Application of Cockle (*Anadara granosa*) Shell Waste as an Adsorbent of Heavy Metal Cadmium (Cd), Copper (Cu), and Lead (Pb)

Akbar Falah Tantri¹*, Mirni Lamid² and Sugijanto³

¹Study Programme of Fisheries and Marine Biotechnology, Faculty of Fisheries and Marine, Universitas Airlangga, Jl. Mulyorejo, Mulyorejo, Surabaya 60115, Indonesia
²Department of Farm, Faculty of Veterinary, Universitas Airlangga, Jl. Mulyorejo, Mulyorejo, Surabaya 60115, Indonesia
³Department of Pharmaceutical Chemistry, Faculty of Pharmacy, Universitas Airlangga, Jl. Mulyorejo, Mulyorejo, Surabaya 60115, Indonesia

*Correspondence :
akbarfalah74@yahoo.com

Received : 2021-05-19
Accepted : 2021-10-06

Keywords :
*Anadara granosa, Adsorbent, Heavy metal*

Abstract

Heavy metal is one of the water pollutants that are harmful to the environment and humans. Cockle (*Anadara granosa*) is only used for meat so that the shells become waste that pollutes the environment. This study examines the ability of cockle shell powder as an adsorbent in the process of adsorption of heavy metals cadmium (Cd), copper (Cu), and lead (Pb). The ability of the adsorbent was tested through the batch method, using a glass beaker (100 ml) at a speed of 90 rpm; initial metal concentration 20 ppm; adsorbent weighing 0.1 – 0.5 grams; contact time of 20 minutes and 30 minutes. The results showed that the adsorbent weighing 0.5 grams can reduce > 75% concentration of cadmium (Cd), copper (Cu), and lead (Pb). Freundlich and Langmuir adsorption isotherms of cadmium (Cd), copper (Cu), and lead (Pb) had $R^2 > 0.9$.

INTRODUCTION

Water pollution by heavy metals has significantly increased over the last decades. Heavy metals in the water environment mostly come from anthropogenic activities such as smelting, mining, and electronic manufacturing. The toxicity of heavy metals constitutes a great risk to the environment and human health. Today, about 80% of the global wastewater has untreated. Once water is contaminated, it is difficult, costly, and often impossible to remove the pollutants. The nature and amount of pollutants in water determines the suitability of water for many human uses such as drinking, bathing, and agriculture (United Nations Environment Programme (UNEP), 2021).

United Nations (UN) (2021) reported that 1 in 3 people live without safe drinking water, and approximately 5.7 billion people in 2050 could be living in areas where water is scarce for at least one month a year. Therefore, the removal of heavy metal pollutants from contaminated water and wastewater has received increasing attention among the scientific community.

Indonesia as a maritime country with a coastline of 81,000 km, has the potential for abundant shellfish. Cockle (*Anadara granosa*) has a delicious taste, easy to find in the market, has high and complete nutritional content, and is an affordable price. Cockle meat contains:
crude protein (15.95 %), carbohydrates (1.33 %), crude fat (1.6 %), water (78.69 %) and ash (2.44 %) (Bhara et al., 2018). Financially, the cockle farming industry has considerably boosted the Indonesian economy. However, the disposal of cockle shell waste has led to environmental problems, namely blocks access roads, reduces the aesthetics of an area, and causes bad odor. Therefore, the recycling of cockle shell waste has become an issue of concern. To date, a portion of cockle shell waste has been recycled for use as souvenirs, fertilizers, and animal feed. Hence, alternative approaches are required for the recycling of cockle shell waste.

Several studies have been conducted in Indonesia to evaluate possible means of reusing bivalve shell waste material for heavy metals removal from contaminated water. Anugerah dan Iriany (2015) used cockle (Anadara antiquata) shell waste to remove cadmium (Cd) and lead (Pb) from an aqueous solution. Pridyanti et al. (2018) used blue mussel (Corbula Faba) shell waste to remove chromium (Cr) from batik liquid waste. While Matondang (2019) used windowpane oyster (Placuna placenta) shell to remove lead (Pb) from electroplating liquid waste. Therefore, in this study, we examined the use of cockle shell waste as an adsorbent of heavy metal cadmium (Cd), copper (Cu), and lead (Pb) from an aqueous solution.

METHODOLOGY

Place and Time

The research was conducted from January to October 2020 at Laboratory of Multipurpose I, Faculty of Pharmacy, Airlangga University, Surabaya.

Research Materials

The materials used in this research were cockle (A. granosa) shell waste from a traditional market in Surabaya, East Java; (CH₃COO)₂Cd.2H₂O 99 % p.a (Merck, Germany); CuSO₄ 99 % p.a (Merck, Germany); (CH₃COO)₂Pb.3H₂O 99.5 % p.a (Merck, Germany), HNO₃ 65 % p.a (Merck, Germany); and aquaest p.a.

The main equipment was magnetic plate (IKA C-MAG HS 10), atomic absorption spectrophotometry (Shimadzu AA-7000), attenuated total reflection (Bruker Alpha II), and analytical balances (Ohaus).

Research Design

The research method used is experimental. The research design used for the adsorbent weight and contact time variable is a non-parametric test, meanwhile, the heavy metal type variable is a randomized block design. The batch adsorption method is applied with various variables. The adsorbent weight used is P1 (0.1 gram), P2 (0.2 gram), P3 (0.3 gram), P4 (0.4 gram) and P5 (0.5 gram). The contact time used is 20 and 30 minutes. Each treatment has triplicate.

Work Procedure

Adsorbent Preparation

Cockle (A. granosa) shell waste was washed with aquaest to remove dust and other debris. Then it was sun-dried for 2 days to reduce moisture. The dried cockle shell was crushed and sieved to particles (200 μm). The sieved powder was stored in the desiccator, and used for the batch experiment.

Adsorbent Characterization

The metal composition of the cockle (A. granosa) shell was determined by x-ray fluorescence (XRF), which was analyzed in Laboratorium Energi-LPPM Institut Teknologi Sepuluh Nopember, Surabaya. The functional group was determined using attenuated total reflectance-fourier transform infrared (ATR-FTIR) (Bruker Alpha II).

Heavy Metal Solution

The solutions of cadmium, copper, and lead ions were prepared by dissolving certain amounts of heavy metal in 1 % HNO₃ into 1000 ml volumetric flasks. The amount of cadmium used is 2.3950 grams,
copper is 2.5370 grams, lead is 1.8408 grams. The initial heavy metal concentration is 20 ppm.

**Adsorption Experiment**

The adsorption experiment was carried out by adding amounts of the adsorbent to 10 ml of heavy metal solution in beaker glass (100 ml), then placed on a magnetic plate and stirred using a magnetic stirrer (0.8 cm) at a speed of 90 rpm. Separation of heavy metal solutions using Whatman 42 filter paper. The initial and final heavy metal concentrations were determined by atomic absorption spectrophotometer.

**Adsorption Ability**

The adsorption ability was calculated according to the following equations (Mustapha et al., 2019):

\[
R = \left( \frac{Co - Ce}{Co} \right) \times 100%
\]

\[
Qe = \frac{(Co - Ce) \times v}{m}
\]

Where:
- \( R \) = removal (%)
- \( Qe \) = adsorption capacity (mg/kg)
- \( Co \) = initial metal concentration (ppm)
- \( Ce \) = final metal concentration (ppm)
- \( v \) = volume of metal solution (ml)
- \( m \) = mass of adsorbent (g)

**Adsorption Isotherm**

The adsorption isotherm and constant were calculated according to the following equations (Mustapha et al., 2019):

**Freundlich Isotherm:**

\[
\log Qe = \log KF + \frac{1}{n} \times \log Ce
\]

**Langmuir Isotherm:**

\[
Qe = \frac{q_{max} \times KL}{q_{max} + Ce}
\]

Where:
- \( Qe \) = adsorption capacity (mg/kg)
- \( Ce \) = final metal concentration (ppm)
- \( KF \) = maximum adsorption capacity (mg/kg)
- \( q_{max} \) = maximum adsorption capacity (mg/kg)
- \( n \) = affinity parameter
- KL = affinity parameter

**Data Analysis**

Statistical analysis was performed with SPSS (version 22). The results are expressed as mean±SD. Kruskal-Wallis test was used to analyze the correlation between adsorbent weight with adsorption ability. Mann-Whitney test was used to analyze the correlation between contact time with adsorption ability. The effect of heavy metal type was examined using One-Way ANOVA, then followed by Duncan’s multiple range test. The isotherm model and constant were analyzed using Microsoft Excel (version 2013).

**RESULTS AND DISCUSSION**

**Adsorbent Characteristics**

Cockle (A. granosa) shell contains chitin–protein fiber that is associated with various amounts of CaCO₃ and other minerals (de Paula and Silveira, 2009), representation of cockle shell as given in Figure 1. Mineral composition and certain functional groups are responsible for the heavy metal uptake from an aqueous solution. Figure 2 shows that the most mineral element which is contained in adsorbent is calcium (93.315 %). The amount of other mineral is aluminium (0.74 %); silicon (1.55 %); sulfur (0.08 %); titanium (0.255 %); vanadium (0.013 %); manganese (0.17 %); iron (3.065 %); copper (0.086 %); strontium (0.691 %); barium (0.04 %); and zirconium (0.0025 %).

Figure 3 shows the ATR-FTIR analysis result of adsorbent, which was further confirm to contain CaCO₃ phase with a characteristic peak at 699, 712, 765, 861, and 1470 cm⁻¹, which indicates the CO₃²⁻ group. Besides that, the peak was shown at 1785 and 2508 cm⁻¹ also attributed to the combination modes of different CO₃²⁻ spectrum (Khiri et al., 2016). Adsorbent had the characteristic peak which indicates polymorph form of CaCO₃, that is aragonite at 699 and 861 cm⁻¹, calcite at 712 cm⁻¹, vaterite at 765 cm⁻¹. The peak at 3201 until 3703 cm⁻¹ corresponds to N-H stretching group.
present in chitin and protein. The peak at 3819 and 3849 cm\(^{-1}\) is related to O-H stretching group present in CaO (Konwar and Baruah, 2017). Based on the adsorbent characteristics, it can be concluded that the cockle \textit{(Anadara granosa)} shell contains various mineral oxide compounds (such as SiO\(_2\), Al\(_2\)O\(_3\), Fe\(_2\)O\(_3\), CaCO\(_3\), and MnO) and functional groups (such as CO\(_3^{2-}\), N-H, and O-H) that can be used as heavy metal adsorbent.

**Adsorption Ability**

The highest removal value is Pb.P5.30 (98.44±0.02 %) (lead; 0.5 gram adsorbent weight; contact time for 30 minutes), meanwhile the lowest removal value is Cd.P1.20 (21.76±0.79 %) (cadmium; 0.1 gram adsorbent weight; contact time for 20 minutes). The highest adsorption capacity value is Pb.P1.30 (711.9±51.7 mg/kg) (lead; 0.1 gram adsorbent weight; contact time for 30 minutes), meanwhile the lowest adsorption capacity value is Cd.P5.20 (312.9±0.8 mg/kg) (cadmium; 0.5 gram adsorbent weight; contact time for 20 minutes). The increase in adsorbent weight affects removal and adsorption capacity (P < 0.05; Figure 4; Table 1). This could be due to the increase in adsorbent weight is followed by an increase in the adsorbent surface area, pore size and volume, and the availability of vacant sites (Handayani and Sulistiyono, 2009).

The type of heavy metals affects removal and adsorption capacity (P < 0.05; Figure 4; Table 1). This could be due to the electronegativity of heavy metal. The more electronegative an element, the more it can attract electrons (Shaheen \textit{et al.}, 2018). The contact time does not affect removal and adsorption capacity (P > 0.05; Figure 4; Table 1). This could be due to the contact time has not reached the equilibrium point. The longer the contact time, the more opportunities for the adsorbent to interact with heavy metals (Handayani and Sulistiyono, 2009). Sorption is a general term that refers to all phenomena at adsorbent–heavy metal solution interface, the mechanism of heavy metal adsorption by the adsorbent can be explained by the following examples.

(i) **Van der Waals force:** attraction forces between heavy metals ion and adsorbent surface ion (Than, 2020).

(ii) **Co-precipitation:** the reaction of heavy metals with adsorbents to form water-insoluble substances (Handoko \textit{et al.}, 2013).

\[
\begin{align*}
2\text{CO}_3^{2-} + 5\text{Cd}^{2+} + 6\text{H}_2\text{O} &\rightarrow \text{Cd}_5(\text{CO}_3)_2(\text{OH})_6 + 6\text{H}^+ \\
2\text{SiO}_2 + 5\text{Cu}^{2+} + 6\text{H}_2\text{O} &\rightarrow \text{Cu}_5(\text{SiO}_3)_2(\text{OH})_6 + 6\text{H}^+ \\
2\text{PO}_4^{3-} + 3\text{Pb}^{2+} + 6\text{H}_2\text{O} &\rightarrow \text{Pb}_3(\text{PO}_4)_2(\text{OH})_6 + 6\text{H}^+
\end{align*}
\]
(iii) **Electrostatic Attraction**: attraction interactions between different charges molecules (Yang *et al*., 2019).

(iv) **Ion Exchange**: exchange one or more heavy metals ion with equivalent adsorbent ion (Said, 2010).

**Adsorption Isotherm**

The adsorption isotherm is a relationship between adsorbate in the liquid phase and the adsorbate adsorbed on the surface of the adsorbent at equilibrium at constant temperature (Handayani and Sulistiyono, 2009). The decrease in the value of n and R_L correlated with the lower value of removal and adsorption capacity between the three metals, which indicates favorable heavy metal uptake; as given in Table 1 and 2. The n values measure the favourability of the adsorption process. The n values for the metal ions correspond to the favorable adsorption process of 0 < n < 10. The R_L value describe whether the adsorption is irreversible (R_L = 0), favourable (0 < R_L < 1) or linear or unfavourable (R_L = 1 or R_L > 1) (Mustapha *et al*., 2019).

The Freundlich isotherm showed a better fit to the experimental data with higher correlation coefficients (R^2) for all the heavy metals; as given in Table 2. The Freundlich isotherm was used to reveal chemisorption, while Langmuir isotherm to informed about physisorption (Handayani and Sulistiyono, 2009). The reason behind physisorption is Van der Waals forces, whereas chemical bonds lead to chemisorption. Physisorption is reversible; multilayer adsorption; favor in low temperatures; forming weak bonds; has less activation energy. Chemisorption is irreversible; monolayer adsorption; favor in high temperatures; forming strong bonds; has high activation energy (Murachman *et al*., 2014).

https://e-journal.unair.ac.id/JAFH

Tantri *et al*.

(2022)
Figure 1. The prismatic layer of the Bivalve shell, fractured in a plane perpendicular to its outer surface (SEM, 25 kV) (de Paula and Marina Silveira, 2009). A. The aragonitic simple prisms, about 1 mm high, were cut at different levels. B. End-on view of the crystals showing hexagonal or pentagonal bases; their polycrystalline character is evident. C. Periodic growth steps (*) and remains of the biological matrix decorate the lateral surfaces of all prisms. D. Illustration of a mineral-chitin-protein complex in cockle shell.

Figure 2. XRF analysis result of adsorbent mineral element composition.

Figure 3. ATR-FTIR analysis result of adsorbent functional group.
Cadmium (Cd), copper (Cu), and lead (Pb) average removal value of 98.44%. The treatment had the highest removal value for Pb (lead), Cu (copper), Cd (cadmium); contact time for 20 minutes (20) and 30 minutes (30).

Table 1. Adsorption ability.

| Treatments | Removal (%) | Adsorption Capacity (mg/kg) |
|------------|-------------|-----------------------------|
|            | Lead (Pb)   | Copper (Cu) | Cadmium (Cd) | Lead (Pb) | Copper (Cu) | Cadmium (Cd) |
| t: 20      |             |              |              |           |              |              |
| P1         | 34.76±1.68  | 33.67±0.68   | 21.76±0.79   | 690.2±33.1 | 666.6±13.0  | 430.7±15.6   |
| P2         | 62.93±0.42  | 60.94±0.19   | 40.40±0.66   | 627.6±3.3  | 606.5±2.8   | 401.9±6.3    |
| P3         | 83.48±0.26  | 80.57±0.20   | 56.00±0.45   | 556.2±0.9  | 535.4±0.5   | 372.1±2.7    |
| P4         | 94.04±0.19  | 91.60±0.09   | 68.76±0.44   | 470.2±0.6  | 456.9±0.3   | 343.0±2.0    |
| P5         | 98.22±0.02  | 96.63±0.04   | 78.37±0.21   | 392.7±0.1  | 385.8±0.1   | 312.9±0.8    |
| t: 30      |             |              |              |           |              |              |
| P1         | 35.88±2.57  | 33.99±0.70   | 22.53±0.79   | 711.9±51.7 | 673.0±12.8  | 446.4±14.9   |
| P2         | 64.11±0.51  | 61.74±0.38   | 41.79±0.58   | 639.4±5.3  | 614.3±3.3   | 415.8±5.0    |
| P3         | 84.55±0.17  | 81.55±0.21   | 57.86±0.43   | 562.9±1.4  | 542.0±1.0   | 384.4±2.6    |
| P4         | 94.65±0.17  | 92.59±0.06   | 70.55±0.29   | 473.4±0.9  | 461.9±0.2   | 351.8±0.9    |
| P5         | 98.44±0.02  | 97.22±0.03   | 80.00±0.19   | 393.5±0.4  | 388.1±0.5   | 319.3±0.9    |

*abcd*: different superscript letters within the same column indicate significant differences (p < 0.05).

Description: adsorbent weight at P1 (0.1 gram), P2 (0.2 gram), P3 (0.3 gram), P4 (0.4 gram), P5 (0.5 gram); Pb (lead), Cu (copper), Cd (cadmium); contact time for 20 minutes (20) and 30 minutes (30).

Table 2. Isotherm model and constant.

| Isotherm Model | Isotherm Constant | Contact Time for 20 Minutes | Contact Time for 30 Minutes |
|----------------|-------------------|-----------------------------|-----------------------------|
|                |                   | Lead (Pb) | Copper (Cu) | Cadmium (Cd) | Lead (Pb) | Copper (Cu) | Cadmium (Cd) |
| Freundlich     | Kf (mg/g)         | 461       | 416.1       | 217.4        | 472.2      | 432.1       | 226.6        |
|                | n                 | 6.39      | 5.43        | 4.03         | 6.35       | 5.78        | 4.03         |
|                | R²                | 0.9999    | 0.9999      | 0.9999       | 0.9999     | 0.9999      | 1            |
| Langmuir       | qmax (mg/g)       | 1111      | 769.2       | 175.4        | 1111       | 909.1       | 188.7        |
|                | Rₜ                 | 0.07      | 0.05        | 0.02         | 0.07       | 0.06        | 0.02         |
|                | R²                | 0.9968    | 0.9964      | 0.9977       | 0.9958     | 0.9967      | 0.9978       |

CONCLUSION
Cockle (A. granosa) shell waste can be used as an adsorbent for cadmium (Cd), copper (Cu), and lead (Pb). Pb.P5.30 (lead; 0.5 gram; contact time for 30 minutes) treatment had the highest average removal value of 98.44%. Cadmium (Cd), copper (Cu), and lead (Pb) tend to exhibit the Freundlich isotherm pattern.

Based on the results of the research, it is recommended to modify the preparation of cockle (A. granosa) shell waste as an adsorbent to increase its effectiveness. Then, further research is needed through in vivo tests on fishery products to confirm the quality of the product.
adsorbent in order to qualify food-grade standards.

ACKNOWLEDGMENT
The authors would like to express a great attitude to everyone who supported this research.

REFERENCES
Anugerah, A.S. and Iriany, 2015. Pemanfaatan limbah cangkang kerang bulu sebagai adsorben untuk menyerap logam kadmium (II) dan Timbal (II). Jurnal Teknik Kimia USU, 4(3), pp.40-45. https://doi.org/10.32734/jtk.v4i3.1480

Bhara, A.M., Meye, E.D. and Kamlasi, Y., 2018. Analysis of bivalves nutrient content consumed in The Coastal Coast of Arubara, Ende. Jurnal Biotropikal Sains, 15(3), pp.38–48. http://ejurnal.undana.ac.id/index.php/biotropikal/issue/view/no3

de Paula, S.M. and Silveira, M., 2009. Studies on molluscan shells: Contributions from microscopic and analytical methods. Micron, 40(7), pp.669-690. https://doi.org/10.1016/j.micron.2009.05.006

Handayani, M. and Sulistiyono, E., 2009. Uji persamaan langmuir dan freundlich pada penyerapan limbah chrom (VI) oleh zeolit. Prosiding Seminar Nasional Sains dan Teknologi Nuklir PTNBR - BATAN Bandung, pp.130-136. https://digilib.batang.or.id/ppin/katalog/file/1858-3601-2009-130.pdf

Handoko, C.T., Yanti, T.B., Syadiyah, H. and Marwati, S., 2013. Penggunaan metode presipitasi untuk menurunkan kadar Cu dalam limbah cair industri perak di Kotagede. Jurnal Penelitian Sains, 18(2), pp.51-58. http://dx.doi.org/10.21831/jps.v18i2.2140

Khiri, M.Z.A., Matorri, K.A., Zainuddin, N., Abdullah, C.A.C., Alssan, Z.N., Baharuddin, N.F. and Zaid, M.H.M., 2016. The usability of ark clam (Anadara granosa) shell as calcium precursor to produce hydroxyapatite nanoparticle via wet chemical precipitate method in various sintering temperature. SpringerPlus, 5(1206), pp.1-15. https://doi.org/10.1186/s40064-016-2824-y

Konwar, R. and Baruah, G.D., 2017. Raman, FT Raman and FTIR Spectra of molluscan shells. International Journal of Advanced Research, 5(6), pp.1408-1415. http://dx.doi.org/10.21747/IJAR01/4551

Matondang, C.D.P., 2019. Pemanfaatan cangkang kerang simping (Placuna placenta) sebagai adsorben logam timbal (Pb(II)) dan aplikasinya pada limbah cair industri elektroplating. Thesis. Jurusan Ilmu dan Teknologi Lingkungan. Fakultas Sains dan Teknologi. Universitas Airlangga. Surabaya.

Murachman, B., Putra, E.S. and Wulandary, 2014. Dekolorisasi dan deoildisasi parafin menggunakan adsorben zeolit, arang aktif dan produk pirolisis batu bara. Jurnal Rekayasa Proses, 8(2), pp.40-48. https://doi.org/10.22146/jrekpros.11371

Mustapha, S., Shuaib, D.T., Ndamitso, M.M., Etsuyankpa, M.B., Sumaila, A., Mohammed, U.M. and Nasirudeen, M.B., 2019. Adsorption isotherm, kinetic and thermodynamic studies for the removal of Pb(II), Cd(II), Zn(II) and Cu(II) ions from aqueous solutions using Albizia lebbeck pods. Applied Water Science, 9(142), pp.1-11. https://doi.org/10.1007/s13201-019-1021-x

Pridyanti, D.D., Moelyaningrum, A.D., and Ningrum, P.T., 2018. Pemanfaatan limbah cangkang kupang (Corbula faba) teraktivasi termal sebagai adsorben logam kromium (Cr⁶⁺) pada limbah cair batik. Hibualamo Seri Ilmu-ilmu Alam dan Kesehatan, 2(2), pp.78-83. http://journal.unhe na.ac.id/index.php/hibualamo/article/view/92
Said, N.I., 2010. Metoda penghilangan logam berat (As, Cd, Cr, Ag, Cu, Pb, Ni dan Zn) di dalam air limbah industri. *Jurnal Air Indonesia*, 6(2), pp.136-148. https://doi.org/10.29122/jai.v6i2.2464

Shaheen, S.M., Niazi, N.K., Hassan, N.E.E., Bibi, I., Wang, H., Tsang, D.C.W., Ok, Y.S., Bolan, N. and Rinklebe, J., 2018. Wood-based biochar for the removal of potentially toxic elements in water and wastewater: A critical review. *International Materials Review*, 64(9), pp.1-32. https://doi.org/10.1080/09506608.2018.1473096

Than, J., 2020. *Van der Waals interactions*. Chemistry LibreTexts. California State University. https://chem.libretexts.org/@go/page/1664

United Nations (UN), 2021. *The importance of water*. https://www.un.org/en/observances/water-day

United Nations Environment Programme (UNEP), 2021. *Tackling global water pollution*. https://www.unep.org/explore-topics/water/what-we-do/tackling-global-water-pollution

Yang, X., Wan, Y., Zheng, Y., He, F., Yu, Z., Huang, J., Wang, H., Ok, Y.S., Jiang, Y. and Gao, B., 2019. Surface functional groups of carbon-based adsorbents and their roles in the removal of heavy metals from aqueous solutions: A critical review. *Chemical Engineering Journal*, 366, pp.608-621. https://doi.org/10.1016/j.cej.2019.02.119