CHEMICAL ENGINEERING TRANSACTIONS
VOL. 63, 2018
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Jeng Shiun Lim, Wai Shin Ho, Jiří J. Klemeš

ISBN 978-88-95608-61-7; **ISSN** 2283-9216
DOI: 10.3303/CET1863070

Optimisation of Wastewater Volume of Single Chamber Biological Cathodic Protection System

Wan Nor Azita W Ali[a], Anis Fitri Afira Azman[a], Mohd Dinie Muhaimin Samsudin[a,b,*], Muaz Mohd Zaini Makhtar[c], Norazana Ibrahim[a], Rafiziana Md Kasmani[a]

[a]Department of Energy Engineering, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[b]UTM-MPRC Institute for Oil and Gas, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[c]School of Chemical Engineering, Universiti Sains Malaysia, 14300, Nibong Tebal, Pulau Pinang, Malaysia

dinie@utm.my

In this study, the concept of Microbial Fuel Cells (MFCs) was applied in the biological cathodic protection (CP) system in order to protect steel pipe. There are various factors affect the performance of the system including the volume of the medium.The purposes of this study were to analyse and optimise the effect of volume ratio of wastewater to the sand on biological CP performance by using Taguchi method. The maximum performance of biological CP in this study was obtained at the largest volume ratio. The orthogonal array and the signal-to-noise ratio (S/N) were employed to study the effect of volume ratio on performance of biological CP. The CP potential vs. copper sulfate electrode (CSE) was -835 mV. It shows that the corrosion of carbon steel pipe was reduced since the native potential of the carbon steel pipe vs. CSE was -531 mV.

1. Introduction

Oil and gas pipelines have been used widely as transportation network in transferring oil and gas. Primary mechanism resulting in oil and gas pipelines failures has been identified as corrosion. Pipeline corrosion is a complex phenomenon where it is resulted from the interaction of multiple reactions and processes occurring simultaneously among material and the environmental interaction (Norsworthy, 2014). Disrupting in the transport process will occur due to damage induced by pipeline corrosion. This problem will increase the direct cost and lead to unfavourable events, such as fires and explosions. For these reasons, cathodic protection (CP) system has been introduced as an alternative of corrosion prevention for underground structures such as oil/gas pipelines (Kuang and Cheng, 2015).
According to International standard ISO 8044, CP is defined as decreasing corrosion potential by electrochemical protection to a level at which the corrosion rate of the metal is significantly reduced. Impressed current cathodic protection (ICCP) is one of the methods used in CP system. In ICCP method, the use of an external supply which is rectifier is introduced to convert alternating current (AC) to direct current (DC) in order to provide the cathodic polarisation of the structure (Ranade et al., 2016). ICCP is more convenient method and popular than sacrificial anode because it provides remarkable protection against corrosion in all types of ships and offshore platforms, pipelines, ports and others. Since the uses of ICCP system will be limited due to the depletion of the fossil fuels to generate electricity in the future, the biological CP system has been introduced as an alternative solution (Cheng, 2015).
In Microbial Fuel Cell (MFC), the electrons generated by the bacteria, which is consuming substrate were used in cathodic reaction. The electrons transfer to the cathode by using external path. The potential of the metal in this system can be shifted to the negative direction as in ICCP due to the capability of electrogenic microorganisms to produce protons and electrons from substances under anaerobic condition (Wang et al., 2016). The potential differences between the electron acceptor and respiratory system in biological CP generates requirement current density and voltage to make electricity. In this study, the concept of a single

Please cite this article as: Wan Nor Azita W Ali, Anis Fitri Afira Azman, Mohd Dinie Muhaimin Samsudin, Muaz Mohd Zaini Makhtar, Norazana Ibrahim, Rafiziana Md Kasmani, 2018, Optimisation of wastewater volume of single chamber biological cathodic protection system, Chemical Engineering Transactions, 63, 415-420 DOI:10.3303/CET1863070

chamber of MFC was applied in the biological CP system, where the principle of ICCP method was practiced. The uses of a power source which is a rectifier to generate the direct current to the CP system was replaced by the generation of electricity using biological CP system. The anaerobic of domestic wastewater was used in this study to fulfil the high potential of biodegradation of organics in anaerobic environment. Domestic wastewater has an energy potential of 1.23 kWh/m^3 in biodegradable organics, where, 0.67 kWh/m^3 (suspended organics) and 0.56 kWh/m^3 (dissolved organics) (Park et al., 2017). The collection of this energy to generate electricity will enable sustainable biological CP system to protect pipe. In MFCs, bacteria are dominant species and the selection of the bacterial inoculum and operating conditions will largely determine the rate of enrichment and biofilm development (Ishii et al., 2013). The volume and moisture content are among the operating conditions that influence the microbial community on the anode and performance on the cathode (Fornero et al., 2010).

This study aimed to investigate the effect of volume ratio and moisture contents on performance of single chamber of biological CP. Taguchi Method was used to optimise the volume ratio in order to obtain maximum power density requirement of a biological CP. A large number of experiments resulted from a full factorial design in most industrial can be reduced to a practical level by selecting a small set from all the possibilities (Pandit et al., 2014). The orthogonal arrays and (signal)/(noise) known as S/N ratio used in this method will give the full information of all the factors that affect the performance parameter (Kumar and Mungray, 2017). This method is suitable in this study to determine the optimum volume ratio and moisture contents variation in single chamber of biological CP simultaneously.

2. Material and Methods

2.1 Sample Preparation

An anaerobic wastewater was collected from gravity thickener pond at Indah Water Konsortium, Taman Bukit Senang, Senai. The anaerobic wastewater sample was kept below 4 °C to deactivate the bacteria growth before feeding to the system. The anaerobic wastewater was chosen because of their microbial communities are definitely valuable at high concentration and high temperature (Lee et al., 2017).

2.2 Material Selection

2.2.1 Anode Selection

An anode electrode of graphite rod was used in this experiment due to its stability in microbial cultures, high mechanical strength and excellent electrical conductivity. The graphite rod with dimension of 150 mm height x 20 mm outside diameter was used.

The graphite rod was undergoing acid treatment before installation. In this treatment, the electrode was placed in nitric acid solution for 24 h. Then, it was removed and washed with deionised water for several times. The main acid treatment purposed were 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, 26.67 mm outer diameter and 20.93 mm internal diameter was used. The pipe length of 120 mm was used according to diameter of beaker. The selected of carbon steel pipe as cathode based on the common pipe material used in a gas pipeline system in Malaysia. The total surface area of the pipe was calculated from the Eq(1).

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

Where:

r: is the external radius of the pipe

l: is the total length of the pipe

2.2.3 Sand Selection

Sand was acted as a backfilling or catholyte in this single chamber system. The volumes of sand used were varied to 2 L, 3 L and 4 L according to the volume ratios. The sand was sieved to 0.105 - 0.250 mm. Sand was used because there were spaces between them that provided oxygen to form water molecule when combine with protons (Venzlaff et al., 2013).

2.3 Substrate Selection

2.3.1 Type of a substrate

A sodium acetate trihydrate (Batch: 11C160007) was a simple substrate and fed to the chamber with the volume of 10 g/L to give power value. Acetate was popular as carbon source in order to encourage electroactive bacteria. As acetate has inertness towards alternative microbial conversion at room temperature, it was extensively used in order to standardise new biological CP components (Pandey et al., 2016).

2.4 Experimental Set Up and Procedure

A membrane-less single chamber biological CP was constructed by used a rectangular acrylic glass beaker in dimension of 30 cm length x 20 cm width x 15 cm height. The copper wire with external resistance of 74 Ω was connected to the digital multimeter (Kyoritsu Model 1009) in order to determine the voltage and current. Figure 1 shows the schematic diagram of the experimental biological CP set up in this study.

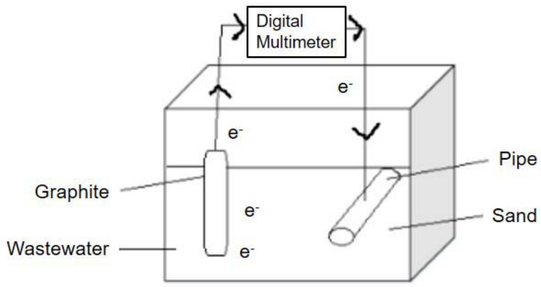

Figure 1: Schematic diagram of the experimental biological CP

Wastewater and sand in a specific volume ratio were filled in the beaker. In this study, L_9 (3^2) orthogonal array was selected according to 2 factors and 3 levels from principle of Taguchi method. In this experimental design, two factors which were volume of wastewater and volume of sand were considered with 3 levels of factor (Pandit et al., 2014). Subsequently, matrix experiments (9 experiments with different combinations) was performed in this study. Then, the graphite rod and carbon steel pipe were immersed in the sand. The acetate with amount of 10 g/L was fed into the wastewater to increase the microbial growth rate.
The experiment was conducted in batch mode and carried out at ambient temperature. The readings of voltage and current were monitored at an interval time until the decreasing outputs were obtained. The stationary outputs readings were important to obtain maximum performance of biological CP. The CP potential vs. CSE at the cathode was also taken regularly to determine the performance of the CP. The values of moisture contents were calculated by Eq(2) based on the volume ratios. Current density and power density were values calculated to determine the performance of biological CP system. The values were then applied in Taguchi method to determine the optimum parameter.

Moisture Contents (%) = (mass (kg) of water)/(mass of sieved sand + mass of water) × 100 % (2)

3. Results and Discussion

3.1 Voltage Potential Reading

The voltage potential readings in biological CP system were related to the activity of bacteria in the wastewater at interval time. The voltages obtained according to the duration were displayed in Figure 2. From Figure 2, it could be seen that the graph trend for all experiments were almost the same. They followed a characteristic pattern of increasing in number, followed by a decrease in number as justified in a bacterial growth pattern. It could be seen that the voltage readings increased at the earlier experiment which represents a period where the population was continuously doubled. This phase is known as an exponential phase. The duration for an exponential phase in these experiments took about 10 to 15 h. This had been continued until the conditions become less favorable (Roy et al., 2013).
From Figure 2, the combinations with low ratio values as shown in Experiment 2, 3 and 6 resulted in a low current density because of poor electrons and protons supplied to the cathode. In this study, the constant amount of acetate feed into the wastewater which is 10 g/L might be stimulated the activation of electrogens in competing for their food to survive. This excitement resulted in the high current density obtained in large volume of wastewater used (Osman et al., 2011). As a result, the wastewater volume of 4 L and sand volume of 2 L combinations gave a high open circuit average voltage of 806 mV with high current density 974.23 mA/m^2. This combination represented the highest ratio value, which was 2. This might be related to the volume of electrogens in the wastewater were increasing proportionally to the wastewater volume (Foad Marashi and Kariminia, 2015). Electrogens acted as the biocatalyst in this system in order to develop an enrich biofilm at the anode. More electrogens might be able to enhance more biofilm development and lower

the activation loss during the electrons transfer. The highest voltage value for each experiment was obtained at stationary phase. In this duration time, the biofilm was fully developed and stabilised at anode electrode. Then, the voltage readings started to drop due to the decline or death phase of bacteria. Eventually a decrease in the number of living cells in the population occured which might be caused by unfavorable conditions (Cai et al., 2016).

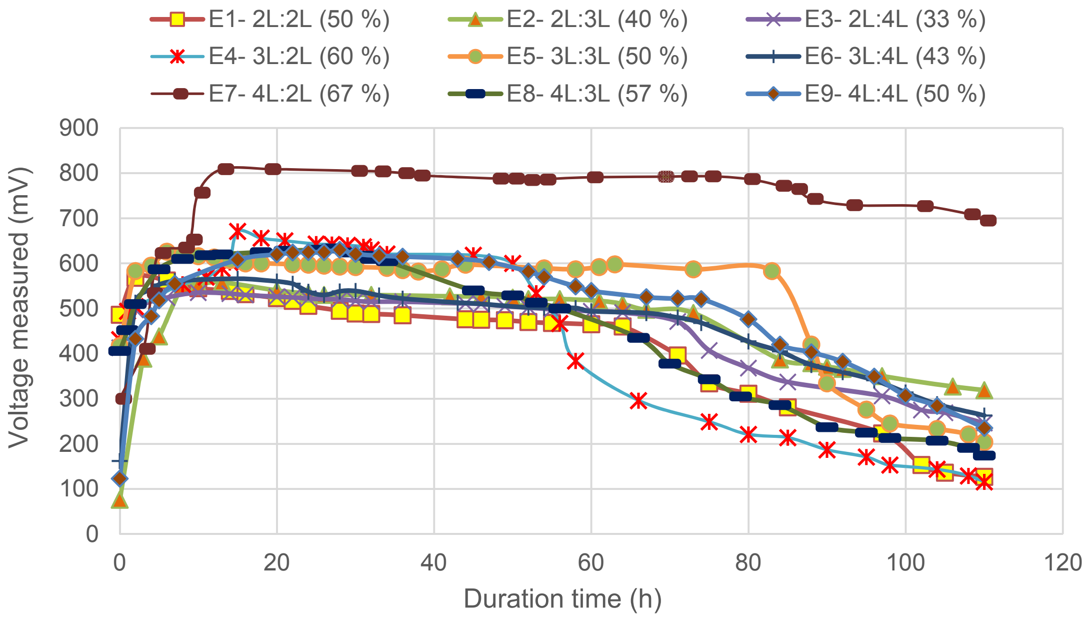

Figure 2: Effect of volume ratio on voltage reading

In Figure 2, the effect of moisture contents was related to the ratio values where they gave high performance at high moisture contents. It shows that the current density in moisture condition was higher than in the case of dry condition. The production of current density might be affected by the bacterial regrowth potential and their activation rate at different level of moisture contents in wastewater (Costa et al., 2014). The rate of bacterial regrowth will be increase proportionally to the moisture contents. Better performance was achieved, and greater current density was produced with higher water content. From the result in Figure 2, the highest performance was observed at the volume ratio of 2, when the moisture contents were 67 %. The lowest performance was obtained at the volume ratio of 0.5, with the level of moisture contents was 33 %.

3.2 Optimisation Study by Taguchi

The optimum volume ratios and moisture contents on the current density requirement were investigated by using Taguchi design. This theory applied the concept of orthogonal array to improve the efficiency and reduce the number of laboratory experiments (Pandit et al., 2014). Controllable (signal) and uncontrollable (noise) were known as S/N ratio which is a factor that affected the performance of biological CP. S/N ratio was determined by calculating the average three highest values for each experiment. Since the experimental design was orthogonal, it was then possible to separate out the effect of power density at different levels. The quality output of this work was the maximum power density, which fitted into the larger-the-better characteristics based on Eq(3) (Kumar and Mungray, 2017).

$$S/_{N} = -10 \times \log 10\left(\frac{1}{n_T}\sum_{i=1}^{n_T}\frac{1}{y_i^2}\right) \quad (3)$$

where
n_T = total number of readings
Y = power density, mW/m^2
The mean S/N ratio for each level of the wastewater and sand volume was summarised and called the S/N ratio response in Table 1. The optimum values of both parameters for obtaining maximum power density were the highest S/N ratio value calculated by Eq(3). Figure 3 was prepared for predicting the influences of parameters on the performance characteristics by using data from Table 1. The numerical values of the maximum point in both graphs which were at 4 L and 2 L of wastewater and sand volume, giving the best

value for that parameter (Kumar and Mungray, 2017). This condition value was same as reported in the L_9 experimental analysis. These should be the optimised condition that produced maximum power density.

Table 1: Response table for S/N ratio based on larger is better

Level	Volume wastewater (L)	Volume Sand (L)
1	51.199	54.6
2	53.133	52.791
3	55.015	51.956
delta	3.816	2.644

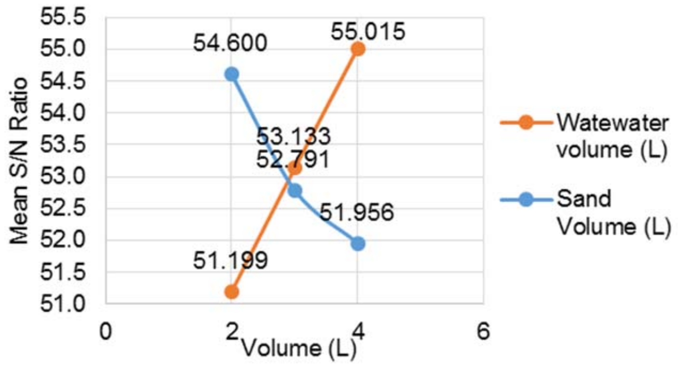

Figure 3: Mean effect plot for S/N ratio

3.3 Performance of 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. The CP potential vs. CSE for each of the experiment were shown in Figure 4. At the highest volume ratio, the initial CP potential vs. CSE which the native potential of carbon vs. CSE was -531 mV. The value was decreasing down to -835 mV. This shows that the corrosion of the carbon steel was reduced as the CP potential vs. CSE was more negative. According to the standard by NACE, the carbon steel pipe was fully protected when this value achieved a minimum of -850 mV (Tsuneyasu et al., 2017).

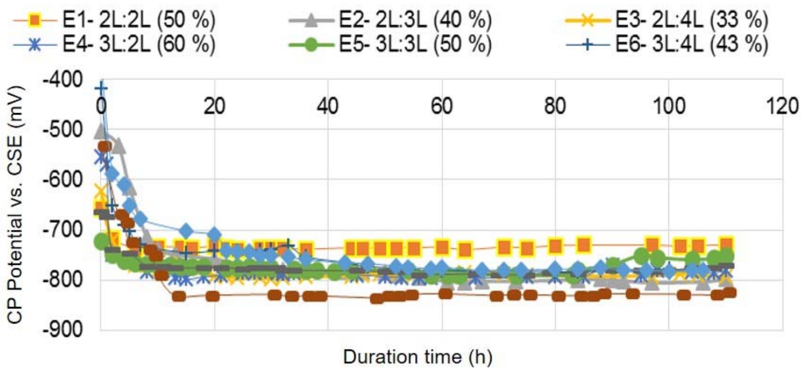

Figure 4: CP potential for each experiment

4. Conclusion

Volume ratio and moisture contents should be kept high for the practical application of composting biological CP and gave the maximum performance of biological CP. Taguchi method could be used to decrease the number of experiments in order to obtain the best combination of volume ratio. An appropriate volume combination was enhanced the performance of biological CP in this study. It was also found that the system could be used to control corrosion of carbon steel pipe where the CP potential versus CSE was decreased from -531 mV to -835 mV.

Acknowledgments

We are grateful for financial support from Ministry of Higher Education Malaysia for Fundamental Research Grant Scheme (RJ130000.7846.4F879) and to Universiti Teknologi Malaysia for Potential Academic Staff grant (QJ130000.2746.02K33).

References

Cai W., Zhang Z., Ren G., Shen Q., Hou Y., Ma A., Deng Y., Wang A., Liu W., 2016, Quorum sensing alters the microbial community of electrode-respiring bacteria and hydrogen scavengers toward improving hydrogen yield in microbial electrolysis cells, Applied Energy, 183, 1133-1141.

Cheng Y.F., 2015, Pipeline corrosion, Corrosion Engineering, Science and Technology, 50, 161-162.

Costa M.M., Queiroz D.M.d., Pinto F.d.A.d.C., Reis E.F.d., Santos N.T., 2014, Moisture content effect in the relationship between apparent electrical conductivity and soil attributes, Acta Scientiarum, Agronomy, 36(4), 395-401.

Foad Marashi S.K., Kariminia H.-R., 2015, Performance of a single chamber microbial fuel cell at different organic loads and pH values using purified terephthalic acid wastewater, Journal of Environmental Health Science and Engineering, 13, 27.

Fornero J.J., Rosenbaum M., Angenent L.T., 2010, Electric Power Generation from Municipal, Food, and Animal Wastewaters Using Microbial Fuel Cells, Electroanalysis, 22, 832-843.

Ishii S.i., Suzuki S., Norden-Krichmar T. ., 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**,** 7120-7130.

Kuang D., Cheng Y.F., 2015, Study of cathodic protection shielding under coating disbondment on pipelines, Corrosion Science, 99, 249-257.

Kumar P., Mungray A.K., 2017, Microbial fuel cell: optimizing pH of anolyte and catholyte by using taguchi method, Environmental Progress & Sustainable Energy, 36, 120-128.

Lee X.J., Hiew B.Y.Z., Lee L.Y., Gan S., Thangalazhy-Gopakumar S., 2017, Evaluation of the Effectiveness of Low Cost Adsorbents from Oil Palm Wastes for Wastewater Treatment, Chemical Engineering Transactions, 56, 937-942.

Norsworthy R., 2014. Understanding corrosion in underground pipelines: basic principles, Underground Pipeline Corrosion, 3-34.

Osman M.H., Shah A.A., Walsh F.C., 2011, Recent progress and continuing challenges in bio-fuel cells. Part I: enzymatic cells, Biosensors and Bioelectronics, 26(7), 3087-3102.

Pandey P., Shinde V.N., Deopurkar R.L., Kale S.P., Patil S.A., Pant D., 2016. Recent advances in the use of different substrates in microbial fuel cells toward wastewater treatment and simultaneous energy recovery, Applied Energy, 168, 706-723.

Pandit S., Khilari S., Roy S., Pradhan D., Das D., 2014, Improvement of power generation using Shewanella putrefaciens mediated bioanode in a single chambered microbial fuel cell: Effect of different anodic operating conditions, Bioresource Technology, 166, 451-457.

Park Y., Park S., Nguyen V.K., Kim J.R., Kim H.S., Kim B.G., Yu J., Lee T., 2017, Effect of gradual transition of substrate on performance of flat-panel air-cathode microbial fuel cells to treat domestic wastewater, Bioresource Technology, 226**,** 158-163.

Ranade S., Forsyth M., Tan M.Y.J., 2016, In situ measurement of pipeline coating integrity and corrosion resistance losses under simulated mechanical strains and cathodic protection, Progress in Organic Coatings, 101, 111-121.

Roy J.N., Luckarift H.R., Sizemore S.R., Farrington K.E., Lau C., Johnson G.R., Atanassov P., 2013, Microbial-enzymatic-hybrid biological fuel cell with optimized growth conditions for Shewanella oneidensis DSP-10. Enzyme and Microbial Technology, 53(2), 123-127.

Tsuneyasu S., Watanabe Y., Nakamura K., Kobayashi N., 2017, In situ measurements of electrode potentials of anode and cathode in organic electrochromic devices, Solar Energy Materials and Solar Cells, 163, 200-203.

Venzlaff H., Enning D., Srinivasan J., Mayrhofer K.J.J., Hassel A.W., Widdel F., Stratmann M., 2013, Accelerated cathodic reaction in microbial corrosion of iron due to direct electron uptake by sulfate-reducing bacteria, Corrosion Science, 66, 88-96.

Wang X., Zhang E., Yu E.H., Scott K., 2016, Low cost materials for the air cathodes in single-chamber microbial fuel cells: A mini review, Chemical Engineering Transactions, 51, 37-42.

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, 4427-4435.