Cadmium (Cd) Metal Adsorption Analysis in Water using Plant Waste Corncobs as Natural Adsorbent

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Abstract

Heavy metals are known to accumulate in the body of an organism, and remain for a long time as toxins.The metal can be distributed to parts of the human body and some will accumulate in the body. If this situation continues, in the long term it can reach an amount that is harmful to human health. Efforts to reduce heavy metals in waste need to be carried out so that industrial contaminants do not pollute the environment too much when discharged into water bodies. So as to minimize the danger of contamination from industrial waste containing heavy metals. The adsorption process is more suitable because the costs required are not too expensive and will not cause new pollutants. Currently, research is being promoted on the use of alternative adsorbents derived from nature. Natural adsorbents in addition to having good adsorption ability, are also more economical. So the aim and target of this research to be achieved is to analyze the content of Cd metal in water using natura1 adsorbent derived from corncobs waste (Zea mays L.). To achieve this goal, the research method that will be carried out is to measure water samples that have been added with natural adsorbent from corncobs which were previously carried out by carbonization, biosorbent activation, and biosorbent characterization using XRD and BET analysis methods, respectively. The results showed that carbon had been carbonized and activated, then the results of XRD characterization analysis were carried out to determine the crystallinity of the layer formed on the biosorbent and activated carbon from corncobs. From the results of the research, the characterization results showed that the carbon and activated carbon from the biosorbent had an amorphous structure with a pore size of micropores. The optimum condition of corncobs activated carbon was at a mass of 5 gram and a contact time of 15 minutes with the absorption capacity of corncobs activated carbon of 56.92 %. The ability of activated carbon from corncobs biosorbent to absorb Cd(II) in water was 0.06 ppm.

Keywords: *Biosorbent, carbonization, activation, adsorption, characterization.*

1. Introduction

In general, heavy metals are toxic to living things, but some of them are required in small amounts. There are several ways how heavy metals enter the environment, such as contaminated air, food or water. The metal can be distributed to parts of the human body and some will accumulate in the body. If this situation continues, in the long term it can reach an amount that is harmful to human health (Sofyan Yatim, et al., 1979).Usually water is more often polluted by inorganic components, for example heavy metals compared to other components. This happens because some heavy metals are widely used in various daily needs, especially for industrial activities whose waste is sometimes are still thrown into the environment. If this situation occurs continuously and has passed the permissible threshold, it will be dangerous for the life of living things and the environment (Darmono, 1995).

Handling and reducing heavy metals in waste needs to be done so that industrial waste does not pollute the environment too much when it is discharged into water bodies. So that it can reduce the danger of contamination from industrial waste containing heavy metals. One way that can be done is an adsorption process, because the costs required are not too expensive and will not cause new pollutants.Currently, research is being promoted on the use of alternative adsorbents derived from nature. Natural adsorbents in addition to having good adsorption capabilities, are also more economical (Rahmi and Sajidah, 2017).

Corn will produce waste, the amount of which will continue to increase along with the increase in post-harvest activities which will result in environmental pollution. Along with the increasing production of corn, it cannot be denied that the presence of waste from corn processing will also increase. The waste generated includes corncobs. Corncobs are the part of the corn that does not contain seeds. Most people only think of corncobs as waste or as animal feed that has no added value. Corncobs contain 41% cellulose, 36% hemicellulose, 16% lignin and 8% other substances (Subekti, 2006).

The contributions of this research in science include the ease with which the materials used in this method can be found in everyday life, in addition, the fruit wastes used are no longer thrown away but can be used to analyze metal content in water. Based on the above background, a research will be conducted to analyze the metal content in water using corncobs biosorbent with UV-Vis spectrophotometry method.

2. Materials and Methods

The instruments used in this study are: UV-Vis spectrophotometer, oven, blender, 70 mesh sieve, furnace, analytical balance, shaker, desiccator, magnetic stirrer, Whatman No 42 filter paper, spray bottle, dropper, beaker, pH meter, funnel, flask 25 mL, 50 mL and 100 mL and a watch glass. All materials and reagents used in this study are: water samples, corn cobs, aquadest, H_2SO_4 1 M, HNO_3 0.6 M, standard solution Cd 1000 mg/L, 1,10-phenanthroline solution 1000 ppm, acetate buffer solution pH 3.5, and acetone.

Experimental Procedure

2.1 Biosorbent Preparation and Carbonization

In this study, corncobs waste were each cleaned by washing until clean and then each waste was dried in the open air (sunlight) for 7-8 days. Then cut into small pieces. Then each waste is ground using a blender. Biosorbent of corncobs were heated at a temperature of 300 ^oC for ± 1 hour, after which they were placed in a closed container. The carbonization results are then ground and sieved using a 70 mesh sieve.

2.2 Biosorbent Activation Process of Corncobs

Charcoal activation was carried out using an acid solution in the form of H_2SO_4 referring to the research of Irmanto and Suyata (2010) and Alfiany, et al., (2013). The biosorbent charcoal was weighed as much as 60 grams, soaked while stirring with a magnetic stirrer for 30 minutes in 250 mL H_2SO_4 solution with a concentration of 1 M as much as 250 mL for 24 hours, then filtered. The solids were washed using distilled water and dried in an oven with time and temperature in stages at an initial temperature of 50˚C for 30 minutes followed by a temperature of 80˚C for 45 minutes then ground first and then at a temperature of 110˚C for 45 minutes, then put in a desiccator.

2.3 Biosorbent Characterization

To see the properties of the biosorbent of corncobs before and after activation using H_2SO_4 characterized by XRD (X-ray Difractometer), to determine the crystalline phase of the adsorbent and to determine the structure of biosorbents of corn coband BET (Brunnaeur-Emmelt-Teller) to determine the size and the pores of the surface area of the adsorbent.

2.4 Water Sample Preparation

Water samples were taken in an industrial area in the Kuala Tanjung area, Batubara Regency. The water sample that has been taken is then added with concentrated HNO_3 until pH 2 is measured using a pH meter. Then the sample was put into a polyethylene bottle filtered with whatman filter paper No. 42 on a filter funnel to clear the sample from impurities such as mud and sand. The sample is ready for analysis.

2.5 Optimum Mass Against Water Purification

The mass variation used in the absorption process of the corncobs adsorbent consisted of 1 g, 2 g, 3 g, 4 g and 5 g. The variation of each adsorbent was then added with 100 mL of water sample, then stirred with a magnetic stirrer at a speed of 125 rpm for 15 minutes. Then filtered using filter paper, the filtrate obtained was then analyzed using a UV-Vis Spectrophotometer instrument.

2.6 Optimum Contact Time Against Water Purification

Each adsorbent with the optimum mass previously obtained was weighed. Then added 100 mL of water sample, then stirred with a magnetic stirrer at a speed of 125 rpm, with time variations of 15 minutes, 30 minutes, 60 minutes and 75 minutes. Then filtered using filter paper, then the filtrate obtained was then analyzed using a UV-Vis Spectrophotometer instrument.

2.7 Water Sample Absorption

Weighed each adsorbent with the optimum mass that has been obtained, then added with 100 mL of water sample, then stirred with a magnetic stirrer at a speed of 125 rpm for the optimum time variation that has been obtained. Then filtered, then the filtrate obtained was then analyzed using a UV-Vis Spectrophotometer instrument.

3. Results and Discussion

3.1 Biosorbent Preparation

In this study, corncobs waste was cleaned by washing it thoroughly to remove impurities that were still in the corncobs. The washed corncobs are then dried in the open air (sunlight) for 7-8 days to reduce the moisture content and to prevent the emergence of microorganisms on the corncobs. Then the corncobs are cut into small pieces and mashed using a blender. Furthermore, dried corncobs are heated in a furnace at a temperature of 300 ^{o}C for ± 1 hour to reduce the water content. After that it is placed in a closed container. The carbonization results are then ground and sieved using a 70 mesh sieve. The goal is to increase the surface area of the biosorbent so that the adsorption ability is higher**.** Corncobs samples used as natural adsorbent. In the preparation process, washing is carried out to remove the remaining impurities that are still present in the corncobs. The washed corncobs were then chopped and washed again with running water to obtain cleaner corncobs. Corncobs that have been washed and chopped and then dried in the sun for 7-8 days to dry to reduce water content and extend the shelf life of corncobs to prevent the emergence of microorganisms on corncobs.

3.2 Carbonization and Carbon Activation

At the carbonization stage, the volatile components contained in the biosorbent samples of corncobs were evaporated. Each biosorbent was carbonized at 500^{o}C for 2 minutes to remove volatile components in order to obtain corn cob carbon. In the carbonization process, the volatile organic content is indicated by the amount of smoke produced. The carbonization process is complete, it is indicated by the sample has changed evenly to black color and has less smoke. The decomposition of organic matter in the corncobs will evaporate the volatile components and will create a pore structure. High temperatures can speed up the reaction but if it is too high, such as above 1000°C, it can cause a lot of ash to close the pores. The activation process of activated carbon was carried out by soaking each of the carbon of corncobs in H_2SO_4 for 24 hours. The activation process aims to activate the carbonized carbon, remove impurity components such as water and volatile components that cover the carbon surface pores, and form new surface pores that will expand the activated carbon surface. This study uses acid activation with H_2SO_4 because H_2SO_4 is widely used as an activator in the manufacture of activated carbon.

3.3 XRD Characterization for Corn Cob Biosorbents and Activated Carbon

XRD characterization was carried out to determine the crystallinity of the layer formed on the biosorbent and activated carbon of corncobs. The results can be seen in Figure 1.

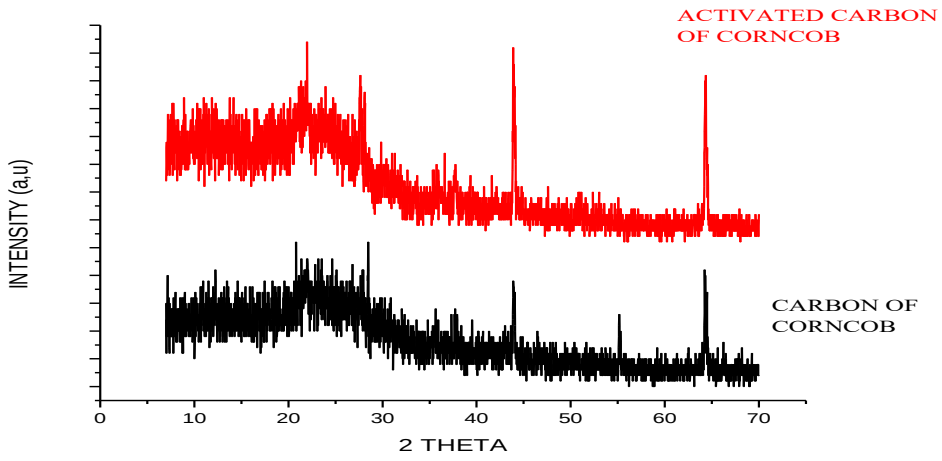

Figure 1. XRD pattern diffractogram of corn cob biosorbent and activated carbon of corncobs

Based on the figure 1, it can be seen that the resulting graphic form is different from corncobs biosorbent and corncobs activated carbon, this is influenced by the degree of crystallinity formed. Based on Figure 1, it can be seen that the shape of the resulting graph is different between corncobs biosorbent and corncobs activated carbon. This is influenced by the degree of crystallinity (%) formed. The smallest degree of crystallinity indicates the most amorphous nature whose structure has an irregular pattern of atomic or molecular arrangement. The higher the degree of crystallinity, the higher the structural regularity of a material. The difference in degree of crystallinity caused by a shift in the diffraction angle (2 theta).

3.4 BET Characterization Analysis for Corncobs Biosorbent and Activated Carbon

The inner surface of carbon has unique criteria, namely on the structure that becomes the absorbent by determining its absorption capacity (Bansal and Golan, 2005). Surface area, pore volume, average pore size and pore type can be analyzed by adsorption-desorption test of N_2 gas using the BET equation (Brunaur, Emmett and Teller). BET Characterization Analysis for corncobs biosorbent and activated carbon can be seen in Figure 2.

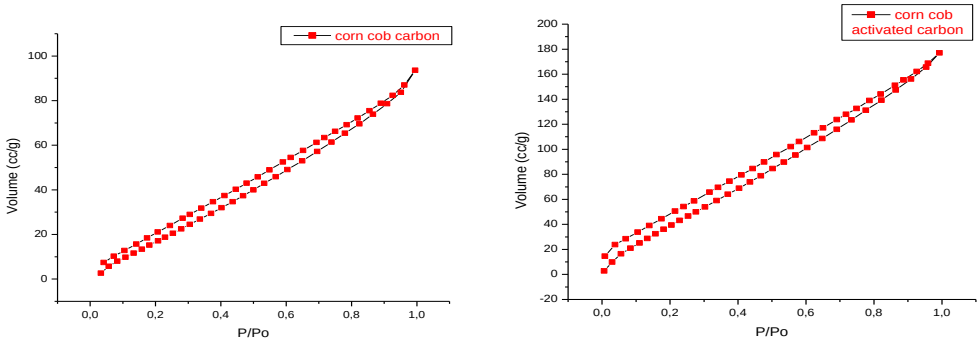

Figure 2. Isotherm Curve (a) corncobs carbon, (b) corncobs activated carbon

Based on the Figure 2 above, we can see that each graph meets the classification of type I, type II, and type V adsorption isotherms, which means that these four carbons have the same type, namely micropores (< 2nm). Carbon characteristics by BET analysis can be seen in Table 1. Referring to the Table 1, it is understood that each unactivated carbon has a lower surface area than the carbon that has been activated with H_2SO_2 acid.

This is caused by the activator that penetrates the gaps or pores in each carbon crystallite plate (activated carbon) which results in a higher surface area.

Table 1. Carbon characteristics by BET analysis

No.	Analysis Result		Sample	
			Corncobs Carbon	Corncobs Activated Carbon
1.	Surface Area	BET (m^2/g)	119.173	228.806
		BJH (m^2/g)	80.601	152.097
2.	PoreVolume (cm^3/g)		1.448	2.739
3.	Average Pore Size (nm)		243.091	239.383
4.	Pore Type		*micropore*	*micropore*

3.5 Effect of Adsorbent Mass on Cd(II) Metal Adsorption Process

The purpose of determining the optimum mass of the adsorbent is to determine the mass of the corncobs adsorbent which is considered very relevant in which the absorption of Cd(II) metal by corncobs activated carbon reaches optimal conditions. The effect of adsorbent mass on the adsorption of Cd(II) metal in this study using the batch method with the adsorbent mass of each activated carbon is 1 g, 2 g, 3 g, 4 g, and 5 g which are interacted with 100 mL of water sample and stirred with a 125 rpm stirrer for 15 minutes. Then each solution was filtered and the filtrate obtained was then analyzed with a UV-Vis spectrophotometer at a wavelength of 511 nm with the aim of knowing the concentration of Cd(II) metal contained in the water sample after the addition of the adsorbent and the results can be seen in Table 2 below.

Table 2. Corncobs Activated Carbon Mass Optimum Cd Metal Adsorption using UV-Vis Spectrophotometer

Corncobs Activated Carbon Mass	Initial Absorbance	Final Absorbance
1 g	0,082	0,011
2 g	0,082	0,019
3 g	0,082	0,025
4 g	0,082	0,027
5 g	0,082	0,031

3.6 Effect of Adsorbent Contact Time on Cd(II) Metal Adsorption Process

The process of determining the optimum contact time is aimed at determining the minimum time taken by the adsorbent of each activated carbon in absorbing Cd(II) metal ions in the maximum time until it reaches saturation conditions. Determination of the impact or contact time of corncobs activated carbon adsorbent to absorb Cd(II) metal present in water samples in this study was carried out using the batch method. The water sample that has been obtained is then added with 5 gram of corncobs activated carbon and shaken with a magnetic stirrer for a variation of time of 15, 30, 45, 60 and 75 minutes, then the solution is filtered and the filtrate obtained is then measured with a UV-Vis spectrophotometer at a length of 511 nm wave, as shown in Figure 3 below.

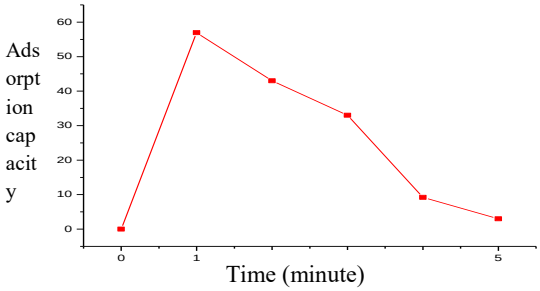

Figure 3. Graph of adsorption of contact time variations

Based on the Figure 3 that has been obtained for the analysis of time variations, it can be seen that the optimum condition of the corncobs activated carbon adsorbent is 15 minutes. Optimum conditions are events that indicate that in these conditions the most effective absorption occurs. On corncobs activated carbon, the contact time was from 15 to 75 minutes, the number of Cd(II) ions adsorbed was greater and reached the optimum point in the 15 minute contact period with an adsorption capacity of 56.92 %.

3.7 Activated Carbon Adsorption in Water Sample

The adsorption process of Cd(II) ions in this study was carried out by taking 100 mL of water samples, where before carrying out the adsorption process, the water sample to be analyzed was first calculated the Cd then added 1 gram of each carbon and homogenized using a magnetic stirrer within 15 minutes, according to the mass and optimum contact time that has been obtained. The initial concentration of the water sample obtained was 0.31 ppm, then calculated using the equation in linear regression that was obtained, namely y = 0.2197x - 0.0037, where the absorbance value of the water sample was 0.065. After adding activated carbon from corncobs, the water sample decreased the absorbance value to 0.052 with the total concentration of Cd(II) absorbed was 0.25 ppm wherein the final concentration of Cd(II) absorbed was 0.06 ppm.

4. Conclusion

The results of the XRD analysis characterization showed that corncobs biosorbent and corncobs activated carbon had amorphous material structure. This material is composed of atoms that are arranged irregularly and randomly scattered.The results of the BET analysis characterization obtained that each graph meets the classification of type I, type II, and type V adsorption isotherms, it means that these carbons have the same type, namely micropores (< 2nm). The characterization results showed that the carbon and activated carbon from the corncobs biosorbent had an amorphous structure with a pore size of micropores. The optimum condition of corncobs activated carbon adsorbent was at a mass of 5 grams and the optimum contact time of corncobs activated carbon was 15 minutes to adsorb Cd(II) metal with a capacity of corncobs activated carbon absorption was 56.92%.The ability of activated carbon from corncobs biosorbent to absorb Cd(II) in water was 0.06 ppm. The initial concentration of the water sample obtained was 0.31 ppm, after adding activated carbon from corncobs, the water sample decreased the total concentration of Cd(II) absorbed was 0.25 ppm where in the final concentration of Cd(II) absorbed was 0.06 ppm.

References

Alfiany, H., Bahri, S. and Nurakhirawati. (2013). Study on The use of Activated Charcoal from Corn Cobs as Adsorbent for Pb Metal with Several Acid Activators, Journal Natural Science, 2(3), 75-86.

A.M. Khah, and R. Ansari.(2009). Activated Charcoal: Preparation, Characterization and Applications, Iran. International Journal of ChemTech Research. Vol.1, No.4 ISSN : 0974-4290, hal. 859-864.

Arora. (2017). Physical, Chemical and Biological Characteristics of Water, Environmental Sciences.1–15

Darmono. (1995).Metals in Living Biological Systems, Universitas Indonesia Pers, Jakarta.

D.Suhedra and E.R.Gunawan. (2010). Making Activated Charcoal from Corn Stems Using Sulfuric Acid Activator and Its use in Copper (II) Ion Adsorption, Makara, Sains, Vol 14(1)

Duffus, J. H. (2002). Heavy Metal, Iupac. Scotland.

Oscik. (1982).Adsorption, England : Ellis Horwood Ltd

Rahmi. Rizna and Sajidah.(2017).Utilization of Natural Adsorbents (Biosorbents) to Reduce Lead (Pb) Levels in Liquid Waste, Proceedings of the National Biotic Seminar, ISBN: 978-602-60401-3-8

Safrianti I, Wahyuni N, Zaharah TA. (2012). Lead(II) Adsorption by Nitric Acid Activated Rice Straw Waste Cellulose: Effect of pH and Contact Time. JKK. 1(1): 1-7.

Sofyan Yatim, dkk. (1979).Distribution of Heavy Metals in Jakarta Bay Seawater, Majalah BATAN XII 3.

Stum,W. & Morgan,J.J.(1996). Aquatic Chemistry : Chemical Equilibria in Natural Water,John Willey and Sonds. Inc. New York.

Subekti, H. (2006). Ethanol Production from the Hydrolysis of Corncob Cellulose Fraction by Saceharomyces Cerevisiae, (Skripsi), Institute Pertanian Bogor.

Sulistyawati. (2008). Modification of Corn Cobs as Adsorbent of Heavy Metal Pb(II),(Skripsi), Institut Pertanian Bogor.