Research Article

Waste *Meretrix meretrix* Shell as Adsorbent of Copper (Cu^{2+})

Encik Weliyadi^{1*}, Afni Nidyasari¹, Tri Paus Hasiholan Hutapea²

¹ Department of Water Resource Management, University of Borneo Tarakan, 77123, Indonesia

² Department of Fisheries Product Technology, University of Borneo Tarakan, 77123, Indonesia

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*Corresponding author:

E-mail:

weliyadianwar098@gmail.com

ABSTRACT

Meretrix meretrix was found to be a very abundant waste at Amal Beach, Tarakan City. *M. meretrix* waste can reduce heavy metals, especially heavy metals copper (Cu^{2+}), by the adsorption process. Research has been carried out on *M. meretrix* as an adsorbent of heavy metals copper (Cu^{2+}) using the adsorption method of Shaker through chemical activation using NaOH bases. The SEM results showed that *M. meretrix* before activation had a rough pore surface that was still closed but *M. meretrix* after activation had an open pore surface that is why it could be used as an adsorbent. *M. meretrix* contains Al (Aluminum), which can be used as an adsorbent. The adsorption results showed that *M. meretrix* with activation in the Freundlich isotherm had the highest ability to absorb Cu^{2+} as much as 9,108 mg/g compared to without activation only 0.051 mg/g. It can be concluded that *M. meretrix* waste can be used as an adsorbent of Cu^{2+} heavy metals.

Keywords: Adsorbent, Adsorption, Copper, Heavy metals, *Meretrix meretrix*

Introduction

The presence of high heavy metals in an area of water can reduce water quality and endanger the environment and aquatic organisms. The existence of minerals in water bodies can come from natural sources and activities carried out by humans. The content of heavy metals in the waters continues to increase along with increasing activities such as transportation, ports, the petroleum industry, and substantial population settlements. These anthropogenic activities produce bulky metal waste, including heavy metals copper (Cu), which can affect the quality of the waters for the life of the organisms in it [1].

Cu is a transition metal (group I B) that is reddish, easy to stretch, and easily forged. Copper is a heavy metal that is toxic to living things [2]. This metal will be sustainably absorbed by aquatic biota if its presence in the waters is always available. One of the efforts to treat copper (Cu) waste is by adsorption (absorption). Adsorption was chosen because it is a relatively simple method and can use natural material adsorbents such as shellfish waste. Research on heavy metal adsorption is car-

ried out to reduce excessive heavy metals [3 - 7].

Shells containing calcium carbonate (CaCO_3), which undergo a calcination process, will produce calcite (CaO). Calcite functions as an adsorbent on absorption [8]. The shell of *Meretrix meretrix* was very abundant on the Amal Beach, Tarakan City. The consumption of *M. meretrix* produces big shells waste which is not managed wisely. Waste of *M. meretrix* can be used as Cu^{2+} heavy metal adsorbent because clam and shell can remove a contaminant from the environment. This study aimed to determine the ability of shell waste as Cu^{2+} heavy metal adsorbent.

Material and Methods

The research procedure was started by doing *M. meretrix* shells sampling at Amal Beach. Samples were cleaned and dried. Then they were mashed and sieved with 80 mesh sieves. The samples were divided into two groups: (1) sample without activation and (2) with activation. The samples were activated by giving 0.1 N NaOH. As much as 50 g of shell powder was given with a 0.1

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N NaOH as much as 250 mL (Sample : NaOH solution was 1 : 5), and it was stirred at a speed of 100 rpm. The activation process is carried out for 24 hours. Then the sample was filtered and dried in an oven at 50°C. After drying, the conch shell powder was stored in a desiccator.

The surface acidity of the shell was determined by the acid-base titration method while the surface characterization of the adsorbent using Scanning Electron Microscopy-Energy Dispersive spectroscopy (SEM-EDS). In determining the adsorption capacity, the concentration of Cu metal ions used is 20 -100 ppm. The concentration of the standard solution of Cu metal ions is 0-5 ppm. The determination of the concentration of Cu metal ions was based on the initial experiment of the adsorption process on 20 ppm Cu metal ions which resulted in the adsorption value in the standard solution adsorption range. Measurement of Cu metal ion concentration was carried out on the filtrate after the adsorption process using the Atomic Absorption Spectrophotometer. To determine the adsorption capability of the Freundlich equation, tests were performed using the following equation Atkins, 1997.

$$\text{Log } W = \text{Log } k + \frac{1}{n \text{ Log } C_e}$$

Information:

Log C_e : concentration of Cu^{2+} ions in solution after adsorption

Log W : mass of Cu^{2+} ions absorbed per gram of adsorbent

n : Fruendlich constant

Log k : Adsorption Capacity (mg/g)

Results and Discussions

Surface acidity of the *Meretrix meretrix* shell

The results of surface acidity on the shells of Asiatic hard clam or *kapah* (in Bahasa) shells (*M. meretrix*) before activation of 4.2 mmol/g and surface acidity on the rounds of *kapah* shells (*M. meretrix*) after activation of 7 mmol/g. The surface of the conch shell (*M. meretrix*) before activation has the lowest surface acidity of 4.2 mmol/g. This is because the shell of the *kapah* shell (*M. meretrix*) before activation still has many impurities on its surface. For samples of *kapah* shells (*M. meretrix*) after activation has an acidity of 7 mmol/g. This is because activation with NaOH can dissolve impurities on the surface of the shell so that the surface pores can open. The value of surface acidity affects the effectiveness of adsorption. The more acidity the copper adsorption by adsorbent is also higher because it has many active sites [9]. The adsorbent pore becomes homogeneous, and the ability to adsorb adsorbate is increased [10]. So that from this study, the head of a mussel shell (*M. meretrix*) after activation is more effectively used as an adsorbent than the head of a mussel shell (*M. meretrix*) without activation.

Surface shell characterization (*Meretrix meretrix*)

The characterization was carried out using a Scanning Electron Microscope (SEM), which aims to determine the surface morphological characteristics of the adsorbent by comparing the surface of the adsorbent before and after activation.

(A)

(B)

Figure 1. Surface Morphology of the Shell (*M. meretrix*) Before (A) and After (B) Activation

The results of the surface characterization of the clamshells (*M. meretrix*) can be seen with a magnification of 5000 times in Figures 1.

From the results obtained can be seen differences in the surface morphology of the adsorbent before and after activation. It appears that the surface of the adsorbent after activation is more homogeneous than before activation with an average

surface area of $1.8 \mu\text{m}$. This is presumably on the surface of the shell of the *kapah* shell (*M. meretrix*) before activation still contains impurities. The addition of NaOH in the activation process can reduce contaminants that are still present in the adsorbent. Adsorbent consists of layers overlapping one another to form a pore. Where the adsorbent pores are usually, there are impurities in

(A)

(B)

Figure 2. Graphs of composition of shells of the shell (*M. meretrix*) before activation (A) and after activation (B)

Figure 3. Contact time graph of adsorbent absorption before (red line) and after (blue line) activation of Cu^{2+}

the form of inorganic minerals and metal oxides that cover the pores. During the activation process, the pollutants also evaporate, causing the pores to get more significant [11]. The results of the analysis of the composition contained in the shells of *kapah* (*M. meretrix*) before and after activation can be seen in Figure 2 which shows that there are O (oxygen), Al (Aluminum), Cl (Chlorine) and Ca (Ca) Calcium). The highest yield found in the shells of *kapah* (*M. meretrix*) is Al. The results of the analysis of the composition contained in the shells of *kapah* shells (*M. meretrix*) before and after activation shows that there are O, Al, and Ca. The highest yield found in the shells of *kapah* (*M. meretrix*) is Al. Characterization was carried out on *kapah* shells (*M. meretrix*) samples before and after activation. The results of the analysis of the composition of *kapah* shells (*M. meretrix*) samples before activation were dominated by O, Al, Cl, and Ca, with the highest yield, namely Al content. The results of the analysis of the composition of *kapah* shells (*M. meretrix*) samples after activation are dominated by O, Al, Cl, and Ca, with the highest yield, namely Al content. The increase in Al composition is caused by the loss of the impurity bonds that cover the Al on the adsorbent. The increase in Al composition is expected to increase the active site of the adsorbent [12 - 15].

The aluminum composition contained in the adsorbent affects the effectiveness of the adsorbent to absorb metal ions [16 - 18]. The results of determining the maximum time on the shells of *kapah* shells (*M. meretrix*) before activation can be seen in Figure 3, which shows that the highest

absorption time of Cu^{2+} 40 ppm is at 30 minutes with the absorption of 39.9818 ppm.

At the maximum time, a determination is done using the shell of the *kapah* shell (*M. meretrix*) activation and without activation. Using Cu^{2+} 40 ppm solution over a span of 15, 30, 45, 60, 75, and 100 minutes. From the measurement results, the maximum time obtained by the mussel shells (*M. meretrix*) without activation absorbing Cu^{2+} is 30 minutes, and the *kapah* shells (*M. meretrix*) with activation is 60 minutes. This maximum time absorption is due to the number of active sides in the shell being fully used so that there is no more active side that can bind Cu^{2+} , and the shell pores are also full by Cu^{2+} .

The absorption ability of Cu^{2+} by *kapah* shell shells (*M. meretrix*) in the adsorption isotherm

Adsorption capacity is the ability of an adsorbent to absorb adsorbate. In this research, various concentrations of Cu^{2+} solutions are used to determine the adsorption capacity. The level of Cu^{2+} solution used was 20, 40, 60, 80, and 100 ppm. The flow time used is the maximum time obtained at the determination of the maximum time, namely in the shell of the conch shell (*M. meretrix*) without activation for 30 minutes and on an eggshell shell (*M. meretrix*) with 60 minutes activation, after that, analyzed at AAS. So we get the remaining Cu^{2+} concentration. The results are then processed to obtain the adsorption capacity from the results obtained. This study uses the Freundlich adsorption isotherms. In *kapah* shells (*M. meretrix*) with out activation using the Freundlich adsorption iso

Figure 4. Freundlich isotherm adsorption graph of Cu^{2+} by *kapah* shells (*M. meretrix*) (A) without activation and (B) with activation

therm. Because this isotherm shows a better value than other isotherms, so this isotherm is used. In the Freundlich isotherm, the data obtained is entered in a graph. The graph on the Freundlich isotherm has components $y = \text{Log } W$ and $x = \text{Log } C_e$, where W is Cu^{2+} absorbed in the shell (mg/g), while C_e is the residual concentration (ppm). After knowing the value, The $\text{log } W$ and the $\text{Log } C_e$ value are entered in a graph, as shown in Figure 4.

From the graph the equation $y = -1.5872x - 1.295$ was obtained with the value $R^2 = 0.7132$. In

the Freundlich equation $\log W = \log k + (1/n) \text{Log } C_e$, where $1/n$ is the slope and $\log k$ is the intercept. If k is the adsorption capacity of the shell (*M. meretrix*) without activation, then the inverse of $\log k$ is 0.0507. adsorption for shellfish without activation was obtained at 0.051 mg/g. The conclusion obtained is that 1 gram of adsorbent shells (*M. meretrix*) without activation can absorb Cu^{2+} as much as 0.051 mg.

From the graph the equation $y = 0.6268x + 0.9594$ with $R^2 = 0.782$ is obtained. In the Freun-

dlich equation, the adsorption capacity for shells with activation was obtained at 9,108 mg/g. The conclusion obtained is that 1 gram of adsorbent from the shells of the mussels (*M. meretrix*) with activation can absorb Cu^{2+} as much as 9,108 mg. The increase in adsorption capacity is caused by the opening of the larger active site so that the adsorbent binds more adsorbate. It causes the adsorption capacity will increase, while the decrease in adsorption capacity is caused by the active site of the adsorbent, which is not all bound to the adsorbate [19].

Conclusion

Shells *kapah* (*M. meretrix*) without activation or activation can be used as an adsorbent because, based on research in addition to having Ca (Calcium) also has Al (Aluminum). *Kapah* shell (*M. meretrix*) without activation in the Freundlich Isotherm can absorb Cu^{2+} as much as 0.051 mg/g. Whereas in the case of *kapah* shells (*M. meretrix*) with activation in the Freundlich isotherm has the highest ability to absorb Cu^{2+} , which is 9,108 mg/g. So based on research, *kapah* shell shells (*M. meretrix*), which through the activation process, are more effective in absorbing heavy metal copper (Cu^{2+}) compared to *kapah* shell shells (*M. meretrix*) without going through the activation process.

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