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Citation: AIP Conference Proceedings **2023**, 020099 (2018); doi: 10.1063/1.5064096
View online: https://doi.org/10.1063/1.5064096
View Table of Contents: http://aip.scitation.org/toc/apc/2023/1
Published by the American Institute of Physics

The Ability of Pensi (*Corbicula moltkiana*) Shell to Adsorb Cd(II) and Cr(VI) Ions

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Abstract. The biosorption of Cd(II) and Cr(VI) ions from aqueous solutions using Pensi (*Corbicula moltkiana*) shell activated with HNO_3 0,01 M was studied in batch method. The optimum conditions were reached at concentration 100 mg/L, particle size 32 µm, and biosorbent mass 0.1 gram for both Cd(II) and Cr(VI) ions. At pH 6 and contact time 120 minutes, biosorbent was warmed at 28°C with the sorption capacity of 6.073 mg/g for Cd(II), while at pH 3, contact time 15 minutes, biosorbent was warmed at 80°C with the sorption capacity of 1.286 mg/g. The adsorption of Cd(II) and Cr(VI) ions follows the Langmuir isotherm models with R^2 0.9389 for Cd(II) ions and 0.9972 for Cr(VI) ions. The Langmuir Isotherm Method indicates an adsorption process occurrs as chemicals formed monolayer. This result showed that Pensi shell can be used to overcome Cd(II) and Cr(VI) content in wastewater.

Keyword : Biosorption, Cd(II) and Cr(VI), Pensi (*Corbicula moltkiana*)shell

INTRODUCTION

Metal is one of toxic unique materials. Metal was found and stayed in the nature, but its chemical state change causes influence on the physicochemical biologist or human activity. Metals in nature were found in compounds with others element and very rare found in singular element. In waters, usually metal was in ionic form that has electron pair or single electron. Heavy metal will destroy mullet and water ecosystem. Heavy metal is toxic substance and generally carcinogenic. Because of that, waste treatment on the heavy metal content is needed.

Realizing the big threat from heavy metal pollution, many kinds of alternative methods have been used, such as diminish the concentration of heavy metal, with chemical process methods like chemical precipitation, ion exchange, adsorption, electrodialysis and reverse osmosis. However, this technique is very expensive concerning heavy metal treatment which minimal content in water [1].

One of technique being developed is bioremoval. Bioremoval can be interpreted as concentrated and accumulation of pollutants or pollutant materials in water body by biological material, in which the biological material can recover the pollutants that can be discharged and friendly to the environment. The principle of this method is using the bioremoval organism for heavy metals. Biosorption terms can not be separated from the bioremoval term, because biosorption is part of bioremoval. Biosorption is the ability of biological material to accumulate heavy metals through the media or track physicochemistry metabolism. Biosorption process can occur because of biological material called biosorbent and their solution containing heavy metals (with high affinity) that is bonded to biosorbent [2].

Biosorbent using biomaterials are already proven and can be used to absorb metals in the waste water stream. Biomaterials are used as absorbent of heavy metals because they contain functional groups such as carboxyl, hydroxyl, amino which the functional groups can bind to the metal [3].

Proceedings of the 3rd International Symposium on Current Progress in Mathematics and Sciences 2017 (ISCPMS2017)
AIP Conf. Proc. 2023, 020099-1–020099-8; https://doi.org/10.1063/1.5064096
Published by AIP Publishing. 978-0-7354-1741-0/$30.00

Compared with other methods, adsorption is considered as the most effective method and has been widely used. Some types of organisms such as algae, bacteria, fungi and yeasts have been proven to have the ability to absorb metal [4]. In addition, now it begins to develop biosorbent use for food waste. These materials generally are not used anymore so it can be obtained cheaply.

Research that uses animals as biosorbent raw materials has not been widely carried out. Pensi shell is used in the study of the mechanism of heavy metal biosorbtion Cd (II) and Cr (VI) in waste water. Determining the type of interaction of this Pensi shell will be done beforehand by performing functional group characterization. This characterization is known from the ability of the Pensi shell to absorb heavy metal Cd(II) and Cr(VI) ions. Biomaterial that has been used for the absorption of heavy metal ions is shells fur [5].

MATERIALS AND METHODS

All chemicals used in this experiment namely Cd(CH3COO)2.2H2O, $K_2Cr_2O_7$, NaOH 0,1 M, HNO3, 0,1 M, HNO_3 0,01 M, Diphenyl Charbazide (DPC), H_3PO_4 p.a, H_2SO_4 2 M, distilled water were obtained from E-Merck (Germany) unless other wise noted. Distilled water was obtained from the laboratory. Analytical balance, AAS (spectraAA-240 VARIAN), Oven (Memmert), Spectrophotometer UV VIS (Thermoscientific SPECTRONIC 200+), pH meter (Metrohm), rotary shaker (Edmun Buhle 7400 Tubingen), XRD (XPert PRO PANalytical), FTIR (ThermoScientific NICOLET iS10), SEM-EDX (Hitachi S-3500N) and glassware, pH meters were used in this experiment. Pensi shells were collected from Padang beach in Padang City, West Sumatra, Indonesia.

Preparation of Biosorbent

Pensi shell washed with water to remove residue of organic material, then dried at room temperature and ground in pestle and mortar, screened to particle size of 425, 160, and 32 µm (Fig. 1 c) and soaked with 0.01 ml/L HNO_3 for three hours, filtered then rinsed with distilled water until neutral. The biosorbent was dried and ready to use.

Batch Adsorption: Powder of Pensi Shell (biosorbent) was entered into 10 mL solution containing Cd or Cr ion and stirred using shaker for several minutes. The experiments were conducted with variety of pH solution, concentration, contact time, biosorbent mass, particle size and warmed biosorbent. To determine the amount of Cd or Cr ion adsorbed by Pensi Shell, the formula used is:

$$q= \frac{(C_o - C_e)V}{m} \quad (1)$$

where Co is the initial concentration of metal ions (mg/L), Ce, final concentration at equilibrium state (mg/L), m, biosorbent mass(g) and *v* is volume solution (L).

RESULTS AND DISCUSSION

Effect of pH solution

The pH solution is one important factor. The pH of solution has a significant impact on the removal of heavy metals, since it determines the surface charge of the adsorbent (has carboxylate, phosphate and amino group) and its degree of ionization. H^+ ion will compete with another metal ion to bind with active side of biosorbent [6]. Based

(a) (b) (c)

FIGURE 1. (a) Pensi (*Corbicula molkiana*) Shell (b) Inner of Pensi Shell (c) Powder of Pensi

on Fig. 2 biosorption capacity of Cd(II) increased from pH 2 to pH 6 and decreased at pH 7. The optimum biosorption capacity for Cd(II) ion is 0.6459 mg/g at pH 6. For Cr(VI) ion, optimum pH is at pH 3. It caused dichromate formed in acid condition with high concentration of Cr(VI). Beside that, in the complexation reaction of Cr(VI) with DPC in acid condition and at pH larger than 6.5, the amount of chromate (CrO_4^{-2}) is dominant. While $HCrO_4^-$ is more dominant at pH smaller than 6.5[7].

Effect of Concentration

The initial concentration of metal ions was studied to determine the ability of the active site of biosorbent to bind [15]. Figure 3 showed an influence of initial concentration at pH 6 for Cd(II) ion solution and pH 3 for Cr(VI) ion. Initial concentration of metal ion solution was studied to know how many metals can bind with the active site of biosorbent [8].

The amount of metal ion adsorbed by Pensi shell powder increased as the concentration of metal solution was up. This can happen because in high concentration many metal ions will compete to bind with active group from biosorbent. However, in certain concentration, adsorption capacity decreased as the initial concentration metal ion solution was up. It can happen because active site on biosorbent surface has been bonded with metal ion, until the biosorbent can be saturated and can not bind with metal ion. The optimum adsorption capacity of Cd(II) and Cr(VI) ions is 10 mg/L.

Effect of Contact Time

Experiment on the contact time of the absorption of metal ions Cd(II) and Cr(VI) was conducted to determine how long it takes for adsorbent to bind with metal ions in the active site. Figure 4 shows that the optimum condition of Cd(II) and Cr(VI) ion by powder of Pensi shell were obtained at 60 and 15 min, respectively. This shows that the sorption capacity of Cd(II) ion rather lower than Cr(VI) ion. In Cr(VI) ion, at 15 minutes the active side of biosorbent is more available so that the metal ions can interact easily. At this time equilibrium between amount of metal ions bind with biosorbent also occurs. Because contact time is too long, Cd(II) ions which has been bonded to the active site becomes loose and the adsorption capacity is low. In Cd(II) ion, the optimum contact time obtained is 120 min. In 15 min to 90 min, the amount of metal ions bind with active side biosorbent is not balanced, and at 120 min the equilibrium occurs between the amount of metal ions bind to biosorbent.

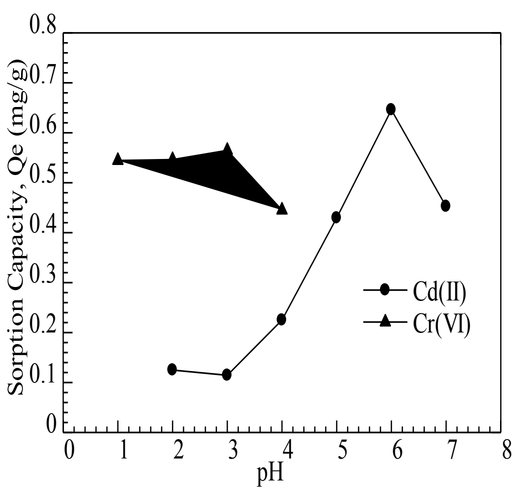


FIGURE 2. Effect of pH on Cd(II) and Cr(VI) ions biosorption of Pensi shell. Experimental condition: concentration 10 mg/L, biosorbent mass 0.1 g, stirring speed 200 rpm, contact time 15 min, and particle size 160 μm

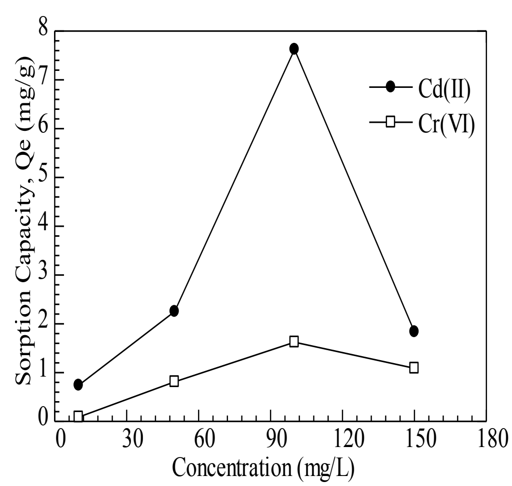


FIGURE 3. Effect of concentration on the sorption capacity of Cd(II) and Cr(II) ions of Pensi shell. Experimental condition: pH solution of Cd(II) 6, pH solution of Cr(VI) 3, biosorbent mass 0.1 g, stirring speed = 200 rpm, contact time = 15 min, and particle size = 160 μm

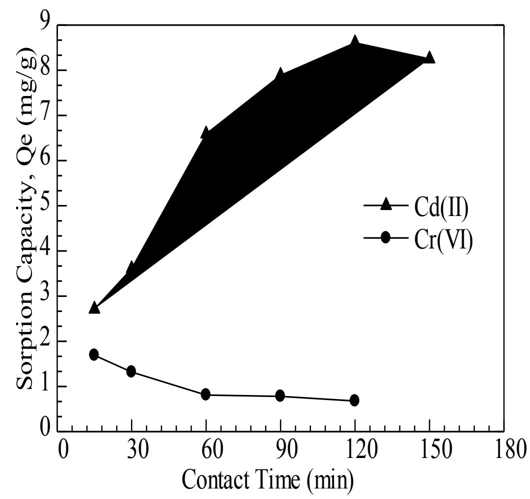


FIGURE 4. Effect of contact time on the sorption capacity of Cd(II) and Cr(VI) ions on Pensi shell. Experimental condition: pH solution of Cd(II) 6, pH solution of Cr(VI) 3, Cd(II) ion concentration 100 mg/L, Cr(VI) ion concentration 100 mg/L, biosorbent mass 0.1 g, stirring speed 200 rpm, and particle size 160 µm

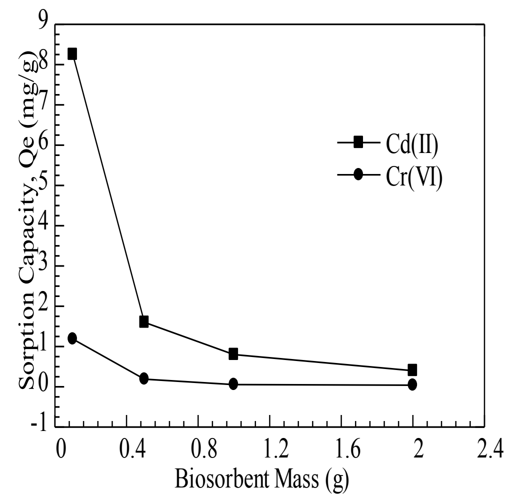


FIGURE 5. Effect of biosorbent mass on the sorption capacity of Cd(II) and Cr(VI) ions on Pensi shell. Experimental condition: pH solution of Cd(II) 6, pH solution of Cr(VI) 3, Cd(II) ion concentration 100 mg/L, Cr(VI) ion concentration 100 mg/L, contact time of Cd(II) 120 min, contact time of Cr(VI) 15 min, stirring speed 200 rpm, and particle size 160 µm

Effect of Biosorbent Mass

Biosorbent mass is an important parameter in the biosorption process to evaluate the adsorption capacity of metal ions on the biosorbent. Biosorption of metal ions depends on the type of adsorbent surface and on the ion forms that metals find in the water solution [17]. If the mass of adsorbent increases the absorption capacity will decrease. This is due to a high number of adsorbent will clot, which causes the surface area of the adsorbent to bind with metal ions decreases. Figure 5 showed the optimum biosorbent mass of Cd(II) and Cr(VI) ion by Pensi shell in the aqueous solution.

Effect of Particle Size

The particle size which has adsorption capacity for Cd and Zn ion were decreased from 32 – 425 µm. the optimum particle size was found at 32 µm. Biosorption capacity of small size biosorbent showed little increase than the medium and big ones, it is very likely that, in the practical application, the biosorbent in big size would achieve a similar performance with the small and medium ones with less cost of pretreatment [9].

Figure 6 shows the effect of heating temperature on the absorption of metal ions Cd (II) and Cr (VI). Variations in temperature were performed at 28, 40, 80, and 120ºC, which is assumed that 28ºC is temperature without any heating. When the temperature is high, then the ion absorption capacity of Cd(II) and Cr(VI) increases due to the evaporation of water molecules, so that the amount of the active side of the Langkitang shell powder increased. Figure 7 shows the effect of heating temperature on the absorption of metal ions Cd (II) and Cr (VI). Variations in temperature were performed at 28, 40, 80, and 120ºC, which is assumed that 28ºC is temperature without any heating. In Pensi shell powder, heating results in the damage of the chemical structure, and the ability to adsorb Cd(II) and Cr(VI) ions is reduced.

Adsorption Isotherm

Adsorption data for various concentrations by biosorbent is most easily explained using adsorption isotherm. Ion absorption experiment data of Cd(II) and Cr(VI) by Pensi shell powder is processed using Langmuir and Freundlich

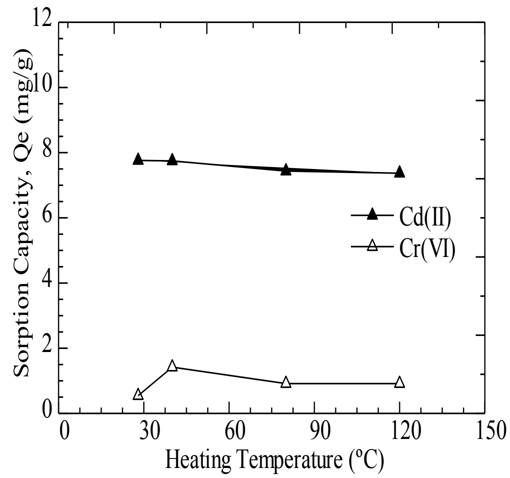


FIGURE 6. Effect of heating temperature on the sorption capacity of Cd(II) and Cr(VI) ions on Pensi shell. Experimental condition: pH solution of Cd(II) 6, pH solution of Cr(VI) 3, Cd(II) ion concentration 100 mg/L, Cr(VI) ion concentration 100 mg/L, contact time of Cd(II) 120 min, contact time of Cr(VI) 15 min, biosorbent mass 0.1 g, particle size 32 µm stirring speed 200 rpm.

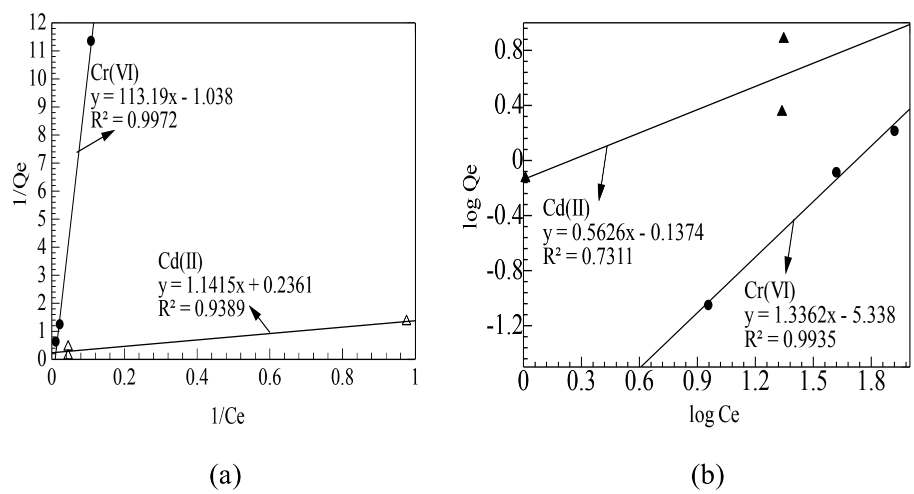


FIGURE 7. Langmuir isotherm model for Cd(II) and Cr(VI) ions biosorption on Pensi shell (a) Langmuir; (b) Freundlich

isotherm models. Langmuir adsorption isotherm is a process that takes place in chemisorption monolayer adsorption. Langmuir constants related to absorption and energy absorption capacity of each other. The surface of shell powder contained Pensi active sites can only adsorb one molecule adsorption of adsorbate would only be limited to the establishment of a single layer (monolayer) [10]. Maximum capacity of biosorbent is denoted by q_{max}. A linear graph in Fig. 8 was obtained by plotting between 1/Ce to 1/qe on variations of the metal ion concentration in accordance with the trail. Freundlich isotherm is the layer model which does not predict the saturation of the Pensi shell powder with metal ions. Freundlich isotherm models can be applied to the absorption process that describes the physical adsorption of Cd(II) and Cr(VI) only.

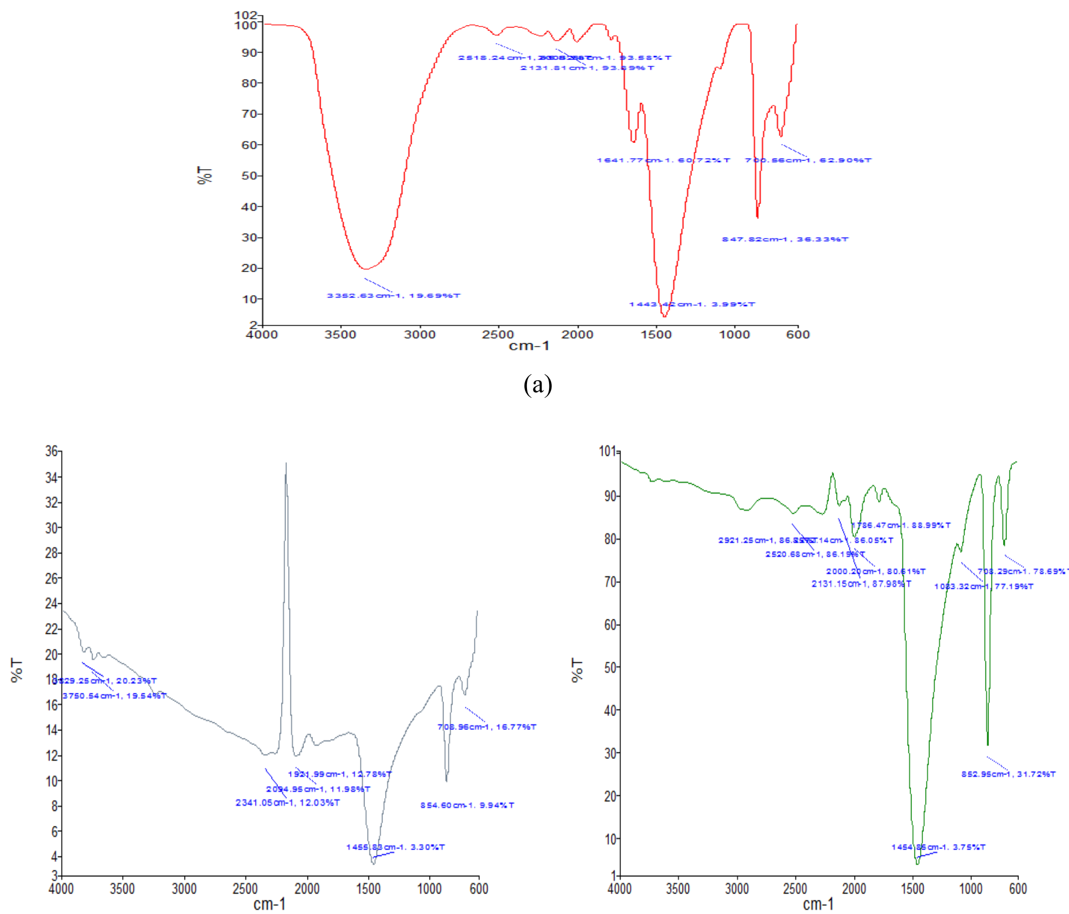
Figure 7 shows that the isotherm graph Cd(II) obtained by the linear correlation coefficient (R^2) approaching is 0.9972. It concluded that the data Cd(II) obtained from this study is in accordance with the Langmuir adsorption equilibrium models. In Fig. 8 the value of R^2 Cd(II) ion for the second isotherm does not occur a significant difference. So, Cd(II) ion can pursue both adsorption equilibrium equation models. In the value of n, the second metal ion obtained >1. This indicates that the bonding process occurs physically [3].

From Table 1 it can be seen Qm for ion Cd(II) takes more than Cr(VI). While the value of K_L for Cd(II) ion is higher than Cr(VI) ion. This means ion affinity of Cd(II) is greater than Cr(VI) so the ability of Cd(II) ion to bind to the active group biosorbent is smaller than Cr(VI) ion.

In order to estimate the functional groups which involved in biosorption process, FTIR analysis was conducted [16]. FTIR analysis is important to confirm the functional groups present in the biosorbents. Furthermore, it provides information on binding mechanism and possibility of functional groups to be involved in the interaction with metal ions [10].

TABLE 1. Data Models Langmuir and Freundlich Adsorption Isotherms

Ion	Langmuir			Freundlich		
	K_L (L/mg)	Q_m (mg/g)	R^2	K_f	N	R^2
Cd(II)	0.20	4.2354	0.9389	0.7287	1.7775	0.7311
Cr(VI)	0.009	0.96339	0.9972	4.73×10^{-6}	0.7483	0.9935



(a) (b) (c)

FIGURE 8. FT-IR spectrum of Pensi shell powder (a) before adsorption
(b) after contacted with metal ion of Cd(II) (c) after contacted with metal ion of Cr(VI)

Fourier Transform Infra Red (FTIR) Spectroscopy Analysis

Figure 8 shows the analysis of functional groups by FTIR. FTIR spectrum of visible shows a shift in wave numbers. The wave number 1020.35 cm^{-1} (Fig. 8a) shifted to 1083.32 cm^{-1} (Fig. 8c) indicates the binding of Cr(VI) to the C-N group. The wave number 3362.62.60 cm^{-1} (Fig. 8a) shifted to 3750.63 cm^{-1} (Fig. 8b) indicates the binding of Cd(II) on the OH group, and the wave number 1715 cm^{-1} (Fig. 8a) indicates carboxyl group, but after absorption (Fig. 8b) a carboxyl group lost a signifies carboxyl group absorbed by adsorbent. From the FTIR spectra, it can be seen that the hydroxyl, carboxyl and amine groups involved during the process of absorption of ion Cd(II) and Cr(VI).

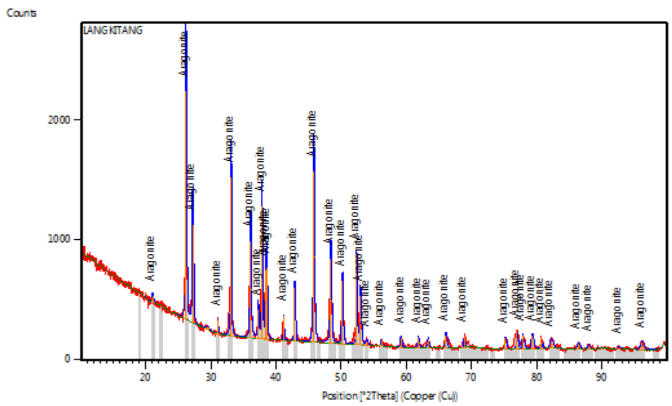


FIGURE 9. XRD of Langkitang (*Faunus ater*) shell before sorption

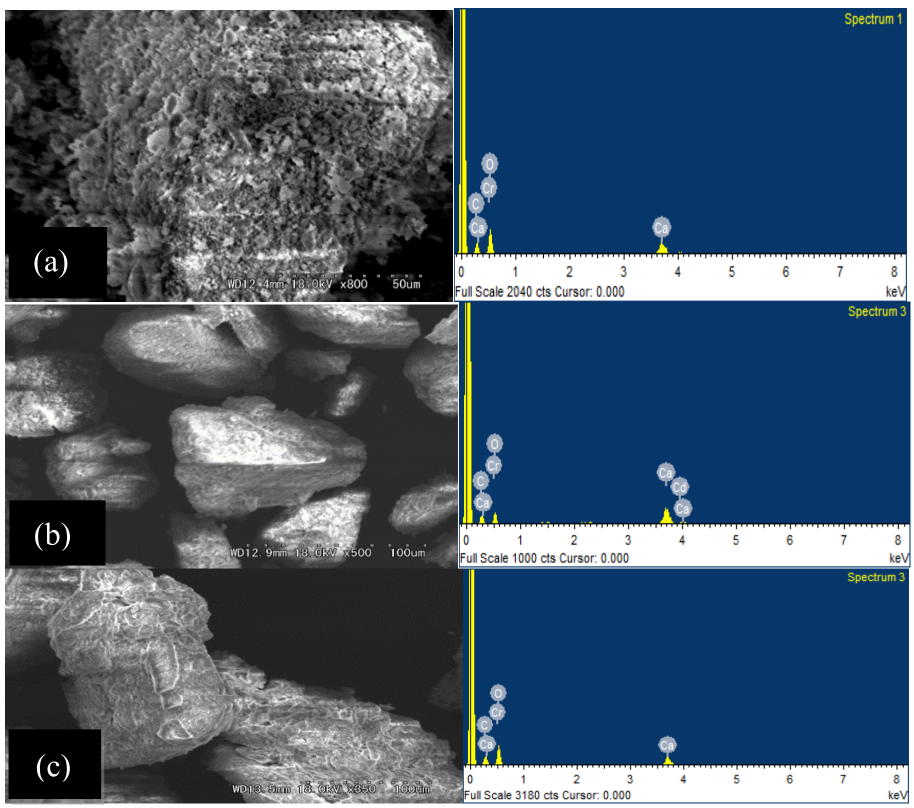


FIGURE 10. SEM-EDX of Pensi (*Corbicula moltkiana*) shell before sorption (a), after Cd(II) ion sorption (b), and after Cr(VI) ion sorption (c).

X-Ray Diffraction (XRD) Analysis

Figure 9 shows the XRD analysis before adsorption that the crystalline structure is aragonite. The basic principle of XRD diffraction of light is through a crack in the crystal.

Scanning Electron Micrograph-Energy Dispersive (SEM-EDX) Analysis

The SEM-EDX analysis was performed to observe the surface morphology and chemical composition of the biosorbents before and after metal ion adsorption [11]. Figure 10a shows the irregular structure of shell art shows as the presence of empty pores as well. These pores facilitate the absorption of metal ions. After absorption of Cd(II) and Cr(VI) ions, the pore is covered by a metal ion. As seen in Fig. 10b and 10c.

CONCLUSIONS

The powder of Pensi *(Corbicula moltkiana)* can adsorb Cd(II) and Cr(VI) ions with the optimum condition for Cd ions at pH 6, concentration 100 mg/L, contact time 120 minutes, mass 0.1 g, particle size 32 µm, and biosorbent temperature at 28 °C with the sorption capacity of 6.073 mg/g and % removal is 72.99 %. While the optimum condition of Cr(VI) ions were at pH 3, concentration 100 mg/L, contact time 15 minutes, biosorbent temperature at 80 °C, with the sorption capacity of 1.286 mg/g and the % removal is 12.86 %. The adsorption of Cd(II) and Cr(VI) ions is following the Langmuir isotherm models with R^2 0.9389 for Cd(II) ions and 0.9972 for Cr(VI) ions. The Langmuir isotherm method indicated an adsorption process is monolayer. FTIR analysis showed the hydroxyl with wave number 3362.62 cm^{-1} shifted to 3750.63 cm^{-1}, carboxyl with wave number 1715 cm^{-1} which after adsorption it was absorbed for Cd(II) ion and amine with wave number 1020.35 cm^{-1} shifted to 1083.32 cm^{-1} for Cr(VI) ion which are the important role in the adsorption process. The SEM-EDX analysis showed the surface morphology has too much pores in Pensi (*Corbicula molkiana*) shell. XRD analysis indicated the aragonite as crystal lattice structure in Pensi (*Corbicula moltkiana*) shell.

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