SEM results with 2500x magnification, it can be seen that hydroxyapatite (HAp) envelops the biochar surface. This is due to differences in size and synthesis methods. Based on the SEM results obtained, it can be seen that the morphology of hydroxyapatite (HAp)-biochar synthesized from *Meretrix meretrix* shells and cassava (*Manihot esculenta*) peel biochar is in the form of cassava biochar surface which is plastered with hydroxyapatite (HAp) particles. There is combination of HAp and biochar, thus exposing active sites favored to of heavy metal ions removal (Fu et al., 2018).

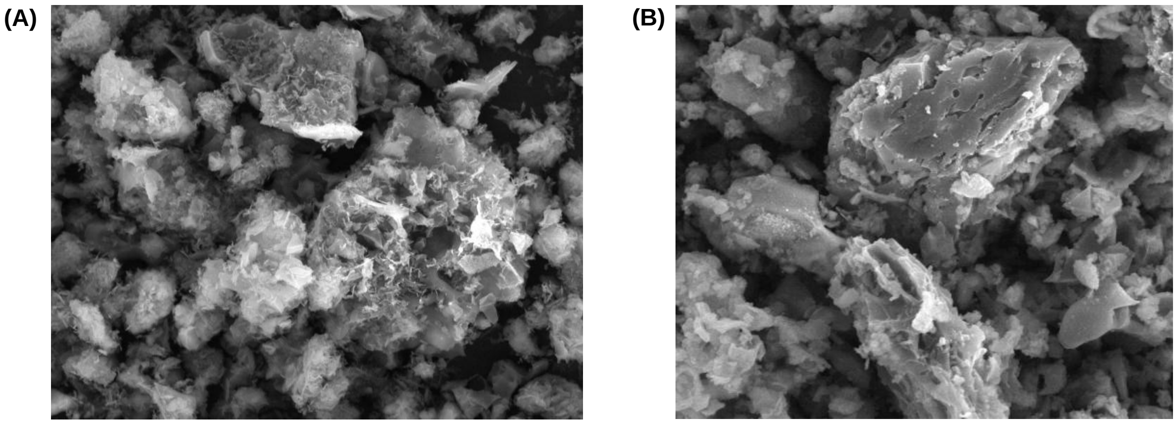

Figure 2: SEM analysis of hydroxyapatite (HAp)-biochar (A) before adsorption (B) after adsorption 2500x magnification

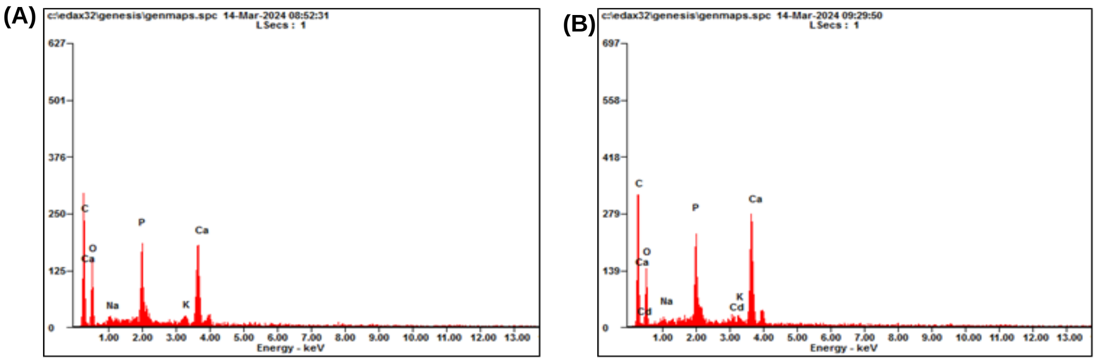

Figure 3: EDX analysis of hydroxyapatite (HAp)-biochar (A) before adsorption (B) after adsorption

Based on Figure 2, morphological differences are found in the appearance of white spots on the adsorbent surface and scattered throughout the adsorbent particles. In the picture before adsorption, there are irregular granules. besides that there are also voids. This cavity can be a place for heavy metal attachment.This shows that there is adsorption of Cd(II) metal on the surface of the adsorbent, namely hydroxyapatite (HAp)-biochar. The SEM morphology results of this study are in line with the other research results (Moirana et al., 2023) which show the morphology of the hydroxyapatite-biochar adsorbent, namely HAp which envelops biochar. In this study, EDX tests were carried out to obtain information about the chemical elements of hydroxyapatite (HAp)-biochar synthesized from *Meretrix meretrix* shells and cassava (*Manihot esculenta*) peel biochar. The elements in the adsorbent before adsorption and after adsorption can be seen in Figure 3. Visible red lines indicate the presence of many elements. The composite of hydroxyapatite (HAp)-biochar before adsorption contains the elements of carbon, calcium, oxygen, sodium, phosphate, and potassium. The presence of Cd metal is very small with a weight percent of 3.54% (after adsorption). This is proof that Cd is adsorbed.

3.2 Effect of pH

pH can affect the charge of an adsorbent and the metal speciation. Figure 4 (A). shows the efficiency of cadmium removal based on pH variation. At pH 2, 3, 4, 5, 6, 7, 8 the average removal efficiency values were 56.21%; 60.32%; 70.66%; 77.03%; 85.67%; 91.34%, 89.93%, respectively. There is significant difference of removal efficiency from pH range of 2 to 8. At acidic pH, cadmium form in the solution is Cd^{2+} so there is competition between protons and the positive charge of Cd^{2+} ions on the adsorbent surface. This causes the small adsorption of Cd^{2+} ions that occur (Le et al., 2018). Adsorption of Cd^{2+} ions increased at pH 6 to 7 with removal efficiency values above 80%. This is due to reduced competition between protons (H^+) and positively charged metal ions (Cd^{2+}) on the adsorbent surface which results in low repulsion of Cd^{2+} ions, so that metal ions can be easily adsorbed in the adsorbent. At pH 8, there is a decrease in the removal efficiency value because the value is close to the pH value of Cd metal precipitation so that the ability of the adsorbent to perform sorption is reduced because the metal will experience precipitation or deposition.

3.3 Effect of concentration

Based on Figure 4 (B), it can be seen the results of Cd (II) adsorption efficiency using adsorbent with variation of adsorbate concentration tends to decrease as adsorbate concentration increases. The lowest Cd (II) adsorption efficiency results (29.26%) occurred at 150 mg/L of adsorbate concentration while the highest efficiency (99.48%) obtained at 5 mg/L adsorbate concentration. This occurs because higher concentration of adsorbate, the ability of adsorbent to bind becomes weaker. The opposite is that the lower the concentration of adsorbate, the adsorbent's ability to bind is higher. There is no significant difference of removal efficiency from the metal concentration data of 0 to 25 mg/L.

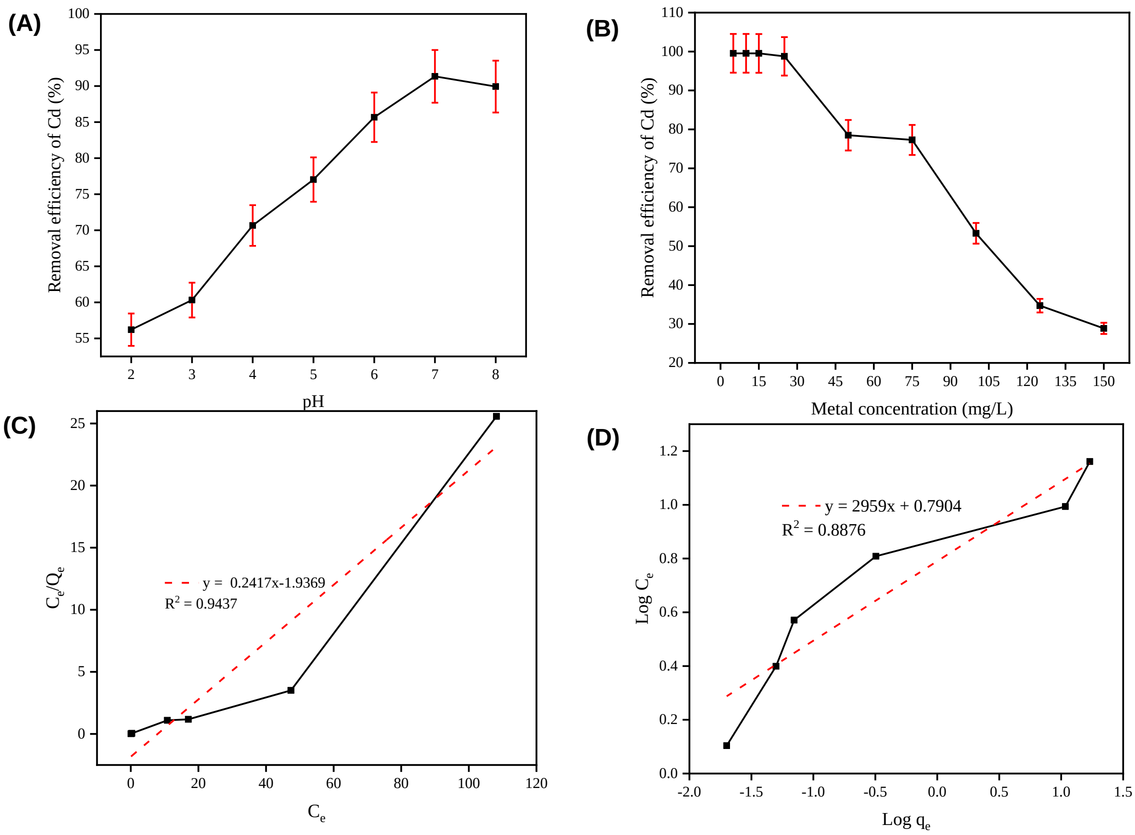

Figure 4: The efficiency of cadmium removal based on (A) pH variation (B) adsorbate variation. (C) Langmuir isotherm model (D) Freundlich isotherm model

Determination of the adsorption isotherm model used data derived from experiments varying the concentration of adsorbate. The most suitable isotherm model is determined based on the coefficient of determination or known as R^2. The coefficient of determination is limited to $0 < R^2 \leq 1$, where the higher the R^2 value, the more linear the curve based on the linear regression equation. Therefore, R^2 values that are closer to 1 indicates a better fit to isotherm model. Based on Figure 4 (C), the result of regression line equation of Langmuir isotherm model is $y = 0.2417x + 1.9369$ with a coefficient of determination (R^2) of 0.9437. Based on Figure 4 (D), the result of regression line equation of Freundlich isotherm model is $y = 0.2959x + 0.7904$ with a coefficient of determination (R^2) of 0,8876. From these results, it is considered that the data follows Langmuir isotherm model.

4. Conclusion

Through the results of characterization, the influence of pH and adsorbate concentration, the composite of hydroxyapatite (HAp)-biochar from *Meretrix meretrix* shells and cassava (*Manihot esculenta*) biochar showed good sorption performance. The results of SEM-EDX analysis show that there are several elements in the adsorbent, namely C, O, Na, P, K, and Ca while the morphology of the adsorbent is hydroxyapatite (HAp) particles envelops the surface of the biochar. The optimum condition of cadmium removal using hydroxyapatite (HAp)-biochar adsorbent is obtained at pH 7 and adsorbate concentration of 50 mg/L. The results showed that the composite of hydroxyapatite (HAp)-biochar from *Meretrix meretrix* shells and cassava (*Manihot esculenta*) biochar shows potential applications as excellent sorbent for the reduction of Cd (II) from polluted waters.

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