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HORN SNAIL (*Telescopium* sp) AND MUD CRAB (*Scylla* sp) SHELLS POWDER AS LOW COST ADSORBENTS FOR REMOVAL OF Cu^{2+} FROM SYNTHETIC WASTEWATER

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ABSTRACT

The use of natural materials like horn snail (*Telescopium* sp) and mud crab (*Scylla* sp) shells as low cost adsorbents for the removal of heavy metal such as Cu from synthetic wastewater has been developed in this research. The experiments were performed in laboratory scale on the 0.025 L wastewater volume; 0.5 g adsorbent mass; and 0.5; 1; 2; 3; and 4 hours contact time variations. The results obtained showed that equilibrium time for adsorption was 2 hours with adsorption capacity of 4.5868 mg g^{-1} with horn snail shell powder and 4.3233 mg g^{-1} with mud crab shell powder. The FT-IR analysis result of horn snail shell powder showed that it contained functional groups of C=O and O-H. The FT-IR analysis result of mud crab shell powder showed that it had same functional groups with horn snail shell powder with addition of N-H bending. The peak of wavelength occurred on 324.04 cm^{-1} because the formation of complex ion between Cu with functional groups that contained in the adsorbents. The SEM-EDX analysis result of horn snail shell powder showed that there was ion exchanging happened between Ca^{2+} and Cu^{2+}.

Keywords: Adsorption capacity of Cu^{2+}, Horn snail (*Telescopium sp.*), Mud crab (*Scylla sp.*), Shell powder, FT-IR analysis, SEM-EDX analysis.

INTRODUCTION

In Indonesia, industrialization developed rapidly over a short period of time that had positive impact in country development. On the other hand, the industries also produced hazardous waste that could contaminated waters, including heavy metal content like Cu that toxic and non-biodegradable in environment.[1] Because of that, heavy metal reduction that has been done from the source got a lot of attention in recent years, including adsorption technique.[1,2]

Adsorption has been used in industrial wastewater treatment, including to reduce components such as toxic components that hard to apart.[2] Adsorption had many advantages, such as high efficiency, low operational cost, and more environmental friendly if compared with conventional treatment.[3] Majority of heavy metal adsorbent that used were from waste that plenty and cheap[4-6], like horn snail shell (*Telescopium* sp.) and mud crab shell (*Scylla* sp.). Horn snail (*Telescopium* sp.) and mud crab (*Scylla* sp.) were animals that had economic value because it could be consumed.[1,7,8]

Horn snail shell powder contained chitin (19-28%) and calcium carbonate (65-70%) that potentially used as heavy metal adsorbent in wastewater that cheap and effective.[9] On the other hand, mud crab shell contained chitin (18.70-32.20%) and calcium carbonate (53.70-78.40%) that had same function.[10] For that reasons, this research was conducted to investigate the adsorption capacity of Cu^{2+} from adsorbents. The obtained results then used to find the adsorption equilibrium time.

The interaction between horn snail shell and Cu ion were determined by SEM-EDX and FT-IR. The interaction between mud crab shell and Cu ion were determined by FT-IR.

EXPERIMENTAL

Material and research equipment

Materials used in this study are horn snail and mud crab shells, $CuSO_4.5H_2O$ (SAP Chemicals), 0.1 M HNO_3, distilled water, filter paper, plastic clip, and labels.
The equipment used in this study are mortar and pestle, oven (Memmert), 50 and 80 mesh sieve, Ohaus analytical balance, glass bottle for sample, spatula, pipette, vacuum pump, Duran Buchner Erlenmeyer and funnel, stopwatch, Wina Instrument type 109 shaker, Shimadzu AA-700 Atomic Absorption Spectrophotometry (AAS), Hitachi TM3000 and SwiftED3000 SEM-EDX, Shimadzu IRPrestige21 Fourier Transform Infrared Spectroscopy (FTIR), and some glassware are commonly used.

Preparation of shell powder from horn snail (*Telescopium* sp) and mud crab (*Scylla* sp) as adsorbents

Horn snail shells were collected from fishpond and waste mud crab shells were obtained from restaurant in Surabaya, Indonesia. The horn snail and mud crab shells were washed several times with distilled water to remove impurities, after which they were dried for two days under the sun. The materials were then crushed manually and passed through 80 mesh sieve to obtain a homogeneous particle size. After that, the materials were dried again at 105.5°C in oven for one hour to reduce the water content. The prepared adsorbents were then stores in a desiccator until further experimentation.

Adsorption experiments based on contact time variation

Synthetic wastewater was prepared individually by dissolving the appropriate amounts of copper sulfate ($CuSO_4.5H_2O$) to obtain Cu^{2+} solution. The initial metal concentrations was set at 100 mg L^{-1}. For the batch experiments, 0.5 g of each adsorbent (horn snail and mud crab shells powder) was mixed with 25 mL of initial metal solution in a 50 mL glass bottle on a shaker at 25°C and 100 rpm. The pH of aqueous solution was at original pH (6.8) and 0.5; 1; 2; 3; and 4 h contact time variations. After that each times, the suspensions were filtered using filter paper and the metal concentrations remaining in the supernatant were analyzed by AAS (Shimadzu AA-700).

Analysis of adsorption capacity

The adsorption capacity is expressed as-

$$Q = \frac{x}{m} = \frac{V(C_0 - C_a)}{m} \quad (1)$$

Where, V is the initial metal solution volume (L), C_o is the initial concentration of Cu solution (mg L^{-1}), C_a is the final concentration of Cu solution (mg L^{-1}), and m is the mass of adsorbent (g). Obtained results can showed the equilibrium time from each adsorbents.

Surface structure and functional group analysis of adsorbents

The surface structure of horn snail shells powder after adsorption was analyzed by scanning electron microscopy (Hitachi TM3000 and SwiftED3000). Additionally, the functional groups of shells powder of horn snail and mud crab were determined by Fourier Transform Infrared Spectroscopy (Shimadzu IR Prestige 21).

RESULTS AND DISCUSSION

Adsorption capacity of Cu ion using horn snail (*Telescopium sp*.) and mud crab shell powder (*Scylla sp*.) based on contact time variation

Adsorption capacity is one of the influential factors in the Cu adsorption process in synthetic wastewater. Contact time variation was done to determine the equilibrium time when Cu adsorbed in 25 mL waste, adsorbent mass of 5.0 g, pH 6.8, and wastewater concentration of 100 mg L^{-1}. The result obtained showed that the adsorption equilibrium time were 2 hours with adsorption capacity of 4.5868 mg g^{-1} for horn snail shells powder and 4.3233 mg g^{-1} for mud crab shells powder. The correlation curve between contact time and Cu adsorption capacity from each adsorbents showed in Fig.-1.

The longer duration of contact time between Cu^{2+} ions with adsorbents affected the Cu^{2+} adsorption by the adsorbents. The longer duration of contact time, then more heavy metal were adsorbed until the adsorbent became saturated. The results kept rising from contact time of 0.5 hour until 2 hours and showed that adsorbents surface could be bonded with Cu^{2+} ion so it could be adsorbed.[11]
At contact time of 2 hours the equilibrium has been reached and it showed by the stagnancy results of adsorption capacity in the further contact. This results occurred because the adsorbents has been saturated so it couldn't be used to adsorb again, even it could cause desorption inside the wastewater.[12]

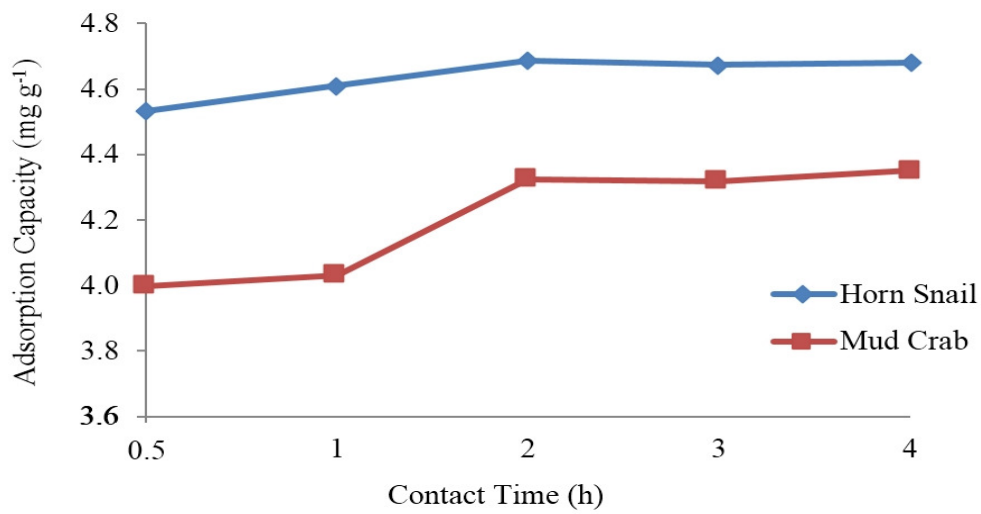


Fig.-1: Correlation curve between contact time and the adsorption capacity of adsorbents

FT-IR characterization of adsorbents
The FT-IR spectrum of horn snail and mud crab shells powder is shown in Fig.-2. The FT-IR spectra for horn snail shells powder was evaluated in the range of 375-4000 cm^{-1} and for mud crab shells powder in the range of 300-4000 cm^{-1}. In both of them spectra, the bands appear to be centered between 2400-3500 cm^{-1} (for O-H), 1550-1640 cm^{-1} (for N-H bending), 1660-1820 cm^{-1} (for C=O), and ≤ 350 cm^{-1} for the bond with heavy. O-H and N-H bending showed that there was chitin in adsorbents, and C=O showed that there was carboxyl that came from calcium carbonate.[13,14]
From the results of FT-IR obtained showed that both adsorbents contained calcium carbonate because there was carboxyl (C=O). Chitin only showed on mud crab shell powder because amine bending (N-H bending) wasn't detected in horn snail shell powder. This could be considerate because horn snail shell only contained few chitin. On the other hand, the calcium carbonate content made horn snail shell still could be utilized as natural heavy metal adsorbent.[15]
The FT-IR result of horn snail shell was different from mud crab shell that often used as one of natural chitin source and heavy metal adsorbent. O-H and N-H bending was detected, completed with the peak of wavelength that occurred on 324.04 cm^{-1}. That could gave information about the possibility of ion complex formation between Cu and the exist functional groups.[14]

Morphology structure and horn snail (Telescopium sp.) shell powder content after adsorbed using SEM-EDX
Adsorption is a general term that includes adsorption processes that occur at the solid/solution interface, as well as those in which a solute (molecule or ion) penetrates the bulk of the adsorbent phase. In this study, adsorption could be known by observing the morphology of adsorbent surface and unsure that contained in horn snail shell powder. Only horn snail shell analyzed using SEM-EDX because from the result of FT-IR,

the functional groups that could be used to indicate the chitin weren't found. The result of SEM-EDX showed in Fig.-3.

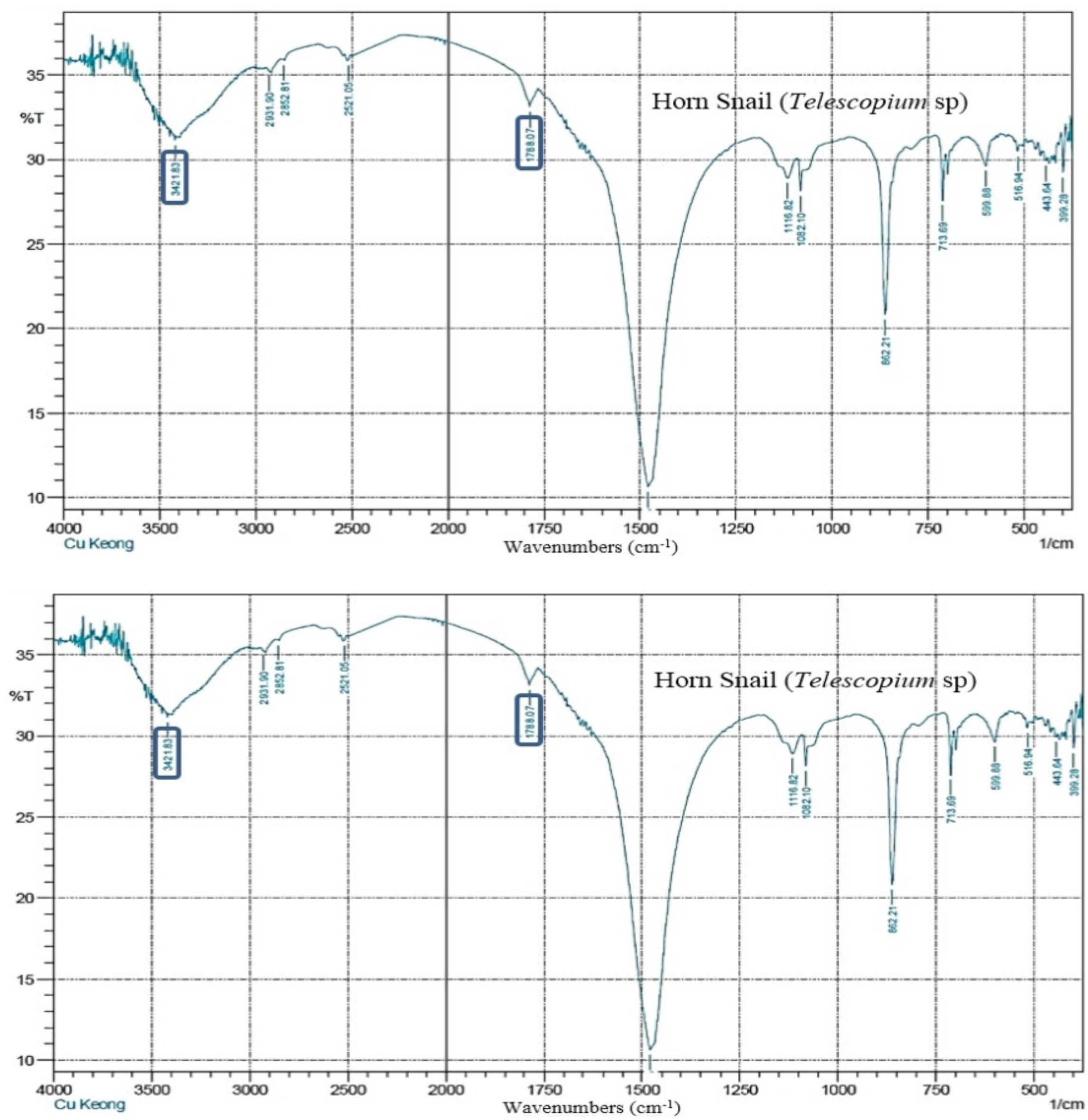
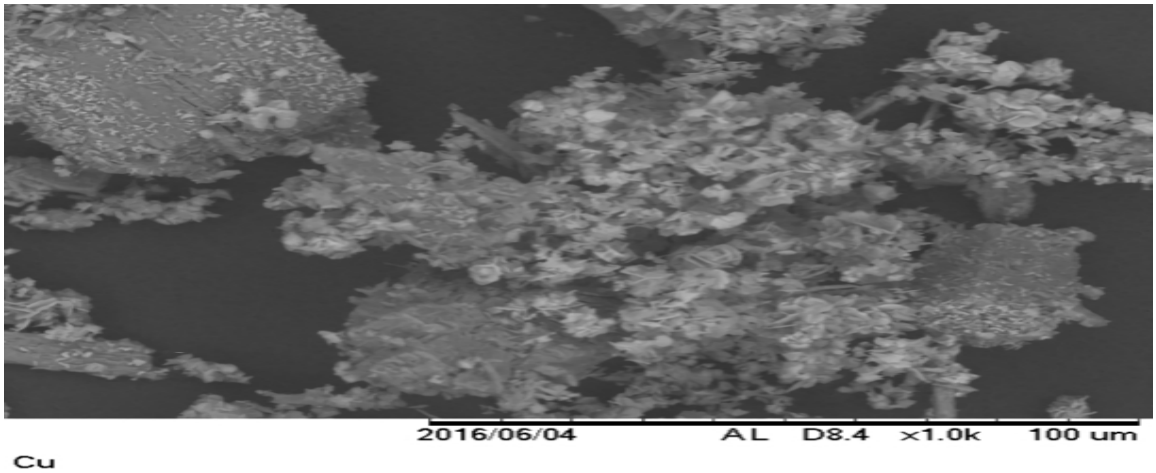


Fig.-2: FT-IR spectra of horn snail and mud crab shells powder used in the experiment

The SEM analysis result showed that the adsorbent surface was hollow and had sharp blob. The EDX analysis result showed that adsorbent after used to adsorb contained Cu unsure besides Ca, C, and O unsure that usually most found in animal shell. Cu unsure that had 3 peaks of energy value at 3.4, 7.8, and 8.8 KeV could showed the existence of Cu ion in the adsorbent. The existence of Cu unsure that contained in adsorbent after contacted with Cu synthetic wastewater could proofed that horn snail shell powder has been adsorbing Cu^{2+}. The percentage of mass for each unsure that contained in adsorbent showed in Table-1.
Cu had bigger content if compared with Ca, proofed the presumption that ion exchange was occurred between Ca and Cu ion. Ion exchange was chemical reaction where Cu ion in synthetic wastewater exchanged with ion in adsorbent that had the same valence with Cu ion, in this research was Ca ion. Ca ion was easier to be replaced by Cu ion because the Cu ion affinity was bigger than Ca ion.[16]



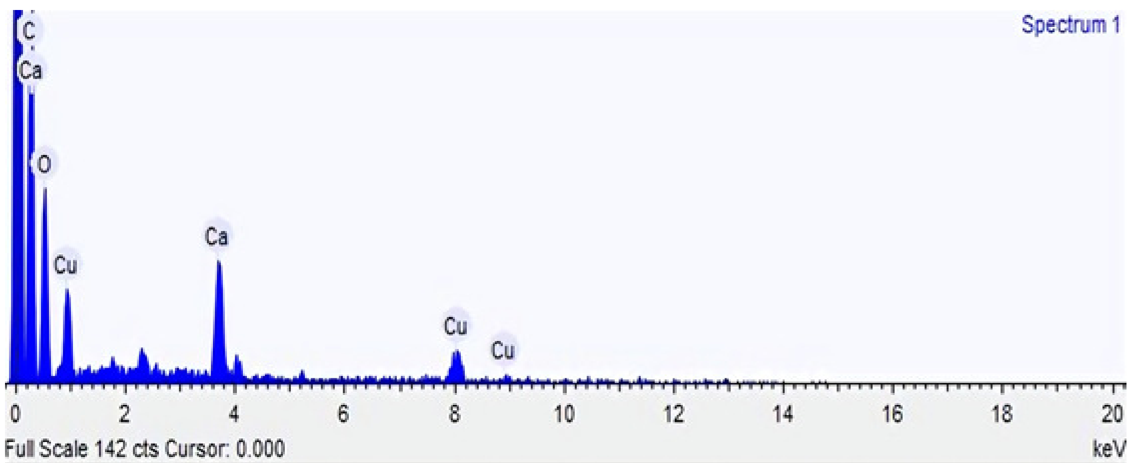


Fig.-3: Scanning electron microscopy (SEM) and energy dispersive X-Ray (EDX) images of horn snail (*Telescopium* sp) shells powder after Cu^{2+} adsorption

Table-1: Elements of horn snail (*Telescopium sp*) shells powder after Cu^{2+} adsorption

No.	Element	Content per 100% Adsorbent Mass (%)
1.	Carbon (C)	46.664
2.	Oxygen (O)	35.126
3.	Calcium (Ca)	6.943
4.	Copper (Cu)	11.266

CONCLUSION

Horn snail and mud crab shell could be used as low cost adsorbents to reduce the Cu^{2+} in synthetic wastewater. The equilibrium time for Cu adsorption in synthetic wastewater was 2 hours with adsorption capacity of 4.5868 mg g^{-1} and 4.3233 mg g^{-1} for each adsorbents. The FT-IR analysis result of mud crab shell showed that there was functional group of C=O that came from calcium carbonate in shell. There were functional groups of O-H and N-H bending that showed that it contained chitin. The FT-IR analysis result of horn snail shell showed that it only contained functional groups of C=O and O-H. The SEM-EDX analysis result indicated that ion exchange has been occurred between Ca^{2+} ions that contained in horn snail shell powder. Future studies will be conducted to evaluate the effectiveness of horn snail (*Telescopium* sp.) and mud crab (*Scylla* sp.) shells powder as an adsorbents on heavy metal removal from contaminated wastewater. The factors affecting the adsorption efficiency including pH, metal competition, temperature, contact time, and adsorbent dose can also be investigated. The experimental results obtained in this study to indicate the potential usefulness of low cost adsorbents for the removal of toxic heavy metals from the environment, especially in aquatic environment.

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