Influence of *Shewanella oneidensis* MR-1 Bacterial Metabolism Process On Waste Treatment Of Cr And Mn Metals In Reactor Microbial Fuel Cell (MFC)

Influence of *Shewanella oneidensis* MR-1 Bacterial Metabolism Process On Waste Treatment Of Cr And Mn Metals In Reactor Microbial Fuel Cell (MFC)

S R Juliastuti, R Darmawan, N Hendrianie, G A Prakoso, T A Bachtiar
Department of Chemical Engineering, Faculty of Industrial Technology, Institut Teknologi Sepuluh Nopember, Campus Keputih-Sukolilo, Surabaya 60111,Indonesia

Email : julizainul@gmail.com

Abstract. Chromium (Cr) and manganese (Mn) are heavy metals which have high oxidation potential and cause mutagenesis and carcinogenic to living organisms. Microbial Fuel Cell (MFC) appears as one of the applications in the processing of Cr and Mn metals. MFC is bioreactor which converts chemical energy of organic compounds into electrical energy through the catalytic reaction of microorganisms in anaerobic conditions. The aim of this research are to find out the role of *Shewanella oneidensis* MR-1 bacteria on manufacture electrical energy by utilizing organic wastes, and to find out the concentration of *Shewanella oneidensis* MR-1 on the most influential anode side for the reduction of metallic Cr, Mn, and its mixed metal on the cathode side by using a MFC. The research method used molasses with bacteria concentration of 10%; 12.5%; 15% (v/v) on the anode side, while on the cathode side was used Cr(VI), Mn(VII) solutions, and mixtures of Cr and Mn solutions with the ratio of 1:0 ; 0:1 ; 1:1 (w/w). 15% bacteria concentration on mixture of metal solution resulted the highest electricity production, which was 46.33 (mW/m^2), and the best reduction of Cr^{6+} to Cr^{3+} 82.15%, while for the reduction of Mn^{7+} to Mn^2 was 61.17%.

1. Introduction

The concentration of Chromium (Cr) and Manganese (Mn) in the environment is increasing as the number of industries developing. Environmental pollution by heavy metals has the potential causing ecosystem damage if the concentration exceeds the threshold. One way of generating alternative energy is bio-based fuel cell based generator. Microbial Fuel Cell is a bioreactor that converts the chemical energy of organic compounds into electrical energy through the catalytic reaction of microorganisms in anaerobic conditions [1]. Microbial Fuel Cell generate electricity by oxidizing anaerobic organic matter through the aid of bacteria [2]. The electricity generated by MFC is relatively low and often power output is fluctuated due to unstable internal resistance presence in the MFC environment [3]. Microbial metabolic activity could as well as be hindered by the macro-environment created by the electrolyte and complexity of the substrate used as the source of fuel [4]. The catalytic activity and proton transfer are carried out using enzymes or bacteria. Microbial Fuel Cell has several advantages that can generate electricity from organic waste and renewable biomass [2]. The electricity generation was then investigated in an air cathode microbial fuel cell, using pure cultures of *E. coli* and *Shewanella sp*. and their mixtures as well [5,6]. Bacteria are able to catalyze and adapt well to different organic materials present in environmental waste to produce electrons. In the cathode

compartment, there is a conductive electrolyte solution. Microbial Fuel Cell working principle is the using of bacteria that perform metabolism of the medium at the anode to catalyze the converter of organic matter into electrical energy by transferring electrons from the anode through a cable and generating current to the cathode. The electron transfer from anode received by free electron at the cathode. Protons transported to the cathode through proton exchange membrane (salt bridge) [7]. In the cathode electrons were received by Cr(VI) and Mn(IV). Then the power density was generated by the electron movement from anodic to the cathode and Cr(VI) and Mn(IV) reduction occurred [8]. In a previous study, pH 4 circumstances Chromium conductive electrolyte solution in cathode chamber were the best for reducing chromium concentration and also generate power density. Previous study, pH 4 circumstances Chromium conductive electrolyte solution in cathode chamber were the best for reducing chromium concentration and also generate power density. The present study has successfully verified that a promising MFC technology can achieve high output power in removing Cr(VI), revealing the enormous potential of scale-up MFCs for heavy metal treatment [9]. MFCs may represent a promising in bioremediation unit by using an anaerobic digestor plants for simultaneous nitrogen removal and electricity generation using digestate as substrate [10]. Using hydrogen peroxide as electron acceptor in the cathode compartment improved the stability of performances and the relation between the time of incubation and the power density of the MFC was showed [11]. The current and voltage output of a *Saccharomyces cerevisiae* based MFC are directly correlated to the cells on the micro-environment of the electrode and to the presence of an electron mediator such as methylene blue (MB). It suggested that reduced methylene blue was entrapped into the cells, enhancing the electron transfer on the graphite electrode as an internal mediator of the cellular metabolism, probably linked to the oxidative electron cascade [12].

2. Experimental Section

2.1. Microbial Fuel Cell Design Instructions

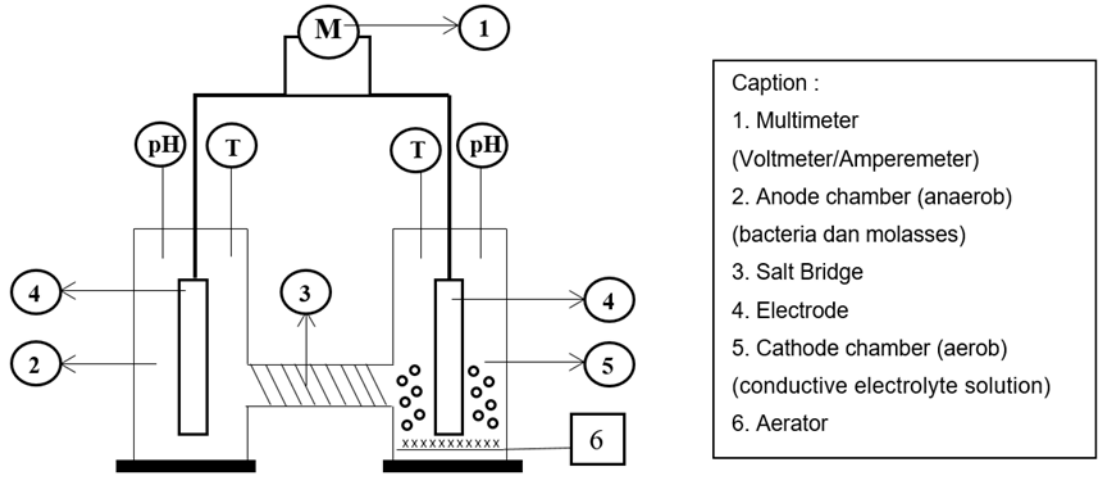

Figure 1. Dual Chamber Microbial Fuel Cell Design

2.2. Electrode Activating preparation

Graphite electrodes need to be submerged into HCl 1 M solution for 1 day, later flush with aquades. After that, submerged again into NaOH 1 M solution for 1 day, then flush with aquades. Electrodes submerged in aquades until the electrodes will be installed

2.3. Buffer solution preparation

For cathode chamber using citrate buffer pH 4 solution, the formula is preparing 0.1 M citric acid solution (21.04 gr of citric acid in 1 L aquades) and 0.1 M sodium citrate solution (29.41 g Sodium citrate / sodium citrate in 1L aquades). Then mixed (33 ml of citric acid solution 0.1 M) + (17 mL sodium citrate solution 0.1 M) and dissolved aquadest until the volume reached 100 mL. For anode chamber using phosphate buffer pH 7 solution, the formula is weighing NaH_2PO_4 0.4063 grams and Na_2HPO_4 0.9247 grams. Then dissolve all in 500 mL aquadest.

2.4. Anode and cathode solution preparation

In cathode chamber was filled with 400 mL conductive electrolyte solution and 400 mL pH 7 buffer mix both solution of them. In anode chamber was inoculated with the bacteria and sugar waste with 5% concentration. phosphate. The conductive electrolyte solution is solution 400 mL $K_2Cr_2O_7$ of 8 mg/L, or solution 400 mL $KMnO_4$ of 8 mg/L, or 400 mL

2.5 *Procedure and measurement*

Digital multimeter was connected on both the electrodes, the postive end at a cathodic chamber and the negative end at a anodic chamber. Recorded power density generated every 24 hour calculated by using equation 1

$$\text{Power density } (mW/m^2) = (I\ (mA) \times V(Volt))/A(m^2) \quad (1)$$

Where P is the power density in milli watts (mW), V is the voltage in milli volts (mV), I is the current density in milli ampere (mA) and A is the surface area of electrode. Voltage and current measurement is carried out by using a multimeter with a system OCV (Open Circuit Voltage) by getting the voltage and the current, then it can be calculated that the resulting power density.

The variable of bacteria concentration of this experiment is 10%, 12.5%, 15% (v/v) with volume of chamber is 800 ml. For example, to obtain the variable of bacteria concentration 10% is measured 10 ml for the volume of bacteria and 790 ml for the wastewater. In anodic chamber was maintain at pH 7 circumtances, otherwise in cathodic chamber was maintain at pH 4 circumtances and measure the Cr and Mn reduction.

3. Result and discussion

3.1. Power density generated

The highest power density production in this experiment at 15% bacteria concentration variable on mixture of metal solution which was 46.33 (mW/m^2). Power density was affected by voltage, electric current and the surface area of electrode. In this experiment, maximum voltage recorded was 1.037 V; an electric current recorded was 0.1 mA; and for the surface area of the electrodes was 22.844 cm^2.

The amount of electrical energy in the Microbial Fuel Cell system was influenced by the rate of metabolism carried out by bacteria. The presence of bacteria in this process becomes very important because the electrons were generated by the bacterial metabolism process. the more microorganisms it would be more electrons were released. The power production were shown in figure 2.

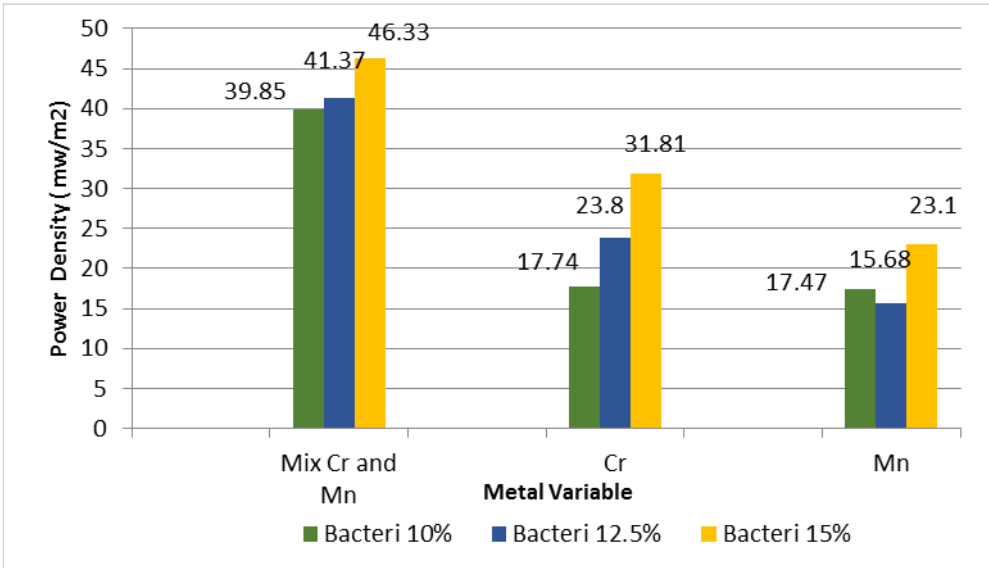

Figure 2. The highest power production relation curve generated with the bacterial population for all variables

3.2 Reduction of metal Cr, Mn and both mix Concentrations

The best reduction of heavy metal Cr^{6+} to Cr^{3+} in mixed metal solution with initial concentration of 8.01 mg/L to 1.43 mg/L and removal percentage of Cr^{6+} was 82.15%. While for the reduction of heavy metal Mn^{7+} to Mn^{2+}, the best result was obtained on mixed metal solution with initial reduction concentration from 8.01 mg/L to 2.95 mg/L and removal percentage of Mn^{7+} was 61.17%.

The reduction of Mn metal concentration was smaller than Cr metal, because the position of Mn metal was on the left of Cr. According to the voltaic series, the more right the position of a metal in the series, the less reactive the metal (it was harder to remove the electrons) and the stronger the oxidant (the easier to reduce).

Oxidation and reduction precisely refered to changes in oxidation numbers due to electron transfer. So that oxidation was better defined as an increase in oxidation number, and reduction as a decrease in oxidation number. The redox reaction could be illustrated in the figure 3 :

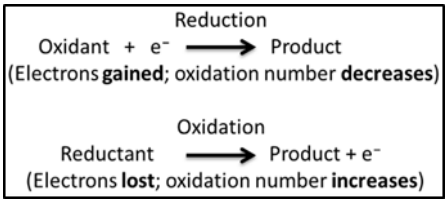

Figure 3: Reduction and oxidation reactions

In cathode chamber, reduction reaction occured, where Cr^{6+} would turn into Cr^{3+}, also Mn^{7+} turned into Mn^{2+} with the help of the electrons coming from the anode as in equation below :

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ E0 = 1.29 V (2)

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ E0 = 1.33 V (3)

$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2^- + 2H_2O$ E0 = 1.70 V (4)

$MnO_2^- + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$ E0 = 1.23 V (5)

In addition to the largest population of bacteria, it also affected the production of electricity generated because in the mixed variable of Cr and Mn metals, the electrode potential (E0) by Mn metal would propose the formation of electrical energy. In the cathode compartment where Cr^{6+} and Mn^{7+} would be transformed into Cr^{3+} and Mn^{2+} with the aid from anode compartment in the form of electron supply through copper wires reacting with protons passing through the salt bridge, and forming water molecules. The longer the cathode side was rich in protons so that the reduction reaction of Cr, Mn, and mixed metal concentrations moved and the concentration decreases.

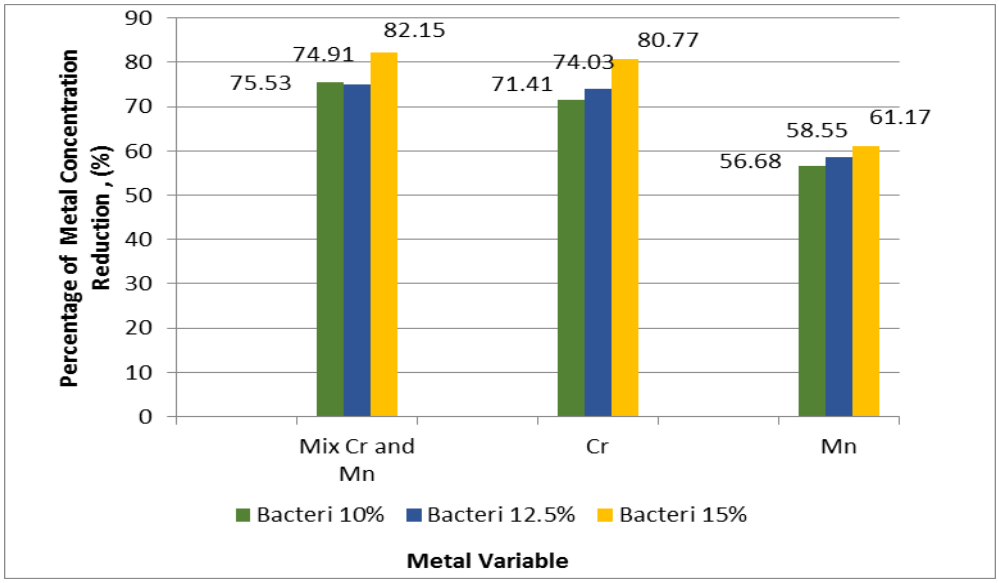

Figure 4. Curve correlation relationship of metal concentration with bacterial population for all variables

4. Conclusion

15% bacteria concentration variable on mixture of metal solution resulted the highest electricity production, which was 46.33 (mW/m^2), and the best reduction of heavy metal Cr^{6+} to Cr^{3+} in mixed metal solution with initial concentration of 8.01 mg/L to 1.43 mg/L and removal percentage of Cr^{6+} was 82.15%. While for the reduction of heavy metal Mn^{7+} to Mn^{2+}, the best result was obtained on mixed metal solution with initial reduction concentration from 8.01 mg/L to 2.95 mg/L and removal percentage of Mn^{7+} was 61,17%.

Acknowledgement
We would like thank to Wastewater Treatment Laboratory, Chemical Engineering Department, Institute of Technology Sepuluh Nopember, for the facilities provided to accomplish the research.

References

[1] Logan B E, Hamelers B, Rozendal R, Schröder U, Keller J, Freguia S, Aelterman P, Verstraete W, Rabaey K 2006 *Env. Sci. & Tech.* **40 (17)** 5181-92.

[2] Lovley, D R 2008 The microbe electric conversion of organic matter to electricity *Current Opinion Biotechnol.* **19** 564-71.
[3] Wang X, Zhang E, Yuc E H and Scott K 2016 *Chem. Eng. Trans.* **51** 37– 42
[4] Mahmood N A N, Khairul A A W, Amirul A A N, Ahmad A M A, Nazlee F G and Eraricar M S 2018 *Chem. Eng. Trans.* **63** 607–12.
[5] Miroliaei M R, Samimi A, Mohebbi-Kalhori D and Khorram M 2014 *J. Ind. Eng.Chem*. **25**, 42-50
[6] Miroliaei M R, Abdolreza Samimi and Davod Mohebbi-Kalhori 2015 *Env. Prog. Sust. Energy* **34 (4)**, 1097-05.
[7] Ramya N, Renganathan K, Barathi S and Venkatraman K 2013 *Int. J. Adv. Res. Technol.* **2 (5)** 326-30
[8] Carmalin Shopia A and Saikanth S 2016 *J. Env. Chem. Eng.* **4** 2402–09.
[9] Meng L, Shaoqi Z, Fuzhen M, Liangliang Z and Xuan Z 2018 *Chem. Eng. J.* **334** 1621-29.
[10] Enea G D D, Gianluca P, Daniele M, Alberto G, Luca D P and Fiorentina A 2015 *J. Biomed. Biotech*. DOI: 10.1155/2015/351014
[11] Ruggero R and Leonardo S 2016 *Env. Eng. Manage J*. **16 (**9), 2011-18.
[12] Ruggero R ,Matia C and Leonardo S 2016 *Chem. Eng. Trans.* **49** 559-64