The Effect of Varying the Hydraulic Retention Time (HRT) and Temperature on the Removal of Sulphates in a Linear Flow Channel Reactor

Jan Witbooi¹, Frans Waanders¹, Andrew Eloka-Eboka², René Bekker¹, Setano Ntwampe³

Abstract— The treatment of acid mine drainage (AMD) is essential to increase the effluent pH, and remove sulphate and heavy metals. Biological treatment methods have been used recently to treat AMD using bioreactors. The sulphate-reducing bacteria (SRB) were used in this study to remove sulphates through the generation of sulphides. Furthermore, the linear flow channel reactor (LFCR) was used and operated at an influent COD/sulphate ratio greater than 0.75. Two experiments were conducted to determine the effect of varying the hydraulic retention time (HRT), temperature and the AMD volume on the reactor performance.The HRT was decreased from 4 days to 2 days, the temperature increased from 21°C to 30°C, and the AMD volume was increased from 6.4 L to 6.6 L. The bioreactor was operated for 38 days for both experiments. A higher sulphate removal efficiency of 98% was achieved for the first experiment and an efficiency of 89% was obtained for the second experiment. Heavy metals, excluding Mn were completely removed after 15 days for the first experiment. Additionally, after 15 days, the concentration of Mn in the effluent was found to be below 7 mg/L for both experiments. It was concluded that high HRT, and low temperature increases the process performance. In addition, treating high AMD volume requires a LFCR with a large volume. 41st Cape Town Homes on Conference of Algorithmental Conference on the Removal and Engineering Cape Cape Town (CCBE) and Conference on the Removal and Engineering Cape Town (CCBE) and Engineering (CCBE) and Engineering (C

*Keywords***— a**cid mine drainage, hydraulic residence time, linear flow channel reactor, sulphate-reducing bacteria, removal efficiency.

I. INTRODUCTION

In South Africa (SA), there is an abundance of acid mine drainage (AMD) production by mines, leading to difficulties in produced AMD management. The AMD consist of toxic components such as low pH, high heavy metal and sulphate concentration, which contribute to pollution of water sources [1]. Water pollution is a major crisis in SA leading to a water scarcity in some provinces, therefore AMD treatment options are required. Treatment processes used in SA include membrane filtration, neutralization and biological methods [2]. AMD treatment bioprocesses have recently been investigated by researchers, and processes such as algal bioremediation, constructed wetlands, and biological sulphate reduction (BSR) are mostly used [3, 4, 5]. These bioprocesses are easier to operate, require less chemical supply, produce less sludge, and are less expensive [6, 7, 8].

²Andrew Eloka-Eboka has left the NWU and is now presiding in the USA.

The BSR process utilizes a sulphate-reducing bacteria (SRB) for AMD treatment. SRB is an anaerobic bacterium that reduces sulphates in AMD as sulphides and require certain growth conditions. Most SRB's are mesophilic (survives at temperatures between 20 C - 40°C) and require a carbon source for growth [9]. Different carbon sources used by SRB include ethanol, lactate, glucose, and activated sludge [10, 11]. The reaction mechanism of the BSR process is given by reaction (1), where the sulphate is reduced to sulphide, and reaction (2) where heavy metals are removed as metal sulphide precipitates [12].

$$
2CH_2O + SO_4^{2-} \to H_2S(g) + 2HCO_3^{2}
$$
 (1)

$$
H_2S + M^{2+} \rightarrow 2H^+ + MS \ (s) \tag{2}
$$

Different bioreactors such as packed bed (PBR), inverse fluidized bed (FBR), submerged anaerobic membrane (AnMBR) and up flow sludge bed reactor (UASB) have been used BSR for AMD treatment [13, 14]. Also, there is a linear flow channel reactor which has been used by researchers from the University of Cape Town (UCT). Previous studies from UCT [6, 15, 16] from UCT have used a larger reactor (25 L) and recent studies [10, 17] have used a small reactor (2 L). These reactors have given satisfactory results, achieving sulphate and COD removal efficiencies above 90%.

In the present study a middle-sized LFCR, with a volume of 10.4 L for the treatment of AMD was used. The aim of the study was to evaluate the effect of changing the HRT, temperature, and AMD volume on the treatment efficiency. Results obtained from this study will provide the optimum conditions required for the SRB growth to improve the reactor performance.

II.MATERIALS AND METHODS

2.1 Acid mine drainage and inoculum

Acid mine drainage (AMD) and an inoculum were used for the two experiments, where the inoculum was provided by Mintek, SA, and characteristics of both AMD samples are given in **Error! Reference source not found.**. The inoculum consisted of a mixed sulphate-reducing bacteria (SRB) community. AMD and inoculum quantities were different for both experiments, and values are given in **Error! Reference**

¹ Jan Witbooi, Frans Waanders and René Bekker and Andrew Eloka-Eboka are with the CoE in Carbon-based Fuels, School of Chemical and Mineral Engineering, NWU, South Africa,

³Setano Ntwampe is with the Dept. of Chemical Engineering technology, UJ, South Africa

source not found.. Ethanol (99%) was used as a carbon source.

2.2 Linear flow channel reactor description

In this study, a linear flow channel reactor (LFCR), as shown in Fig. , was constructed at the North-West University (NWU). The reactor was made from 11 mm thickness Perspex and had 15 sampling ports and 4 inlet and outlet ports. The total reactor volume was 10.4 L, and the working volume was 9 L. The AMD and inoculum were introduced along with ethanol into the reactor using a peristaltic pump via the bottom inlet port. The reactor was continuously operated for a total of 72 days, 36 days for both experiments. The operating conditions for reactor operation for both experiments are presented in **Error! Reference source not found.**.

Fig. 1: Schematic representation of the LFCR used

2.3 Sample analysis

The following parameters: chemical oxygen demand (COD), sulphide, sulphate and heavy metal concentration, and pH were measured to monitor the bioreactor performance. A Hanna multi-photometer instrument was used for COD quantification. Sulphate and heavy metal concentration were measured using UV-spectroscopy [18] and a Thermo Fischer Scientific ICP-OES (iCAP 6000), respectively. The methylene blue method was used to determine the sulphide concentration. A metrohm pH meter was utilized to quantify the effluent pH.

III. RESULTS AND DISCUSSION

3.1 Reactor performance

3.1.1 Effluent COD

The effluent chemical oxygen demand (COD) concentration for both experiments is shown in Fig 2. On day 3, the COD reached peak values of 10545 mg/L and 11471 mg/L for the first and second experiments, respectively. The reason for the sharp increase was the addition of ethanol into the reactor. After 3 days, the COD decreased rapidly due to the SRB being in the high-performance phase, where it is already adapted to the reactor conditions and its growth increased exponentially and the trend continued until day 18 and day 15 for the first and second experiments, respectively. After this period, the COD started to decrease slowly due to the SRB being in the sustained phase. The addition of inoculum (250 mL) on day 30, led to a rapid COD decline. The final COD removal efficiency for the first experiment was 72%, and 69% for the second experiments.

3.1.2 Sulphate and heavy metal removal

The effluent sulphate concentrations for both experiments are shown in Fig. . The initial sulphate concentrations for both experiments were not the same due to differences in the AMD volume in the reactor. The sulphate concentration decreased rapidly for the first experiment compared to the second experiment due to the exponential SRB growth. However, from day 18, the SRB was at the sustained phase for both experiments leading to a slow sulphate reduction. The addition of the inoculum led to rapid sulphate reduction, and final removal efficiency of 98% was achieved for the first experiment and for the second experiment removal efficiency of 89% was achieved.

experiments after 36 days

Heavy metals concentrations that were measured for 15 days are given in TABLE . For the first experiment, metals such as Fe (II), Ni (II), Zn(II), and Cu (II) were completely removed after 15 days. Small amounts of the same metals were present in the effluent of the second experiment. Both experiments could not reduce the Mn (II) concentration to below 1 mg/L, due to anaerobic conditions in the reactor, as Mn can be removed through oxidation [19].

Period	Fe concentration		Mn concentration		Ni concentration		Zn concentration		Cu concentration	
	First exp.	Second exp.	First exp.	Second exp.	First exp.	Second exp.	First exp.	Second exp.	First exp.	Second exp.
θ	36.7	56.8	9.9	12.4	0.22	0.5	0.59	0.33	0.22	0.68
3		8.03	8.9	12.1	0.02	0.41	0.18	0.28	Ω	0.48
6	0.3	8.03	9.7	9.1	Ω	0.26	$\mathbf{0}$	0.24	$\bf{0}$	0.32
9	Ω	2.53	9	8.9	Ω	0.19	$\mathbf{0}$	0.06	θ	0.17
12	$\bf{0}$	1.27	7.8	7.8	Ω	0.05	$\mathbf{0}$	$\bf{0}$	$\bf{0}$	0.08
15	Ω	0.69	3.9	6.1	Ω	0.03	0.59	Ω	0.22	0.05

TABLE II: EFFLUENT HEAVY METALS CONCENTRATIONS FOR 15 DAYS REACTOR OPERATION

3.1.3 Sulphide production and pH increase

The effluent sulphide concentrations for both experiments are shown in Fig. 4. The sulphide concentration increased rapidly for both experiments, indicating that the SRB efficiently reduced sulphate into sulphide gas. However, after ± 30 days, the sulphide gas concentration was above 200 mg/L, which is remarkably high according to Austigard [20]. Therefore, the top valve was opened to let oxygen into the reactor for sulphide oxidation. The oxygen did not affect the results due to the presence of the floating sulphur biofilm (FSB). Finally, the effluent pH of the first experiment increased from 5.9 to 7.3 and for the second experiment it increased from 5.2 to 6.6. According to Sahinkaya [12], the increase in pH is related to the production of bicarbonate 41st CAPE TOWN Int Conference on Chemical, Biological and Conference of Conference on Chemical, Biological and Southern Cape and Conference of Conference on Chemical and Conference on Chemical and Conference on Chemical a

Fig. 5: pH of the effluent for both experiments during the reactor operation for 36 days

IV. CONCLUSIONS

The performance of the linear flow channel reactor was satisfactory for both experiments. However, the first experiment had higher COD, sulphate, and heavy metal removal efficiencies, and the pH of the effluent was above 7. In conclusion, the sulphate-reducing bacteria (SRB) growth is suitable, when the HRT is above 3 days, and the temperatures are below 25 °C. In addition, the increase in the AMD volume also affected the process performance.

V. ACKNOWLEDGEMENTS

The North-West University (NWU) is recognized for giving assistance with funding, and construction of the experimental equipment, and data analysis. The authors also show appreciation to SARChl chair (Prof. John Bunt), who provided funding and Mintek is also acknowledged for supplying AMD and inoculum.

REFERENCES

- [1] Akcil, A. & Koldas, S. 2006. Acid mine drainage (AMD): causes, treatment and case studies. *Journal of Cleaner Production*, 14(12- 13):1139-1145. https://doi.org/10.1016/j.jclepro.2004.09.006.
- [2] Rambabu, K., Banat, F., Pham, Q.M., Ho, S.-H., Ren, N.-Q. & Show, P.L. 2020. Biological remediation of acid mine drainage: Review of past trends and current outlook. *Environmental Science and Ecotechnology*, 2:100024.

https://doi.org/10.1016/j.ese.2020.100024.

- [3] Bai, H., Kang, Y., Quan, H.E., Han, Y., Sun, J. & Feng, Y. 2013. Treatment of acid mine drainage by sulfate reducing bacteria with iron in bench scale runs. *Bioresource Technology*, 128:818-822. https://doi.org/10.1016/j.biortech.2012.10.070.
- [4] Pat-Espadas, A.M., Loredo Portales, R., Amabilis-Sosa, L.E., Gómez, G. & Vidal, G. 2018. Review of constructed wetlands for acid mine drainage treatment. *Water*, 10(11):1685. https://doi.org/10.3390/w10111685.
- [5] Zhang, Z., Zhang, C., Yang, Y., Zhang, Z., Tang, Y., Su, P. & Lin, Z. 2022. A review of sulfate-reducing bacteria: Metabolism, influencing factors and application in wastewater treatment. *Journal of Cleaner Production*:134109.

https://doi.org/10.1016/j.jclepro.2022.134109.

- [6] van Hille, R., Van Wyk, N., Motleleng, L. & Mooruth, N. 2011. Lessons in passive treatment: Towards efficient operation of a sulphate reduction– sulphide oxidation system*.* In. International Mine Water Conference. pp. 4-11.
- [7] Neale, J.W., Muller, H.H., Gericke, M. & Mühlbauer, R. 2017. Low-cost biological treatment of metal-and sulphate-contaminated mine waters. *Mine Water and Circular Economy*, 453:453-460.
- [8] van Rooyen, M., Staden, P.J.V. & du Preez, K.A. 2021. Sulphate removal technologies for the treatment of mine-impacted water. *Journal of the Southern African Institute of Mining and Metallurgy*, 121(10):523-529. http://dx.doi.org/10.17159/2411-9717/1541/2021 .
- [9] Torbaghan, M.E. & Torghabeh, G.H.K. 2019. Biological removal of iron and sulfate from synthetic wastewater of cotton delinting factory by using halophilic sulfate-reducing bacteria. *Heliyon*, 5(12), https://doi.org/10.1016/j.heliyon.2019.e02948.
- [10] Marais, T.S., Huddy, R.J., Harrison, S.T.L. & van Hille, R.P. 2020. Demonstration of simultaneous biological sulphate reduction and partial sulphide oxidation in a hybrid linear flow channel reactor. *Journal of Water Process Engineering*, 34:101143. https://doi.org/10.1016/j.jwpe.2020.101143 *Water*, 14(1), https://doi.org/10.3390/w14010032.
- [11] Siddiqui, M.A., Biswal, B.K., Heynderickx, P.M., Kim, J., Khanal, S.K.,

Chen, G. & Wu, D. 2022. Dynamic anaerobic membrane bioreactor coupled with sulfate reduction (SrDMBR) for saline wastewater treatment. *Bioresource Technology*, 346:126447. https://doi.org/10.1016/j.biortech.2021.126447.

- [12] Sahinkaya, E., Isler, E., Yurtsever, A. & Coban, I. 2019. Sulfidogenic treatment of acid mine drainage using anaerobic membrane bioreactor. *Journal of Water Process Engineering*, 31:100816. https://doi.org/10.1016/j.jwpe.2019.100816.
- [13] Oztemur, G., Basaran, S.T., Tayran, Z. & Sahinkaya, E. 2020. Fluidized bed membrane bioreactor achieves high sulfate reduction and filtration performances at moderate temperatures. *Chemosphere*, 252:126587. https://doi.org/10.1016/j.chemosphere.2020.126587.
- [14] Cunha, M.P., Ferraz, R.M., Sancinetti, G.P. & Rodriguez, R.P. 2019. Long-term performance of a UASB reactor treating acid mine drainage: effects of sulfate loading rate, hydraulic retention time, and COD/SO 4^{2} ratio. *Biodegradation*, 30(1):47-58.

https://doi.org/10.1007/s10532-018-9863-8.

- [15] Mooruth, N. 2013. *An investigation towards passive treatment solutions for the oxidation of sulphide and subsequent removal of sulphur from acid mine water.* University of Cape Town. (Thesis-PhD).
- [16] Molwantwa, J.B. & Rose, P.D. 2013. Development of a linear flow channel reactor for sulphur removal in acid mine wastewater treatment operations. *Water Sa*, 39(5):649-654. https://doi.org/10.4314/wsa.v39i5.9.
- [17] Horn, E.J., Oyekola, O.O., Welz, P.J. & van Hille, R.P. 2022. Biological desulfurization of tannery effluent using hybrid linear flow channel reactors.
- [18] Thangiah, A.S. 2019. Spectrophotometric determination of sulphate and nitrate in drinking water at Asia-Pacific International University Campus, Muak Lek, Thailand. *Rasayan Journal of Chemistry*, 12(03):1503-1508. http://dx.doi.org/10.31788/RJC.2019.1235201.
- [19] Tobiason, J.E., Bazilio, A., Goodwill, J., Mai, X. & Nguyen, C. 2016. Manganese removal from drinking water sources. *Current Pollution Reports*, 2:168-177.
- [20] Austigard, Å.D., Svendsen, K. & Heldal, K.K. 2018. Hydrogen sulphide exposure in waste water treatment. *Journal of Occupational Medicine and Toxicology*, 13:1-10.

https://doi.org/10.1186/s12995-018-0191-z.

Author Contributions

Conceptualization, S.T, A.E-E, F.W.; writing—original draft preparation, J.W.; writing—review and initial editing, F.W.; supervision, F.W.; project administration, F.W, R.B.; funding acquisition, F.W. All authors have read and agreed to the published version of the manuscript. 41. Start Conference on Conference on Chemical and Chemical, Biological and Chemical, Biological and Environmental Engineering (CCBEE-24) Nov. 21-22, 2024 Cape Town (CCBEE-24) Nov. 21-22, 2024 Cape Town (South African En