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Utilization of Yellow Shells (*Cypraea moneta*) in the Treatment of Cadmium Heavy Metal (Cd) Waste

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ABSTRACT

Cadmium (Cd) metal is a heavy metal that can cause environmental pollution if its levels are above the environmental quality standard value. Generally, industrial wastes such as paper industry waste contain heavy metal Cd with levels reaching 0.026 ppm. Meanwhile, the quality standard for Cd metal in the environment is 0.005 ppm. For this reason, it is necessary to process it to reduce the levels of Cd metal in the waste before being discharged into the environment. One way that can be used to reduce the levels of Cd metal is by adsorption method using *Cypraea moneta* clamshells containing chitin. This study used variations in the particle size of the shellfish adsorbent of 6 and 12 mesh. In addition, the ratio of the amount of adsorbate and adsorbent (mg:mg) is 1 : $0.5x10^6$; 1 : $1x10^6$; and 1 : $1.5x10^6$. Based on the results obtained, it showed that the use of shellfish as an adsorbent was able to reduce Cd metal content up to 89%.

***Keywords*:** Adsorption, cadmium, *Cypraea moneta*, shellfish, waste.

1. INTRODUCTION

Industrial waste that contains heavy metals and is not treated correctly is a major problem in environmental pollution that is difficult to handle and can negatively affect the surrounding environment. One of the industries that produce waste with high levels of heavy metals is the paper industry. In addition to produce waste containing organic substances such as lignin, cellulose, and hemicellulose, paper industry waste also contains inorganic materials such as heavy metals. The heavy metal contents in the waste come from the raw material used for pulp production. The types of heavy metals contained in the paper industry waste are Cadmium (Cd), Chromium (Cr), Nickel (Ni), Lead (Pb), and Mercury (Hg) with levels that are quite high when compared to the environmental quality standards as presented in Table 1.

Table 1. The content of heavy metals in paper industry water treatment waste compared to environmental quality standards.

Type of Metal	Content in waste (ppm)	Quality standard (ppm)*
Lead (Pb)	0.01127	0.050
Cadmium (Cd)	0.02623	0.005
Chromium (Cr)	0.01844	0.050
Nickel (Ni)	0.02450	0.050
Mercury (Hg)	0.00955	0.001

Information :
*Regulation of the Minister of Health of the Republic of Indonesia No. 32, 2017 [1]

These heavy metals are non-essential or toxic, where if they enter the body intentionally or unintentionally, their presence in the body is still unknown or even toxic. These heavy metals can cause health effects for humans such as physical discomfort, inhibition of metabolic processes in the body, life-threatening

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diseases and permanent damage to the body's vital systems [2,3]. Therefore, it is necessary to handle or prevent it to reduce the levels of heavy metals in the waste before being discharged into the environment. This research is focused on reducing the levels of heavy metal Cd by using the adsorption method.

Adsorption is the process of separating certain components by moving to the surface of a solid that can adsorb (adsorbent). Adsorption is basically the process of mass transfer of a substance from the liquid phase to a solid surface through physical and/or chemical interactions [4]. Adsorption has a high selectivity so that it can be used to separate materials with small concentrations from mixtures containing other ingredients with higher concentrations [5]. The adsorption process is generally related to the surface tension of a solid, where the active surface will attract or absorb other gas or liquid molecules. The material used in the adsorption process is referred as an adsorbent, which is a solid material that has a very large surface area and is useful as an adsorbent. The large surface is formed due to the presence of fine pores on the solid surface [6].

The removal of heavy metals using low-cost adsorbents is more desirable because there are several locally available and abundant materials such as natural materials or organic wastes that can be utilized as low-cost materials [7]. The adsorbent material that will be used in this study is yellow clam shell (*Cypraea moneta*) because it contains 54.8% (w/w) chitin compounds. Chitin $(C_8H_{13}NO_5)_n$ is a polysaccharide compound that has a hydroxyl group and an active primary amine, is white in color in the form of crystals, semi-transparent, insoluble in ordinary solvents and insoluble in water. This compound is widely used as a coagulant, flocculant, and adsorbent for metal ions because it can form complex bonds with some transition metals well in the periodic system [8].

2. RESEARCH METHODS

2.1. TOOLS AND MATERIALS

The tools used include a set of the adsorber column (Figure 1), beaker glass, volumetric flask, mortar, pipette, balance, stirrer, and UV-Vis spectrophotometer single beam. While the materials used were water treatment waste from paper industry, clam shells, pH 7 buffer, tetrahydrofuran (THF), and tri-butyl phosphate (TBP).

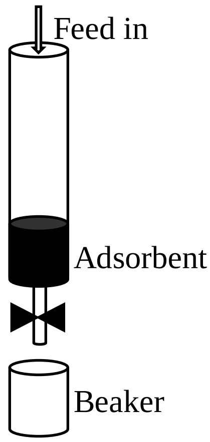

Figure 1. Schematic diagram of adsorber column in this study.

2.2. ADSORPTION PROCESS

The shells were cleaned by washing and soaking, then dried at a temperature of 50-70°C for 1 hour for the activation process. After the clam shells were dry, they were crushed using a crusher and sieved with particle sizes of 6 and 12 mesh. The shells that have been sieved were then put into the adsorption column. Then, the waste sample has flowed at a flow rate of 30 mL/minute and the treatment results were accommodated in a glass beaker every 100 mL for further analysis of Cd metal content using UV-Vis spectroscopy.

2.3. Cd METAL ANALYSIS

Cd metal analysis was carried out using a UV-Vis spectrophotometer with reagents consisting of a mixture of 10 mL tetrahydrofuran (THF) and 16 mL tri-butyl phosphate (TBP). The analysis procedure was carried out by measuring 5 mL of the sample, then adding 5 mL of pH 7 buffer to maintain the pH of the solution. Then put in a cuvette and add 2 mL of reagent THF and TBP. Let stand for 30 minutes, and observe the absorbance using a UV-Vis spectrophotometer at a wavelength of 460 nm [9]. Determination of the concentration of Cd in the sample was calculated using the standard Cd curve.

2.4. BACKWASH PROCESS

The backwash process aims to regenerate the adsorbent that has been used. The procedure was carried out to alternately wash the adsorption column using water and a dilute acid-base solution from the bottom of the column, so that the solution becomes neutral and metal ions form salts. Next, the salt solution formed was removed through the valve at the bottom of the column and collected in a holding container. After the regeneration process, analysis using UV-Vis spectrophotometer was also carried out.

3. RESULTS AND DISCUSSION

Based on the data that has been obtained, the decrease in the concentration of Cd metal in the waste can be done through the adsorption method using an adsorbent from yellow clam shells. This can be done because based on the analysis in this study, it shows that the yellow shell contains a chitin of 54.8% (w/w). Following the statement of Stephen [8] which states that chitin and chitosan can form complex bonds with several transition metals well. As it is known that Cd metal is included in the transition metal in the periodic system of elements, shells can be used as an alternative to reduce Cd metal levels in waste.

The adsorption mechanism that occurs is that the Cd metal ions contained in the waste will be bound to the surface of the adsorbent. The principle of metal absorption in chitin contained in clam shells is ion exchange, where the amine group (-NH-) in chitin will bind metal ions from the liquid waste mixture and release H^+ ions (Figure 2). This is because metals in general in electrolyte solutions are positively charged particles, while chitin is a cationic polyelectrolyte [6].

This research was conducted by using variations in the size of the shellfish adsorbent of 6 and 12 mesh. In addition, variations in the ratio between the amount of Cd metal in the liquid waste and the amount of shellfish adsorbent were also carried out by 1 : $0.5x10^6$; 1 : $1x10^6$; and 1 : $1.5x10^6$ (w/w). From the data obtained as presented in Table 2, at a ratio of 1 : $1x10^6$ the use of shellfish adsorbent with a size of 6 mesh is known to reduce the concentration of Cd metal by 88.6% (w/w). Meanwhile, using 12 mesh shells as adsorbents with the same ratio is known to reduce the concentration of Cd metal by 89.5% (w/w).

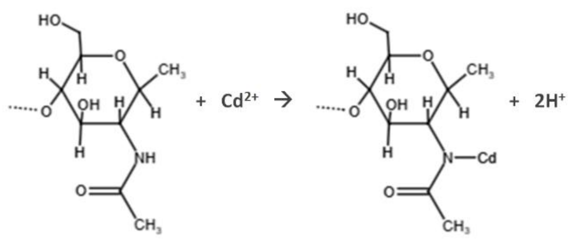

Figure 2. Cd^{2+} binding reaction by chitin.

At a different ratio, namely 1 : $1.5x10^6$ using 6 mesh sized shellfish adsorbent, the data obtained for decreasing the metal concentration of Cd was 89.0% (w/w). And, on the use of calm shell adsorbent with a size of 12 mesh, data obtained for a decrease in Cd metal concentration of 89.6% (w/w).

Based on the results of the analysis of these data, it can be concluded that the shellfish adsorbent can reduce Cd metal levels from industrial wastewater to below the Environmental Quality Standards determined by the government in the Regulation of the Minister of Health of the Republic of Indonesia No. 32 of 2017, which states that the permissible quality standard value for Cd metal is 0.005 ppm [2]. For the results of the analysis at a ratio of 1 : $0.5x10^6$, the use of shellfish adsorbents with a size of 6 and 12 mesh is known to only be able to reduce the concentration of Cd metal by 71.6% to 72.2% (w/w). Based on these data, it can be concluded that the use of a ratio of 1 : $0.5x10^6$ is not optimal in reducing the concentration of Cd metal from liquid waste because it still leaves Cd metal with levels above the established environmental quality standards.

Based on the data in Figure 3, it shows that the ratio of the amount of adsorbate to the adsorbent affects in decreasing the concentration of Cd metal. According to research conducted by Cundari, et al. [10], by increasing the surface area of the adsorbent, the more metal ions bound to the surface of the adsorbent, then the higher ability to reduce the Cd metal. But, in this study, the different particle size of adsorbent (6 and 12 mesh) have a similar ability to reduce Cd metal content.

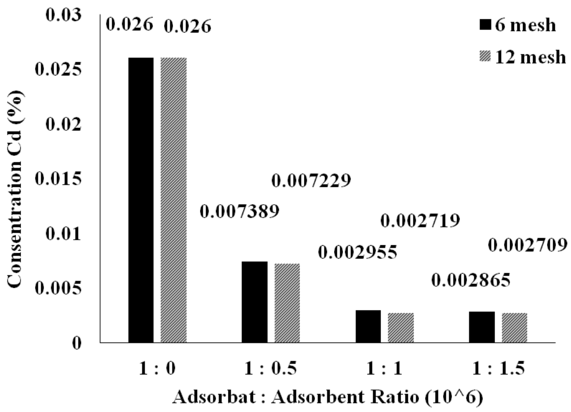

Figure 3. Graph of the decrease in Cd metal concentration.

In this study, a continuous adsorption process was also carried out to determine the saturation level of the shellfish adsorbent in absorbing Cd metal. The level of saturation of the adsorbent is shown in the breakthrough curve, which is the curve of the relationship between the adsorbate concentration from the adsorption column and the adsorption time.

The adsorption time variable is the time measured at certain intervals during continuous contact between the adsorbate and the adsorbent [11]. According to Kawamura, et al. [12], the breakthrough curve is a curve that describes the range of conditions where there is a drastic increase in the amount of metal adsorbed by the adsorbent before the adsorption process approaches equilibrium conditions.

Based on the breakthrough curve for Cd metal in Figures 4 and 5, the stability of the initial concentration of the adsorption process does not appear to occur, this can be seen by the increasing value of Cd concentration even though the increase is very small. This situation occurs between 0 to 120 minutes. However, between 120 to 240 minutes, the increase in concentration values seems to be getting bigger with increasing time. The condition at this time is known as the breaking point. According to Sundstrom [13], this condition is called the breaking point, the point where the concentration in the effluent begins to increase.

Table 2. The adsorption ability of shells

Ratio	**Diameter**	**Absorbansi**		**Concentration**	**%**
		A.1	**A.2**	**Cd (ppm)**	**reduction**
1 : 0.5x10^6	6 mesh	0.03299	0.03298	0.0074	71.6
	12 mesh	0.03254	0.03254	0.0072	72.2
1 : 1x10^6	6 mesh	0.02058	0.02057	0.0030	88.6
	12 mesh	0.01992	0.01991	0.0027	89.5
1 : 1.5x10^6	6 mesh	0.02032	0.02033	0,0029	89.0
	12 mesh	0.01988	0.01989	0,0027	89.6

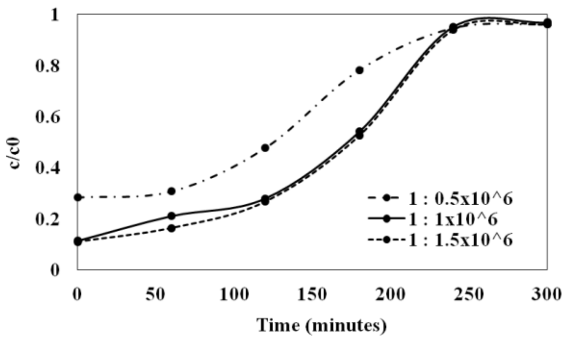

Figure 4. The breakthrough curve of 6 mesh shell adsorbent on Cd metal analysis results.

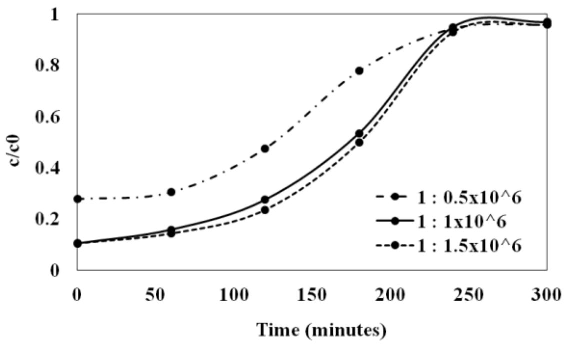

Figure 5. Breakthrough curve of 12 mesh shell adsorbent on Cd metal analysis results.

In addition, based on the breakthrough curve above, the use of shellfish adsorbent at a ratio of $1.5x10^6$ to $1x10^6$ did not have a significant difference. So when viewed from the estimated process cost, the use of shells with a ratio of $1x10^6$ can already be applied as an increase in WWTP improvements. Meanwhile, the ratio of $0.5x10^6$ cannot be applied because the concentration of effluent in the adsorption process is still above the standard value of environmental quality standards.

After going through the adsorption process for a certain time, the adsorbent will experience saturation which is indicated by a decrease in the number of adsorbed molecules. That was known by conducting metal analysis by sampling using a UV-Vis spectrophotometer. If the adsorbent has experienced its saturation point, it is necessary to carry out a regeneration process for the adsorbent. The adsorbent regeneration process can be carried out in two ways, namely by heating and backwashing. The most commonly used method is through a heating process that aims to reactivate the adsorbent [14,15]. However, when viewed in terms of the estimated cost of the heating process with the use of steam, it requires a large cost.

Based on the data in Table 3, the results of the analysis of the output of the adsorption process using the adsorbent after the regeneration process still can reduce Cd metal levels to below environmental quality standards. Although the ability of the adsorbent to absorb Cd metal begins to decrease when compared to the use of new adsorbents, this backwash process can be used as an alternative to the reactivation of previously used adsorbents. The decrease in the ability of the adsorbent after the backwash process is due to the presence of metal ions attached to the adsorbent so that the adsorbent becomes saturated faster.

Table 3. The adsorption ability of mussel shells during the first use and after the regeneration process by backwashing.

Ratio	Size	First use		After regeneration	
		Concentration Cd (ppm)	% reduction	Concentration Cd (ppm)	% reduction
$1 : 0.5x10^6$	6 mesh	0.0074	71.6	0.0080	69.2
	12 mesh	0.0072	72.2	0.0073	71.8
$1 : 1x10^6$	6 mesh	0.0030	88.6	0.0030	88.4
	12 mesh	0.0027	89.5	0.0030	88.4
$1 : 1.5x10^6$	6 mesh	0.0029	89.0	0.0031	88.0
	12 mesh	0.0027	89.6	0.0028	89.2

4. CONCLUSION

Based on the results of the study, it can be concluded that the adsorption process using clam shells can be used as an alternative in the method of reducing Cd metal levels in liquid waste. The adsorption process using clam shells can reduce the metal content of Cd up to 89.6%. The best particle size used to adsorb Cd metal in this study was 12 mesh. While the ratio of the ratio of adsorbate and adsorbent best to meet the Cd metal content below the environmental quality standards is to use a ratio of 1 : $1.5x10^6$. However, when viewed from the economic value, the use of a ratio of 1 : $1x10^6$ has been able to reduce the Cd metal content up to below the value of environmental quality standards.

REFERENCES

[1] Peraturan Menteri Kesehatan Republik Indonesia, *Peraturan Menteri Kesehatan No. 2406 Tahun 2011 tentang Pedoman Umum Penggunaan Antibiotik*, 2011.

[2] S. Martin, W. Griswold, Human Health Effects of Heavy Metals, in *Environmental Science and Technology Briefs for Citizens*, issue. 15, 2009.

[3] T. Can, Introduction to Bioinformatics, in *miRNomics: MicroRNA Biology and Computational Analysis*, Totowa, NJ: Humana Press, vol. 1107, pp. 51–71, 2014.

[4] C. T. Chiou, Fundamentals of the Adsorption Theory, in *Partition and Adsorption of Organic Contaminants in Environmental Systems*, New Jersey: John Wiley & Sons, Inc., pp. 39–52, 2002.

[5] M. Sperling, S. Xu, B. Welz, Determination of chromium(III) and chromium(VI) in water using flow injection on-line preconcentration with selective adsorption on activated alumina and flame atomic absorption spectrometric detection, *Anal. Chem.*, vol. 64, no. 24, pp. 3101–3108, 1992.

[6] W. L. McCabe, J. C. Smith, P. Harriott, Unit operations of chemical engineering, New York: McGraw-Hill Education, 1982.

[7] S. N. A. Abas, M. H. S. Ismail, M. L. Kamal, S. Izhar, Adsorption process of heavy metals by low-cost adsorbent: A review, *World Appl. Sci. J.*, vol. 28, no. 11, pp. 1518–1530, 2013.

[8] A. M. Stephen, Food polysaccharides and their applications, 2nd Edition, Boca Raton: CRC Press, 2006.

[9] A. Marlina, Pengembangan Metode Penentuan Kadar Timbal Dalam Kerang Hijau (Perna viridis L) Secara Spektrofotometri UV-Vis, in *Prosiding Industrial Research Workshop and National Seminar*, pp. 521–524, 2019.

[10] L. Cundari, M. F. Melsi, C. Fiat, Pengaruh Waktu Sampling dan Ukuran Partikel Adsorben Terhadap Adsorpsi Kontinyu Limbah Kain Jumputan, *Jurnal Teknik Kimia*, vol. 22, no. 4, pp. 19–26, 2016.

[11] Y. Sahan, K. Despramita, Y. Sultana, Penentuan Daya Serap Bentonit dan Kesetimbangan Adsorpsi Bentonit Terhadap Ion Cu(II), *Chem. Prog.*, vol. 5, no. 2, pp. 93–99, 2012.

[12] Y. Kawamura, H. Yoshida, S. Asai, H. Tanibe, Breakthrough curve for adsorption of mercury (II) on polyaminated highly porous chitosan beads, *Water Sci. Technol.*, vol. 35, no. 7, pp. 97–105, 1997.

[13] D. W. Sundstrom, H. E. Klei,

Wastewater treatment. Englewood Cliffs, N.J: Prentice-Hall, 1979.

[14] J. H. Nasution, I. Iriany, Pembuatan Adsorben dari Cangkang Kerang Bulu yang Diaktivasi Secara Termal sebagai Pengadsorpsi Fenol, *Jurnal Teknik Kimia USU*, vol. 4, no. 4, pp. 51–57, 2015.

[15] Y. Suprianti, A. S. Kurniasetyawati, Regenerasi In-Situ Adsorben Karbon Aktif Tipe Granul dengan Metode Termal, *J. Tek. Kim. Ling.*, vol. 3, no. 1, pp. 1–9, 2019.