CASSAVA PEEL BIOSORBENT (*Manihot utilissima*) FOR REMOVAL CHROMIUM (VI) WITH MICROBIAL FUEL CELL SYSTEM OF COMBINATION TECHNIQUES BIOADSORPTION AND BIOELECTROCHEMISTRY

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Article Info

Article history:

Received Jul 12th, 2017
Revised Aug 20th, 2017
Accepted Oct 26th, 2017

Keyword:

Bioelectrochemical-biosorption
Biosorbent
Heavy Metal Chromium (VI)
Microbial Fuel Cell
Zymomonas Mobilis

ABSTRACT

Cassava peel biosorbent as heavy metal adsorbent of chromium (VI) has active organic compound. The active cellulose compound for adsorption of chromium metal is evidenced by FTIR activated carbon having an absorbent band at 3412 cm^{-1} wave number which is an OH functional group reinforced by absorbing band at 1323 cm^{-1} which is OH (bending) and 1109 cm^{-1} Which indicates the presence of CO vibration from secondary OH, and the absorption band at 3000-2750 cm^{-1} which is CH sp^3. The effect of combination technique on the best microbial fuel cell system is bioelectrochemical-biosorption method. The result of the reduction of Cr (VI) content by the bioelectrochemical-biosorption method on the best pH (1,4,7,10 and 13) variations was at pH 1 with a 10 min contact time of 0.285 mg / L, 15 minutes at 0.253 mg / L, and 20 minutes of 0.177 mg / L in accordance with Standard of Industrial Waste Water Quality Standard of KEMEN LH RI. 5 Year 2014 is the maximum limit of chromium levels is 0.5 mg / L.

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I. INTRODUCTION

Electroplating is the process of coating metal plating with other metals with the help of electricity (Akmad, 2001). The electroplating wastewater industry contains various types of heavy metal ions such as Cr (III) and Cr (VI) ions, Lead (Pb), Copper (Cu), Zinc (Zn), and so on. Chromium is a heavy metal present in two stable forms such as Cr (III) and Cr (VI), from which Cr (VI) is carcinogenic and genotoxic to living things (Sheng, 2015).

Research of adsorbent from biomass at the end of this much done, one of cassava peel biosorben. Cassava peel biosorbent has a unique ability, absorption can be through active binding and passive. Active binding involves metabolic reactions occurring in live cassava biosorbent peel while passive binding occurs only in dead cassava biosorbent (Nur, 2010). In passive binding, absorption occurs on the surface of the cell wall and other external

surface through chemical and physical mechanisms such as ion exchange, complex formation, and overall adsorption (Nur, 2010).
In recent years, Microbial Fuel Cell (MFC) has emerged as one of the best applications in the reduction of heavy metal Cr (VI). MFC is a promising method to convert chemical energy into electricity using the help of microbes in generating eletron (electricity). This treatment process uses the reduction of microbiological biocatalysts to reduce Cr (VI) to Cr (III), which has received widespread attention recently (Feng, et al 2008). In research Shang Shang et al (2016) has been studied MFC with monochamber system that is anode and cathode in one container, but this system has weakness that is saturated easily bacteria when chromium (VI) concentration increase. Then research by Zhang et al (2014) has researched MFC with dual chamber system using Proton Exchange Membrane (PEM), but membrane price is very expensive. Then research by Shingvi et al (2014) has been studied MFC with dual chamber system using bridge of KCl salt, so in this research using bridge of KCl salt as substitute of expensive PEM.
This study aims to reduce Cr (VI) wastewater in MFC using bioadsorption and bioelectrochemical combination techniques, in which microbial fuel cells as bioremediation and bioelectrochemical by using manihot utilissima biosorbent for analyzing the heavy metal Cr (VI) reduction activity. Using ethanol production bacteria (Zymomonas Mobilis and Saccaromyches sp) can make a new breakthrough in reducing Cr (VI). The objective of this research was bioremediation and bioelectrochemistry by using biosorbent of cassava peel (manihot utilissima) for the analysis of reduction activity of heavy metal chromium (VI) with bioadsorption and bioelectrochemical combination technique.

II. RESEARCH METHODOLOGY

2.1 Tools and Materials
The tools used in this research are U Pipes, Pipette Volume, Pipette Drops, AAS, Sieve 80 mesh, Reaction Tubes, Measuring Glass, Color pH, Erlenmeyer, Oven, Timepiece, Bunsen, Beaker glass, Pipet Measure, Mixer, Statip, Mortar Grinder, AVO meter, Graphite Electrode, Buret, Clamp Holder Cable Aligator, FTIR, Petridis, Funnel, Desiccator, and Analytical Scales. The materials used in this research are Zymomonas Mobilis, Cassava Peel, KCl, Broth Nutrition, NaOH, Buffer pH1,4,7,10 and 13, Plastic wrap, $K_2Cr_2O_7$, Agar, Sucrose, Ethanol 70%, HCl 2M, Aqua DM, and Whatsman Filter Paper no.41.

2.2 Preparation of Cr (VI) Standard Solution and Chromium Metal Calibration Curve (VI)
A total of 0.0048 grams of $K_2Cr_2O_7$ salt were diluted in a 100 ml measuring flask with 1% HCl to the limit mark, so that Cr solution was obtained with concentration of 1.7 mg / L. Then chromium parent solution 1.7 mg / L dipipet as much as 80; 60; 40; And 20 mL, was then fed into a 100 mL measuring flask and diluted by adding 1% HCl to the limit marking to obtain a chromium solution of concentration 1.36; 1.02; 0.68; And 0.34 ppm for the measured value of absorption with AAS 359.4 nm so that will be obtained chromium metal calibration curve. Then characterized by FTIR.

2.3 Making of Biosorbent from Cassava Peel
White cassava peel is dried, cut into small size and ground until smooth powder. Then the cassava peel powder was heated with dry to dry, sifted with 85 mesh sieve. Then washed with aqua demineralate to remove the levels of cyanide and other impurities in it. After that, strain with buchner funnel so as to produce residue 1. Then the residue is dioven with temperature 100^0C to dry, soaked in HCl 1 M for 24 hours for the activation process, so that the suspension and filtered with buchner funnel. After that, washed with aqua demineralata to remove impurities, resulting in residue 2. Then the residue is heated with oven at a temperature of 100^0C to dry. Then mashed with mortar grinder, so as to form a cassava peel biosorben activated HCl 1 M. Then biosorben in characterization with FTIR.
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2.4 Microbial Fuel Cell Preparation
1. Preparation of Bacterial Culture
Taken 1 ose zymomonas mobilis and saccaromyches sp. Then diceluplan ose in a beaker glass that has been given nutrient broth. Give 1 g of glucose as a nutrient. Then tightly closed the beaker glass in order for the bacteria to metabolize.
2. Salt Bridge Preparation
First boil aqua DM, then pour the agar in moderation and KCl as much as 3 grams in 1 liter of aqua DM. Then pour in the pipe U. Then chill in the aquades until used.
3. Electrode Preparation

Prepare the carbon electrode. Then the electrode was immersed in a 100 ml HCl 2 M and 100 ml NaOH 2 M solution, each for 1 day. Before using electrodes, store electrodes in aquades.

2.5 Applications of Bio Process (electrochemical adsorption) In Electroplating Waste with Variation of Contact Time and Degree of Acidity (pH)

Prepared two glass bekker, then separated the anode compartment and cathode compartment by using the salt bridge of KCl. Then prepared two glass beaker, put 10 ml bacterial culture, and 15 ml aqua DM on the anode compartment. In the cathode compartment is filled by Cr (VI) solution. In the first test was analyzed combination variation (Bioelectrochemical, Biososorption and Bioelectrochemical-biososorption). Both tests on bacterial variation (Zymomonas Mobilis) with bioelectrochemical-biososorption model. Third test of pH variation (1, 4, 7, 10 and 13) with bioelectrochemical-biososorption model. All testers measured the resulting electrical potential for 0 minutes, 5 minutes, 10 minutes, 15 minutes, and 20 minutes using a controlled biosorbent mass of 0.1 gram. The resulting filtrate is then filtered by whatman filter paper no. 41 to separate the biosorbent particles and Cr (VI) solution, and then the chromium metal concentration in the filtrate was analyzed using AAS.

III. RESULTS AND DISCUSSION.

4.1 FTIR Characterization Test on Biosorbent of Cassava Peel

The infrared spectrum of Cassava peel biosorbent can be seen at figure 3.1. The biosorbent in FTIR spectrum has an absorption band at 3412 cm^{-1} wave number which is an OH functional group, reinforced by an absorbing band of 1323 cm^{-1} which is OH (bending) and 1109 cm^{-1} which indicates the presence of CO vibration from secondary OH, And the absorption band at 3000-2750 cm^{-1} which is CH sp^3.

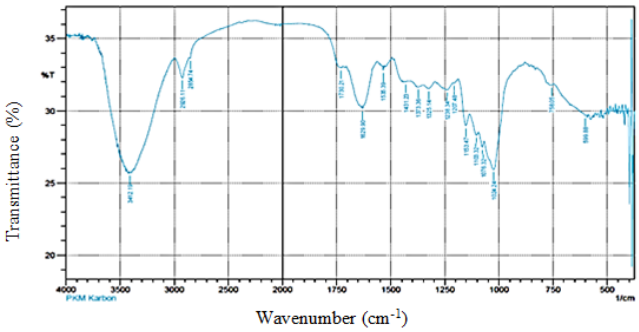

Figure 3.1 Results of FTIR Characterization on Cassava Biosorbent Peel

4.2 Percentage of Activity of Reduced Metals Cr (VI) on Bioelectrochemical Method and Bioelectrochemical-Biosorption Method

In adsorption by bioelectrochemical method and bioelectrochemical-biosorption method can be determined peresentasi activity of reduction of level on metal Cr (VI). The Percent image result of reduction of Cr (VI) metal content by bioelectrochemical method and bioelectrochemical-biosorption method represented at figure 3.2.

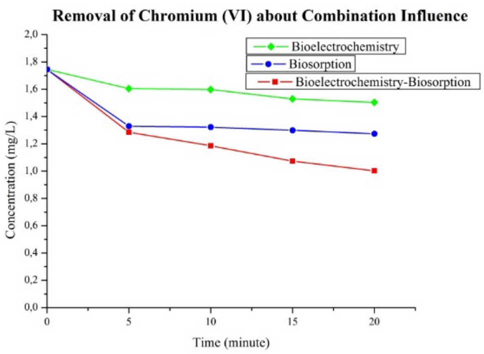

Figure 3.2 Curve Percent Result of Cr (VI) Reduction of Metals by Bioelectrochemical and Biosorption Method

4.3 Potential Electricity of Bioelectrochemical-Biosorption and Bioelectrochemical
Microbial Fuel Cell is aimed at lowering Cr (VI) levels with a very fast time with ditandainya reduction of electrical potential generated. The reactions as the theoretical basis are as follows.

Anode: $C_6H_{12}O_6$ (l) + $6H_2O$ (l) $\xrightarrow{\text{Bakteri}}$ $6CO_2$ (g) + $24H^+$(aq) + 24 e
Cathode: $Cr_2O_7^{2-}$(aq) + $14H^+$(aq) + 6e- → $2Cr^{3+}$(aq) + $7H_2O$(1)

C6H12O6 (l) + 4 CrO72- (aq) + 40 H + (aq) $\xrightarrow{\text{Bakteri}}$ 6 CO2 (g) + 8Cr3 + (aq) + $22H_2O$ (1)
The relationship with the electric potential is by using the Nernst Equation.

$$E_{sel} = E^0_{sel} - \frac{R\,T\,In\,Q}{N\,F}$$

(Zhang, 2015)

With the theory of chemical equilibrium that is denoted (Q) is as follows.
Q = Products / Reactants

$$Q = \frac{(pCO_2)^6 . (Cr^{3+})^8}{(Cr_2O_7^{2-})^4 . (H^+)^{40}}$$

(Zhang, 2015)

From figure 3.3 it is clear that with the combination bioadsorption-bioelectrochemical technique to decrease Cr (VI) or $Cr_2O_7^{2-}$ (aq), Cr levels (III) will increase due to the effect of Cr (VI) reduction to Cr (III). So make the potential of electricity generated to be down at a certain time (Sheng, 2016).

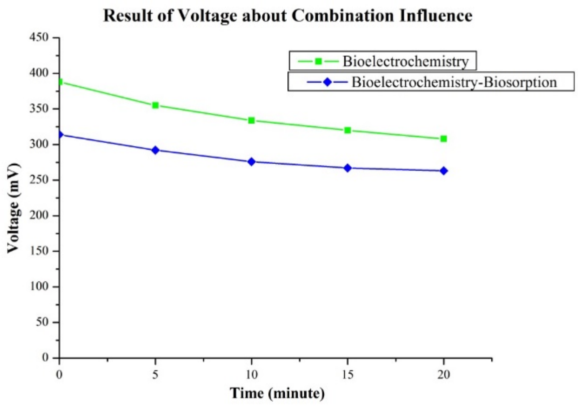

Figure 3.3 Potential Electricity Bioelectrochemistry-Biosorption and Bioelectrochemistry

IV. CONCLUSION

The cellulose active compound for adsorption of chromium metal is evidenced by FTIR of activated carbon having an absorbent band at 3412 cm^{-1} wave number which is an OH functional group reinforced by absorbing band at 1323 cm^{-1} which is OH (bending) and 1109 cm^{-1} indicating the presence of a CO from secondary OH vibration, and the absorption band at 3000-2750 cm^{-1} which is CH sp^3. The result of the reduction of Cr (VI) metal content with the best combination engineering technique is bioelectrochemical-biosorption method. The result of the reduction of Cr (VI) content by the bioelectrochemical-biosorption method on the best pH (1,4,7,10 and 13) variations is at pH 1 with 10, 15, and 20 minutes contact time corresponding to Standard Quality Standard of Industrial Water Waste Metal Coating KEMEN LH RI No. 5 Year 2014.

V. ACKNOWLEDGEMENT

This work was carried out in the frame of research projects funded by Minsitry of Research, Technology and Higher Education (Kemenristekdikti) in form Program Kreativitas Mahasiswa (PKM). The FTIR measurements were carried out using spectrophotometer Shimadzu-8400S that was provided by Instrumentation and Analytical Science of Chemistry Department ITS.

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