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Effect of pH at Anode and Cathode Chamber on the Performance of Biological Cathodic Protection

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A new corrosion control system which is biological cathodic protection (CP) system was developed using the concept of microbial fuel cells (MFCs). Microorganisms available in domestic wastewater was utilised to generate electrons and supplied to the carbon steel pipe, and as consequence, protect the pipe from corrosion. There are various factors affect the performance of the system including the pH at the anode and cathode chamber. This study aims to analyse the optimum pH at anode and cathode. In this study, wastewater was used as the electrolyte and graphite rod as the electrode in the anode compartment while cathode compartment was filled with sand and carbon steel pipe acts as the cathode. Both compartments were connected by a plastic tubing and separated by the membrane. It was found that optimum pH at anolyte and catholyte were 8 and 6. The CP potential versus copper sulfate electrode (CSE) was -752 mV. It shows that the corrosion of carbon steel pipe was reduced since the native potential of the carbon steel pipe versus CSE was -560 mV.

1. Introduction

Corrosion in pipelines has been identified as one of the major mechanism that gives rise to failures in oil and gas pipelines (Cheng, 2015). Coatings in pipelines usually are not perfect and may have defects such as scratch of the coatings, pinholes, and flaws. These problems may occur during coating manufacturing, transportation, and pipeline construction. Chemical species, groundwater, and corrosive gases may pass through the defects and reach the pipe surface. This phenomenon can cause coating disbonding and eventually corrosion of pipe at the defected area (Kuang and Cheng, 2015). To overcome this problem, all buried steel gas pipelines applied the concept of cathodic protection (CP) system, which can reduce the corrosion in pipelines (Tsynaeva, 2015).CP is a procedure to minimise the corrosion or oxidation of metal surface by constructing an electrochemical cell and making that surface of metal the cathode. There are two types of CP systems which are sacrificial anode CP system and impressed current cathodic protection (ICCP) system (Orazem, 2014). The concept of sacrificial anode is the driving voltage is provided by the natural potential difference that occurs between the structure and a second metal in the surrounding without the need of power source. By this method, the steel pipe can be protected from corrosion while other metal that is used will corrode. Opposite to the concept of sacrificial anode, in ICCP method, the driving voltage for protective current is supplied from a power source. The power supply is usually a rectifier that converts alternating current (AC) power to direct current (DC). The anodes (graphite, high-silicon cast iron, lead-silver alloy, etc.) are connected using an insulated cable to the positive terminal of a DC source (Ashworth, 2010).
However, the concept of microbial fuel cells (MFCs) can be used as an alternative to represent a new method in CP system. MFCs are sustainable energy technology which microorganisms present in the wastewater

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work to convert chemical energy into electrical energy. Electricity is generated by MFCs as the microbes in the anode compartment consume substrates and thus generating electron and protons (Molognoni et al., 2014). The transfer of electrons to the cathode through the external circuit and proton through the internal membrane will produce electricity (Lu et al., 2009). The capability of the microorganism to generate electricity can be used as a new approach for biological CP in order to protect the pipelines.

In order to make this concept reliable, it is very important to ensure that the system is in its optimum condition. There are various factors that can affect the performances of the system and improper selection of these factors will result in losses.

For instance, the performance of the microorganisms vary at difference pH at the anode and cathode (Kumar and Mungray, 2016). Choosing an appropriate pH condition is crucial to make the condition favorable for the efficient transfer of electron and eventually can maximise the power output produced. According to Mahmood et al. (2017), bacteria respond differently when there are changes in their environment, especially pH changes. In this study, optimum pH at the anode and cathode and the performance of biological CP for corrosion control system were studied.

2. Material and methods

2.1 Sample preparation

The electrolyte used at the anode compartment was wastewater from the Indah Water Gravity Thickener Pond at Taman Bukit Senang. After the collection, the wastewater was kept in a freezer at the temperature below 4 °C to deactivate the bacterial growth before conducting the experiment (Ishii et al., 2013).

2.2 Material selection

2.2.1 Anode selection

A graphite rod was used as the anode electrode due to its stability in microbial cultures, high mechanical strength and excellent electrical conductivity (Zhou et al., 2011). The dimension of the graphite rod was 15.0 cm height x 2.0 cm diameter. The graphite rod was undergoing acid treatment before installation. The graphite rod was immersed in the nitric acid (Analytical Reagent-65%, R&M Chemicals) for 24 h. After that, the graphite rod was washed with distilled water for a few times and then dried at the suitable temperature. The purpose of this treatment is to clean the electrode surface from impurities and to increase the active area on the anode surface (Zhou et al., 2011).

2.2.2 Cathode selection

Carbon steel pipe (schedule 40 pipe dimension) with size of 1.905 cm was used. This pipe as the cathode was cut with the length of 120 mm according to diameter of the designed rig. The carbon steel pipe was chosen as a cathode in resulting from common gas pipeline material used in Malaysia (Khattak et al., 2016). The total surface area of the pipe is calculated from the Eq(1). The total surface area of the carbon steel pipe is 0.01118 m^2.

$$\text{Total surface area, } A\left(m^2\right) = 2\pi r(r + l) \quad (1)$$

where

r is the external radius of the pipe in m

l is the total length of the pipe in m

2.2.3 Backfilling selection

In the cathode compartment, sand was used as a backfilling. The size of the sand between 0.105 - 0.250 mm was used. Sand was selected because there were spaces between them that provide oxygen to form water when combine with protons (Kim et al., 2007).

2.2.4 Membrane selection

A proton exchange membrane, Nafion-117 (Sigma Aldrich) with 3.2 cm internal diameter, and 183 μm thickness was used due to its good mechanical durability and high cation conductivity (Logan et al., 2006)

2.3 Experimental rig design and set up

Two compartment of biological CP system were constructed by joining two equal cylindrical Plexiglas in dimension of 16 cm diameter x 20 cm height with plastic tubing. The plastic tubing with 20 cm length x 3.2 cm internal diameter was connected to the both side of the compartment. The Nafion-117 membrane with the thickness of 183 μm (Sigma-Aldrich) was placed in the middle of the plastic tubing plus a rubber gasket that was used for sealing to avoid leakage. The anode compartment of the rig was designed with a tight cap to avoid any addition of unwanted materials throughout the operation.

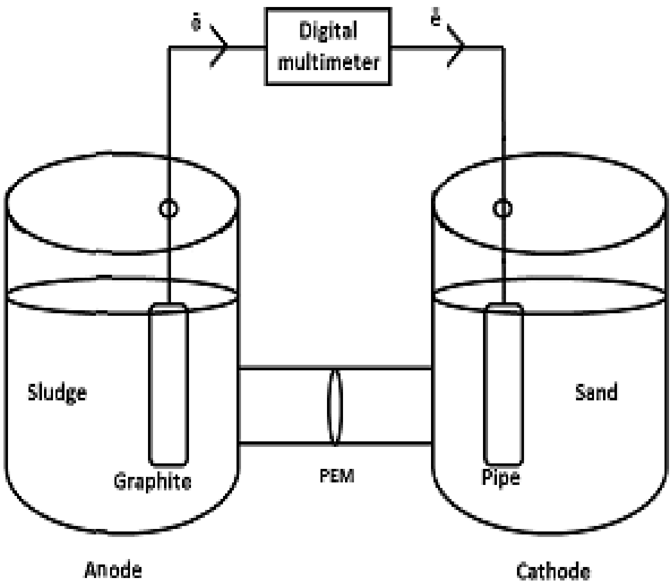

Figure 1: Schematic diagram of the experimental set up

3 L of wastewater and 3 kg of backfilling sand were filled in anode and cathode compartment. The graphite rod was immersed in the wastewater, while carbon steel pipe was inserted into the sand. The copper wire was used to connect both anode and cathode electrodes to the multimeter. 30 g of sodium acetate (Sigma Aldrich-11C160007) was fed into the anode compartment to increase the microbial growth rate. Sodium acetate is a simple substrate and popular as a carbon source in order to encourage electroactive bacteria (Pant et al., 2010). The experiment was conducted in batch mode and carried out at room temperature. Voltage and current readings were taken regularly every three hours until the values taken were decreasing which mean the microbes has reached its death phase (Yates and Smotzer, 2007). The CP potential vs. CSE at the cathode was also taken regularly to determine the performance of the CP. The digital multimeter (Kyoritsu Model 1009) was used to take the voltage and current response of the biological CP system. Figure 1 shows the schematic diagram of the experimental biological CP set up used in the study.

2.4 Study on the effect of the pH on the system

Different pH at the anode and cathode will affect the performance of the biological CP system as this will give different value of power density. In this study, the pH value at the anode and cathode was adjusted using 1.0 M sodium hydroxide (Emsure-UN1823) and 0.1 M hydrogen chloride (Fisher Chemicals,H-1200NC-17) solutions. The reading of pH at the anode and cathode compartment was taken using digital pH meter (Checker by Hanna). The performance of this biological CP system was analysed by comparing the power density output of each run. The reading of the voltage and current in the circuit were taken to calculate the current density. Table 1 shows the number of runs at different pH value of anode and cathode.

Table 1: List of experimental runs

Run	pH at anode	pH at cathode
1	7	6
2	7	7
3	7	8
4	8	6
5	8	7
6	8	8
7	9	6
8	9	7
9	9	8

3. Results and discussion

3.1 Voltage output

The voltage output for all runs is plotted in Figure 2. Based on Figure 2, the voltage output curves were almost the same for all of the runs. The pattern is similar to the typical microbial growth curve. The typical microbial growth curve can be divided into four phases which are lag phase, exponential phase, stationary phase and death phase. The lag phase was the phase when the microbes adapt themselves to the growth conditions. The next phase was the exponential growth as shown in the early stage in Figure 2 which occurred approximately between 0 to 15 h. Run 5 with the pH of 8 and 7 at anode and cathode showed the highest slope among all of the runs. During this phase, the microbes grew rapidly and divided at the maximal rate as possible (Yates and Smotzer, 2007).

During 15 to 50 h period of the experiment, most of the line in the graph showed the stationary phase. During this phase, the growth rate of the microbes was limited due to the limiting factors such as the depletion of nutrients. The growth rate of the microbes was also equal to the death rate (Yates and Smotzer, 2007). Based on Figure 2, the highest voltage output during the stationary phase was shown by the Run 5. This might be due the pH combination of Run 5 is the most favorable for the bacteria growth. From 50 until 90 h period, most of the lines were decreasing gradually which represented the death phase. During this phase, the microbes declined in population because the surroundings cannot maintain the population.

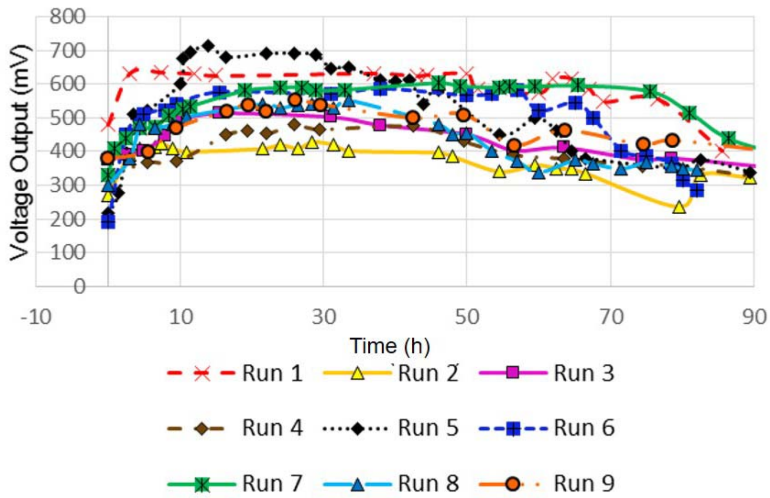

Figure 2: Voltage output for all runs

Based on Figure 2, three runs that had the highest voltage output were Run 1, Run 5, and Run 7. The similarities between these three runs were the systems were in alkaline condition for anode and a little acidic condition at cathode. Higher voltage was obtained from this condition because alkaline condition at anode can enhanced the electron transfer efficiency while a little acidic condition at cathode is favorable for denser biofilm formation (Kumar and Mungray, 2016).

3.2 Effect of anodic pH on the system

In order to study the effect of pH at the anode compartment on the performance of the system, a graph of current density produced was plotted against the different values of pH at anode as shown in Figure 3a. In this study the value of anodic pH were 7, 8 and 9 while the cathodic pH was kept constant at 7. It was observed that alkaline condition of anode produced higher current density. This was because the acidified anode could reduce the bacterial activity and therefore affect the performance and stability of biofilm formation (Oliveira et al., 2013). However, based on Figure 3a, pH 8 showed the highest current density output which was 863 mA/m^2, 29 % higher than the current density produced at pH 9. This showed that the optimal conditions for this system in terms of current power production corresponded the pH at anode in the range between 7 and 8. Alkaline ones with an anolyte pH higher than 8, induced a decrement in the current density production. This is because bacterial metabolism constantly produces weak acid compounds. As a result, the high pH was decreased over the current generation process by uptaking protons (He et al., 2008). Besides the study discussed above, a research done by Yuan and co-worker (Yuan et al., 2011) found that biofilm at alkaline showed enhanced electron transfer efficiency with respect to the electrocatalytic current, electron transfer rate, exchange current density, and charge transfer resistances, compared with the biofilms at neutral and acidic.

3.3 Effect of cathodic pH on the system

In order to analyse the effect of pH at the cathode compartment on the performance of the system, a graph of current density produced was plotted against the different values of cathodic pH as shown in Figure 3b. In this study the value of cathodic pH were 6, 7 and 8 while the anodic pH was kept constant at 7. Figure 3b shows the current density produced at different pH value at cathode. The highest current density recorded was 768 mA/m^2 at pH equal to 6 which was 24 % higher compared to the highest value at pH 8. This was due to protons were available in high concentrations at low catholyte pH and thus gave better performance of the system. The presence of high concentration of protons in the cathode compartment will reduce the ohmic losses problem in the system (Kumar and Mungray, 2016).

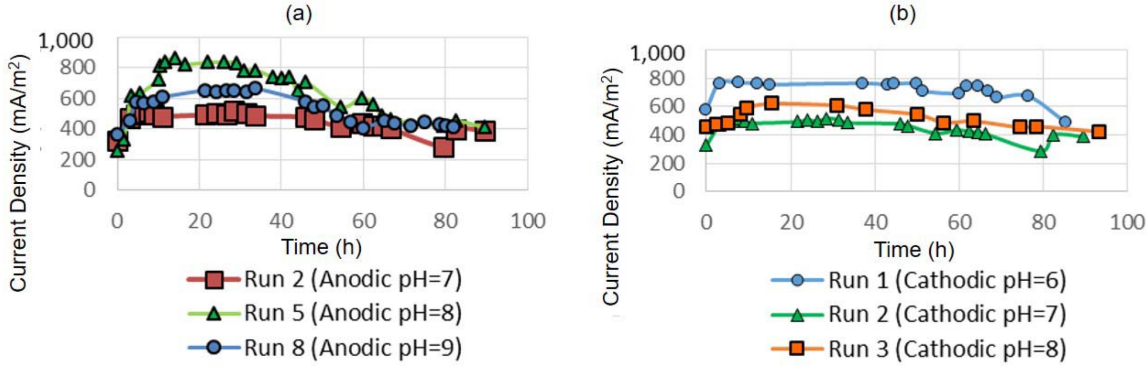

Figure 3: (a) Current density produced at different anodic pH; (b) Current density produced at different cathodic pH

3.4 Performance of the system in reducing corrosion of carbon steel pipe

The performance of the system in order to reduce the corrosion of steel pipe was analysed by monitoring the CP potential vs CSE (Liu and Cheng, 2017). Figure 4 shows the CP potential vs. CSE for each of the run conducted. The initial CP potential vs. CSE which is the native potential of carbon vs. CSE was -560 mV. The value was decreasing down to -752 mV. This shows that the corrosion of the carbon steel was reduced.

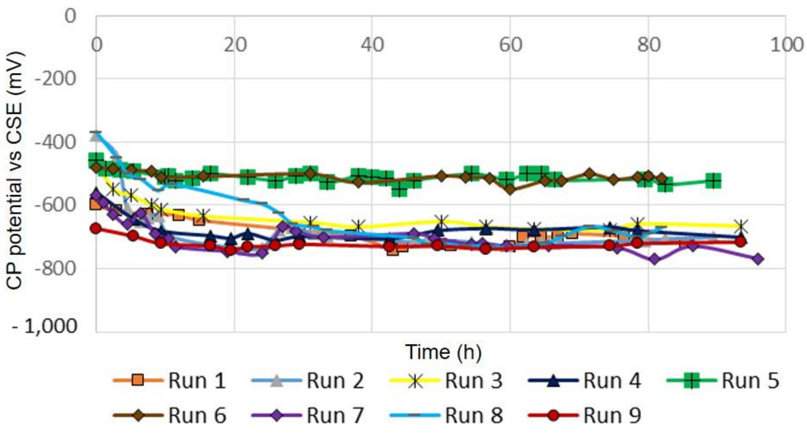

Figure 4: CP potential for each runs

4. Conclusion

It is important to optimise the operating condition of a biological CP system. Based on the study, the optimum pH at anolyte and catholyte for maximum power density were 8 and 6 as the highest power and voltage output were produced in alkaline anode and acidic cathode condition. It was also found that the system could be used to control corrosion of carbon steel pipe where the CP potential vs. CSE was decreased from -560 mV to -752 mV.

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Reference

Ashworth V., 2010, Principle of Cathodic Protection, 2, 2747-2762.

Cheng Y. F., 2015, Pipeline Corrosion, Corrosion Engineering, Science & Technology, 50(3), 2.

He Z., Huang Y., Manohar A. K., Mansfeld F., 2008, Effect of electrolyte pH on the rate of the anodic and cathodic reactions in an air-cathode microbial fuel cell, Bioelectrochemistry, 74(1), 78-82.

Ishii S.i., Suzuki S., Norden-Krichmar T.M., Wu A., Yamanaka Y., Nealson K.H., Bretschger O., 2013, Identifying the microbial communities and operational conditions for optimized wastewater treatment in microbial fuel cells, Water Research, 47(19), 7120-7130.

Khattak M.A., Zareen N., Mukhtar A., Kazi S., Jalil A., Ahmed Z., Jan M.M., 2016, Root cause analysis (RCA) of fractured ASTM A53 carbon steel pipe at oil and gas company, Case Studies in Engineering Failure Analysis, 7, 1-8.

Kim B.H., Chang I.S., Gadd G.M., 2007, Challenges in microbial fuel cell development and operation, Applied Microbiology and Biotechnology, 76(3), 485.

Kuang D., Cheng Y.F., 2015, Effect of alternating current interference on coating disbondment and cathodic protection shielding on pipelines, Corrosion Engineering, Science and Technology, 50(3), 211-217.

Kumar P., Mungray A.K., 2016, Microbial fuel cell: optimizing pH of anolyte and catholyte by using taguchi method, Environmental Progress & Sustainable Energy, 36(1), 120-128.

Liu T., Cheng Y.F., 2017, The influence of cathodic protection potential on the biofilm formation and corrosion behaviour of an X70 steel pipeline in sulfate reducing bacteria media, Journal of Alloys and Compounds, 729, 180-188.

Logan B.E., Hamelers B., Rozendal R., Schröder U., Keller J., Freguia S., Aelterman P., Verstraete W., Rabaey K., 2006, Microbial fuel cells: methodology and technology, Environmental Science & Technology, 40(17), 5181-5192.

Lu N., Zhou S.-g., Zhuang L., Zhang J.-t., Ni J.-r., 2009, Electricity generation from starch processing wastewater using microbial fuel cell technology, Biochemical Engineering Journal, 43(3), 246-251.

Mahmood N.A.N., Ghazali N.F., Ibrahim K.A., Ali M.A., 2017, Anodic pH Evaluation on performance of power generation from palm oil empty fruit bunch (EFB) in dual chambered microbial fuel cell (MFC), Chemical Engineering Transactions, (56), 1795-1800.

Molognoni D., Puig S., Balaguer M.D., Liberale A., Capodaglio A.G., Callegari A., Colprim J., 2014, Reducing start-up time and minimizing energy losses of Microbial Fuel Cells using Maximum Power Point Tracking strategy, Journal of Power Sources, 269, 403-411.

Oliveira V.B., Simões M., Melo L.F., Pinto A.M.F.R., 2013, Overview on the developments of microbial fuel cells, Biochemical Engineering Journal, 73, 53-64.

Orazem M.A. (Ed.), 2014, Underground pipeline corrosion: Detection, analysis and prevention, Woodhead Publishing, United Kingdom.

Pant D., Van Bogaert G., Diels L., Vanbroekhoven K., 2010, A review of the substrates used in microbial fuel cells (MFCs) for sustainable energy production, Bioresource Technology, 101(6), 1533-1543.

Tsynaeva A.A., 2015, Cathode Protection Systems of Cross-country Pipelines, Procedia Engineering, 111, 777-782.

Yates G.T., Smotzer T., 2007, On the lag phase and initial decline of microbial growth curves, Journal of Theoretical Biology, 244(3), 511-517.

Yuan Y., Zhao B., Zhou S., Zhong S., Zhuang L., 2011, Electrocatalytic activity of anodic biofilm responses to pH changes in microbial fuel cells, Bioresource Technology, 102(13), 6887-6891.

Zhou M., Chi M., Luo J., He H., Jin T., 2011, An overview of electrode materials in microbial fuel cells, Journal of Power Sources, 196(10), 4427-4435.