

Bioreduction Adsorbent (Biosorbent): Recovery Technology Of Heavy Metal Pollution (Cadmium/ Cd) In Polluted Lapindo Water Sources Using Bacteria And Durian Leather

Dr. Sueb, M.Kes¹, Eka Imbia Agus Diartika², Khasanah Sripalupi³, Achib Irmawati²

¹ Lecturer Departement of Biology: Mathematic and Science Faculty, State University of Malang, Malang, Indonesia

² Departement of Biology Student: Mathematic and Science Faculty, State University of Malang, Malang, Indonesia

³ Departement of Physics Student: Mathematic and Science Faculty, State University of Malang, Malang, Indonesia
eka.imbia@gmail.com

Abstract— Sources of water in three villages in Sidoarjo can no longer be consumed because it has been contaminated with heavy metals, one of them is Cadmium (Cd). Cadmium is a heavy metal that is dangerous after Mercury (Hg). Cadmium is dangerous because this element has high risk for blood vessel. Cadmium effects on humans in the long term and can accumulate in the body, especially the liver and kidneys. Handling heavy metal pollution can use biological organism, such as microbes and agricultural wastes. Previous research has identified indigenous bacteria that can reduce heavy metals Cd. From research Wildana et al. (2015) note that the efficiency of Cadmium biosorption by *Lactobacillus acidophilus* that has been immobilized can be seen from the percentage of removal of metal ions (% R) and the value biosorption capacity (qe). At the inlet concentrations low of 0.5557 ppm, the percentage of removal of metal ions (% R) obtained is the highest at 49.763%. Other researches have also demonstrated the ability of activated charcoal durian leather which can reduce Cd. Therefore, the authors took the initiative to combine both the adsorbent to the hopes will be more effective at absorbing heavy metals Cd. Bacteria must be isolated prior to the media Na. Durian leather used to be carbonized and activated in advance with KOH.

Keywords: Durian leather, Bacteria, Cadmium

INTRODUCTION

Porong and the surrounding is a watery marsh area throughout the year, including the lowland areas of East Java North Section. High ground is almost equal to the height of sea level with elevation difference of 1-1.5 meters^[1]. On May 29, 2006 happened mudflow in Porong, Sidoarjo result of the leaking pipeline drilling at Brantas Inc. Mudflow in Sidoarjo until now not been able to overcome^[2]. Water sources (wells, and rivers) in three villages (Siring, Renokenongo, Jatirejo) can no longer be consumed because it has been contaminated. The color turns yellow. Research results show that the well BAPEDAL Jatim population exceeds water quality requirements. Water wells in the village contains some heavy metals, one of which Cadmium (Cd)^[3]. Initial testing of the content of Cadmium (Cd) in soil contaminated leach Lapindo mud around the village area Renokenongo which has been tested in Chemical Engineering ITS Surabaya shows Cd value of 28.84 mg/kg. Said contaminated soil when Cd content reaches more than 3.0 ppm or equal to 3.0 mg / kg^[4]. Heavy metals that contaminate the soil can also contaminate water wells and if consumed continuously will cause health problems. Therefore, treatment and removal of heavy metals from water is indispensable^[5].

One of the short-term efforts that can be done to reduce levels of heavy metals in the water is the adsorption process using an adsorbent. As adsorbent, commonly used activated charcoal. This material is composed mainly of carbon, porosity and surface area and higher. But in terms of price, including the activated charcoal is expensive^[6] and its effectiveness is not too high to heavy metals. One other alternative in the treatment of heavy metal waste that is using biological materials. The process is called biosorption. Biosorption demonstrate the ability of biomass to bind heavy metals from solution through a metabolic step chemical-physics^[7]. Another advantage in using biosorbent are abundant raw materials, cheap, and efficient waste treatment process. Biological material which has been investigated is able to adsorb heavy metals such as Cd is bacteria and agricultural wastes.

Results of preliminary research note that the efficiency of Cadmium metal biosorption by bacteria *Lactobacillus acidophilus* which has mobilized can be seen from the percentage of removal of metal ions (% R) and the value biosorption capacity (qe). At the inlet concentrations low of 0.5557 ppm, the percentage of removal of metal ions (% R) obtained is the highest at 49.763%^[8].

In addition to the group of microorganisms, there are agricultural wastes that can be used as adsorbent, which

is derived from the skin of durian. Research from the University Chulalongkom Thailand mention that durian skin have the highest cellulose content of about 50% - 60% carboxymethylcellulose and 5% lignin. Cellulose can be applied because it can bind the metal^[9]. Durian skin can be used as a potential raw material in the manufacture of activated charcoal can be used as adsorbent. Based on research note the maximum adsorption capacity of Cd metal ions by activated charcoal durian leather is equal to 0.4951 mg to 1 gram of activated charcoal durian skin. The use of bacteria and waste durian skin is very safe because it comes from biological materials that are environmentally friendly. Therefore, bacteria and activated charcoal adsorbent durian skin is highly prospective for further applied to reduce the levels of heavy metals, especially cadmium in polluted areas Lapindo mud^[10].

In connection with the application opportunities adsorbent combination of bacteria and activated charcoal durian skin, the authors also design prototype adsorbent packing a combination of bacteria and activated charcoal leather durian in the batch process^[11]. This combination is done so that the adsorption of Cd is more optimum. The results are expected to contribute to the application of a combination of bacteria and the use of adsorbent activated charcoal as an adsorbent durian skin to reduce the levels of heavy metals Cd in water.

MATERIAL AND METHODS

The method used is book study method, namely the search for reviews of books, articles, and journals that are correlated with the material.

The preparation phase includes the manufacture of activated charcoal adsorbent bacteria and skin durian and manufacture of prototype packaging and activated charcoal adsorbent bacterial skin durian for batch process. The initial phase includes the identification and characterization of bacterial adsorbent activated charcoal durian skin using a spectrophotometer. The application stage Cd metal adsorption on adsorbent batch process by a combination of bacteria and activated charcoal durian skin. Phase analysis using AAS spectrophotometer to determine the amount of Cd metal that has been adsorbed by the adsorbent a combination of bacteria and activated charcoal durian skin.

a. Material

Tools and materials used for making adsorbent Cd Metals using bacteria are test tubes, autoclave, digital scales, measuring cups, beakers, wire loop (round), a pipette, Whatman filter paper, spatula, Bunsen,

erlenmeyer, cotton, gauze, aluminum foil, incubators, centrifuges, freeze dry, plastic clips, laminar air flow, the syringe 1 cc, spatula, pH meters, infusion sets, refrigerators, glass bead, jerry cans 3 L, stopwatch, ruler, flask, pipette volume, cling wrap, sample vials, test equipment SSA (atomic absorption spectrophotometry), column chromatography with a height of 30 cm in diameter and 1 cm, CaCl₂ anhydrous, Sodium Alginate, distilled water, powder MRS-broth strains of *Lactobacillus acidophilus* in the medium MRS-agar, a solution of nitric acid (HNO₃), a solution of sodium hydroxide (NaOH), the standard solution of Cadmium (Cd), and distilled water^[8].

The tools used for making adsorbent metal Cd using active charcoal leather durian (*Durio Zibethinus L.*) in this study among sieve size of 200 mesh, beaker glass, plastic bottles, spray bottle, cup porcelain, funnel glass, erlenmeyer, furnace, measuring cup, flask, mortar and pestle, analytical balance, oven, micro pipette, pipette, pipette volume, shakers, spatula, glass containers and Atomic Absorption Spectrophotometer (AAS). The materials needed in the study include durian skin, 0.1N HCl, HNO₃ solution 0.1N, 0.1N NaOH solution, 3CdSO₄.8H₂O, HNO₃ (70%), pH universal, filter paper, aquades and aluminum foil^[8].

b. The process of Immobilized Bacteria

CaCl₂ solution made of 5%, the ratio of 5 grams of CaCl₂ in 100 ml of distilled water. 2 g Sodium Alginate comparison was mixed with 0.3 grams of *Lactobacillus acidophilus* in the beaker was then added 100 ml of distilled water. Then homogenized using a magnetic stirrer for a few minutes. 2% Sodium Alginate solution that has been mixed with the bacteria *Lactobacillus acidophilus* is dripped slowly into a solution of CaCl₂ 5% using a 1 cc syringe to a solution of Sodium Alginate exhausted. Settling for one night and then washed using distilled water^[8].

c. Preparation of Waste Artificially and Testing Column biosorption

Preparations solution of metal cadmium (pure) is converted to 2 mg / l, 1.5 mg / l and 0.5 mg / l with dilution technique. Then the pH of the solution metal is set using 4% NaOH solution and HNO₃ (1: 1) to pH to 6^[10].

Column chromatography will be used distilled water to be washed in aseptic conditions before being installed on the static to the desired position, then filled bacterial alginate as high as 8 cm, with coated glass bead each about 1 cm at the base and the surface of the bacterial alginate. Column chromatography then flowed through the IV tube with a solution of 2 ppm Cd metal, as artificial waste solution, the valve opening is set infusion at a speed of influent 2.5 ml / min with the help of a stopwatch. Effluent taken every 60 minutes until considered saturated. The absorbance of the metal will be tested at SSA test equipment based on ISO 6989.16: 2009 on water and wastewater. The above step is repeated in the process biosorpsi for metals Cd concentration of 1.5 ppm and 0.5 ppm^[8].

1. Making Adsorbent Metal Cd Using Active Charcoal Leather Durian (*Durio zibethinus L.*)

a. Sample Preparation

In this process the durian skin will carbonized first cleaned, then cut to the size of 1x2 cm². Then the durian skin were burnt to ashes shaped. carbonization process

Carbonization process is carried out using a furnace as media authoring at a temperature of 400°C for 2 minutes. Then charcoal cooled, after cold charcoal pulverized using a mortar and then sieved with a 200 mesh sieve^[10].

b. Activation process

This process uses HCl as the activating substance. Charcoal that has been sifted taken as much as 25 grams dissolved in 250 mL of aqueous KOH and stirred simultaneously heated using stirrer. Then filtered with filter paper. Activated charcoal is then washed with distilled water to pH neutral. After the charcoal dried at 100 ° C for 3 hours^[10].

c. Testing Characterization of Active Charcoal

Determination of the yield of activated charcoal is done by calculating the weight ratio of activated charcoal that is produced by the weight of the raw materials used. A total 1gram activated charcoal put in a cup of known weight, then put in an oven at 110°C for 3 hours. Furthermore, cooled and weighed. A total of 1 gram of activated charcoal put in a cup of known weight. Then put into the furnace and burned at a temperature of 650°C for 2 hours. After it cool in a desiccator and weighed. A total of 1 gram of activated charcoal put in a cup of known weight. Then put into the furnace and burned at a temperature of 900°C for 7 minutes. After it was put into an oven at 105°C for 10 minutes. Further cooled in a desiccator for 30 minutes, then weighed. Determination of the carbon content of activated charcoal is not held directly but derived from the calculation indirectly, namely: FC = 100% (% moisture content + % ash content of volatile matter content). Prepared by 30 mL of solution with a concentration of metal ions Cd 20, 30, 40, 50 and 60 mg / L which has been set pH at optimum pH and incorporated into the Erlenmeyer flask. Activated charcoal is added as much as 1 gram in each of the Erlenmeyer flask) and closed with aluminum foil. Shaken solution by using a shaker for optimum contact time. Filtrate is filtered using filter paper and then measure its concentration using AAS^[10].

2. Manufacture Prototype Packaging Batch Adsorbent Combination Skin Bacteria and Carbon Durian (*Durio zibethinus L.*)

The prototype bacterial packaging adsorbent combination with activated charcoal in batch process consists of three main parts: a container where the adsorbent, the adsorbent and the barrier between the effluent pipe. The prototype is made of plastic material types Polyethylene High Density (HDPE) food grade. Tubular container where the adsorbent is made by arrangement from the bottom up, respectively, are anchoring the bottom, activated charcoal, anchoring the middle, the bacteria (which had been dried and immobilized), and retaining top. Retaining the bottom, middle and top made of HDPE plastic with the top and bottom side are small holes so that water can exit the process result. Retaining coated with a sieve. Water containing adsorbent Cd inserted into the bottom of the container. It aims to optimize the adsorption of pollutants by the adsorbent^[11].

Results and Discussion

There are three mechanisms that occurs when microorganisms took the metal in the solution, ie the accumulation / deposition of extracellular, adsorption or complex formation on the cell surface and intracellular accumulation. The process of accumulation / deposition of extracellular to do with living microorganisms, adsorption or complex formation on the cell surface can be done with living and dead microorganisms while requiring the accumulation of intracellular microbial activity. In living cells, then the parameters that influence the adsorption process is the age of the cell, the availability of nutrients for growth and during the process biosorpsi conditions (such as pH, temperature and the presence of certain co-ions). Absorption efficiency is also greatly influenced by the chemical characteristics of the metal to be processed^[12].

Accumulation of heavy metals Cd by bacteria can occur by way of binding heavy metals in cell structure. This binding can occur due to the interaction of metal ions to the surface of bacterial cells. This occurs because of the size of the bacterial cells are relatively minor cause greater surface area, so the possibility of effective interaction between the metal ions to the surface of the cell wall of the larger^[12]. The ability of bacterial accumulation is also affected by the bond so that the metal cation anion will easily be adsorbed^[13]. In the study showing the rest of the Cd of 0.3 mg / l to be like 0.13236 mg./l within an interval of 24 hours. These results indicate that bacteria can reduce the concentration of heavy metals especially those of Cd^[14].

Durian skin can become activated charcoal because it contains cellulose is high (50% - 60%), lignin (5%) and starch (5%) to form carbon. By looking at the structure and characteristics of the skin micro durian, but could include the use of the durian skin as activated charcoal to absorb cadmium that pollute the water. The amount of activated charcoal leather adsorbansi durian one of them caused by the morphological structure of the carbon is porous so that the larger surface area that magnifies the power absorbed anyway.

Biosorbent that comes as a byproduct of agricultural products, such as durian skin, there are two models, namely the absorption of the intrinsic adsorption and interaction colombik. On the intrinsic adsorption process is a major factor is the area. It can be seen by observing the effect of the size of the adsorbent to the adsorption capacity. While on kolombik interaction electrostatic energy resulting from the interaction of the adsorbent and adsorbate. The intensity of this interaction will depend on the strength of the charge of both materials. Kolombik interactions can be observed on the adsorption of cationic and anionic adsorbent material. The study mentions that in biosorbent generally contain β -D-glucose repeatedly as a major component of the cell wall. This cellulose polar hydroxyl groups that play a role in chemical reactions and bind heavy metals from solution. Modification of functional groups can change the surface properties that will ultimately affect the ability of the adsorption material^[12].

In a scientific paper is to collaborate between the use of two types of adsorbents, which is derived from the bacterium *Bacillus* sp. and activated charcoal durian skin. This is done in order to optimize the work of each adsorbent. *Bacillus* sp. were able to absorb various types of heavy metals such as Cd, Hg, and Pb, while the activated charcoal is able to absorb metal Fe with a certain level. Thus, the content of heavy metals present in the water source wells and rivers in the area of the Lapindo mud can be reduced.

CONCLUSION

The bacteria *Bacillus* sp. and durian peel waste can be used as a biological adsorbent through several steps, such as the manufacture of activated charcoal leather durian and the isolation of bacteria with medium Cd. Both the adsorbent material is used simultaneously so that the result is more optimal.

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