

THE STUDY ON THE EFFECTIVENESS OF ORGANIC MATERIAL IN ACID MINE DRAINAGE TREATMENT

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Graphical abstract



Abstract

The objective of this study is to find suitable weight quantity of organic material and retention time of acid mine drainage (AMD) treatment in column experiment. Hopefully the study will assist the miners to reduce the maintenance and operating cost after the treatment. The study using experimental column was carried out in the laboratory to investigate the effectiveness of organic material in treating acid mine drainage. Four different organic material weights were used; 50 g, 100 g, 200 g and 300 g. Five different retention times for each weights were used; 15 minutes, 30 minutes, 45 minutes, 60 minutes and 75 minutes. Analysis results showed that pH value of water sample had increased between 3.2 and 7.2 after the treatment. The lowest sulphate and sulphur contents after treatment were 967 mg/L at retention time of 75 minutes and 607 mg/L at retention time of 15 minutes respectively. Both experiments used 50 g organic material.

Keywords: Organic material, sulphate, sulphur, acid mine drainage, column experiment

Abstrak

Objektif kajian ini adalah untuk mendapatkan kuantiti berat Bahan organik dan masa penahanan yang sesuai bagi rawatan asid saluran lombong (AMD) dalam eksperimen kolum. Diharap kajian ini dapat membantu pemilik lombong untuk mengurangkan kos penyelenggaraan alat dan operasi lombong selepas rawatan. Kajian ini menggunakan eksperimen kolum yang dijalankan di makmal untuk mengkaji keberkesanan bahan organik dalam rawatan saluran asid lombong. Empat parameter berat bahan organik yang berbeza digunakan; 50 g, 100 g, 200 g dan 300 g. Lima waktu penahanan yang berbeza pada setiap berat berbeza digunakan; 15 minit, 30 minit, 45 minit, 60 minit dan 75 minit. Keputusan analisis menunjukkan bahawa nilai pH telah bertambah selepas rawatan iaitu di antara 3.2 hingga 7.2. Kandungan sulfat dan sulfur yang paling rendah selepas rawatan adalah 967 mg/L pada masa penahanan 75 minit dan 607 mg/L pada masa penahanan 15 minit masing-masing. Kedua eksperimen menggunakan 50 g bahan organik.

Kata kunci: Bahan organik, sulfat, sulfur, saluran asid lombong, eksperimen kolum

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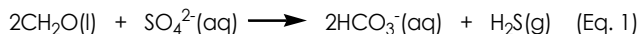
1.0 INTRODUCTION

Organic material is the carbonaceous waste that exists in plant or animal matter originating from domestic or industrial sources [1]. Organic material

can be used to reduce sulphate and heavy metals in acid mine drainage (AMD) for example sheep manure is suitable to be used in sulphate remediation [2]. Sulphate with concentration above 250 mg/L can

cause a bitter or medicinal taste in water and makes the water unpleasant to drink.

In this study organic material was used to treat acid mine drainage because the presence of sulphate reducing bacteria (SRB) in this material. SRB can reduce sulphate and acts as catalyst in the reaction [3, 4]. The reduction of sulphate produces dissolved sulphide and mineralised carbon. Equation 1 shows the reaction.



The use of SRB as biology treatment method has shown successfully developed and practiced at industrial scale in reduce sulphate content in acid mine drainage and industrial water recently [5,6]. The effectiveness of this treatment method depends on the types of organic material chosen to cater carbon source of bacteria [7].

SRB is an anaerobic microorganism that uses sulphate as terminal electron acceptor especially in the decomposition of organic matter, which leads to sulphide release. The bacteria can be easily found in anoxic habitats, which they have important role in sulphur and carbon cycles. SRB can cause negative effect to industries especially in offshore oil industry in which the production of hydrogen sulphide gas can cause corrosion [8]. However, this microorganism can remove sulphate and heavy metals from the waste streams, especially in treatment of acid mine drainage [9]. Previous studies had shown that SRB can be detected at pH as low as 5 [10] and it is sensitive to acidic waters [11, 12].

Acid mine drainage is a global issue and a serious environmental pollution problem in mining activity [13]. Acid mine drainage occurs when sulphide minerals are exposed to water and air [14] with the presence of sulphide oxidising bacteria (SOB) [15, 16]. The sulphide minerals that can cause acid mine drainage are pyrite (FeS_2), arsenopyrite (FeAsS), chalcopyrite (CuFeS_2), chalcocite (Cu_2S), galena (PbS), millerite (NiS), sphalerite (ZnS) and cinnabar (HgS) [17, 18]. AMD can be characterised as polluted water with low pH less than 4, high concentration of iron, sulphate and toxic metals [19, 20].

The objective of this study is to find suitable parameters of organic material in acid mine drainage treatment. The parameters are quantity of organic material and retention time in the experimental column.

2.0 EXPERIMENTAL

2.1 Materials

Goat manure fertiliser was obtained locally and water sample was collected from a tin mine pond tailing in Perak.

2.2 Instrumentations

pH meter (Thermo Scientific Orion Versa Star, Singapore) was used to determine pH value of water sample before and after treatment, ICP-OES (Optima 5300 DV, Perkin Elmer, USA) was used to detect sulphur content, Portable spectrophotometer (DR2800, Hach, USA) was used to detect sulphate content in water samples, Carbon and sulphur analyser (G4 Icarus HF, Bruker, Germany) was used to determine carbon and sulphur content in organic material and Field Electron Scanning Electron Microscope – Energy Dispersive X-Ray (Supra 40VP, Zeiss, Germany) for micrograph and percentage of element content in goat manure fertiliser.

2.3 Column experiment

10 g glass wool was packed into the column. The goat manure with different weights 50 g, 100 g, 200 g and 300 g were packed into the column one at a time. 500 mL water sample was poured into the column. The retention times used for every weight of organic material were 15 minutes, 30 minutes, 45 minutes, 60 minutes and 75 minutes. pH values of water sample before and after treatment were recorded. The experiment was carried out at room temperature. Water sample was analysed before and after treatment to detect sulphate and sulphur. The experimental column is shown in Figure 1.

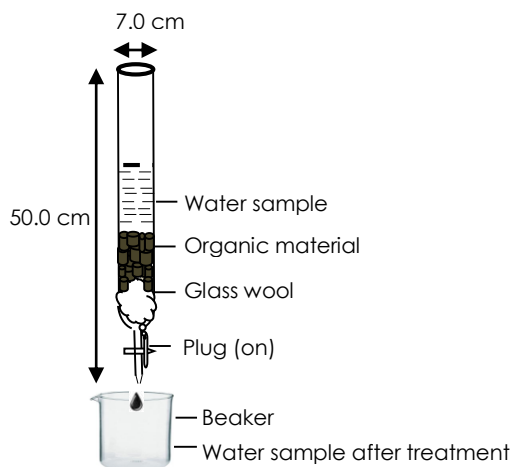


Figure 1 Experimental column

3.0 RESULTS AND DISCUSSION

3.1 Fesem-Edx Result

Organic material was analysed by using Fesem-Edx. Figure 2 shows the micrograph of organic material at 150 times magnification. Table 1 shows the percentage weight of elements in organic material by using Edx result based on micrograph organic material in Figure 2.

The percentage weight of carbon, sulphur and calcium are 57.02%, 0.69% and 1.14% respectively. These three elements are important in reaction between organic material and acid mine drainage.

Table 1 Percentage weight of elements in organic material

Element	Weight (%)
B	14.45
C	57.02
O	19.31
Na	0.20
Mg	0.46
Al	0.98
Si	3.15
P	0.26
S	0.69
K	2.33
Ca	1.14

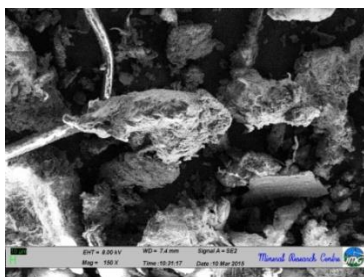


Figure 2 Micrograph of organic material; 150 times magnification

3.2 Carbon and Sulphur Content

Table 2 shows the percentage of carbon and sulphur in organic material that was used in this study. The result indicates that the content of carbon in organic material can be classified as high (32.27%) compared to the content of sulphur (0.68%). The carbon availability is one of the main factors that affects the efficiency of AMD treatment by SRB [7, 21, 22].

Table 2 Percentage of carbon and sulphur in organic material

Carbon (%)	Sulphur (%)
32.27 ± 1.00	0.68 ± 0.04

3.3 Column Experimental Result

Table 3a, 3b, 3c and 3d show the pH values of water sample before and after treatment with 50 g, 100 g, 200 g and 300 g organic material respectively. The result shows the increasing of pH values are affected by weight of organic material used in this experiment. In the experiment that used 50 g and 100 g organic material the retention times are proportional to pH

values. The result shows the reaction between organic material and water sample occurred actively. The result that used 300 g weight of organic material with retention time 60 minutes has the highest pH value, 7.2. The acidic water caused by the presence of hydronium ion, $\text{pH} = -\log_{10}[\text{H}^+]$, show that pH and $[\text{H}^+]$ are proportional to each other. In this experiment bicarbonate ion, HCO_3^- had been produced after organic material reacted to water sample as shown in Equation 1. Bicarbonate can increase pH value of water sample [23]. Equation 2 shows the reaction.

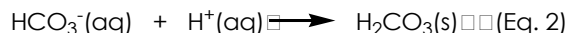


Table 3a Results of pH values before and after treatment with 50 g organic material

Weight of organic material (g)	Retention Time (min)	Before	After
50	15	2.487 ± 0.001	3.167 ± 0.001
	30	2.488 ± 0.001	3.592 ± 0.001
50	45	2.469 ± 0.002	4.392 ± 0.001
	60	2.491 ± 0.002	4.992 ± 0.001
	75	2.501 ± 0.002	5.353 ± 0.001

Table 3b Results of pH values before and after treatment with 100 g organic material

Weight of organic material (g)	Retention Time (min)	Before	After
100	15	2.457 ± 0.001	3.831 ± 0.001
	30	2.449 ± 0.001	4.772 ± 0.000
100	45	2.450 ± 0.002	4.772 ± 0.001
	60	2.497 ± 0.002	5.917 ± 0.001
	75	2.510 ± 0.002	6.260 ± 0.002

Table 3c Results of pH values before and after treatment with 200 g organic material

Weight of organic material (g)	Retention Time (min)	Before	After
200	15	2.464 ± 0.001	4.260 ± 0.002
	30	2.470 ± 0.002	5.801 ± 0.002
200	45	2.468 ± 0.002	6.555 ± 0.001
	60	2.514 ± 0.002	6.238 ± 0.001
	75	2.538 ± 0.001	6.334 ± 0.002

Table 3d Results of pH values before and after treatment with 300 g organic material

Weight of organic material (g)	Retention Time (min)	pH	
		Before	After
300	15	2.463±0.001	5.017±0.001
	30	2.470±0.001	6.503±0.001
	45	2.461±0.001	6.701±0.001
	60	2.465±0.001	7.169±0.002
	75	2.501±0.001	7.012±0.002

3.4 Sulphate Content Before and After Treatment

Table 4 shows the content of sulphate in water sample before and after treatment with retention times 75 minutes. The result shows that the content of sulphate has decreased in water sample after treatment with 50 g and 100 g organic material but the content of sulphate has increased after treatment with 200 g and 300 g organic material. The quantity of organic material at 50 g and 100g are suitable to be used in reducing sulphate content in water sample but the best ratio of quantity of organic material to water sample used in this experiment is 50 g.

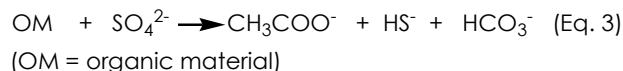
Table 4 Sulphate content in water sample before and after treatment

Weight of organic material (g)	Retention Time (min)	Sulphate concentration (mg/L)	
		Before	After
50	75	1366.7 ± 57.8	966.7±208.2
100	75	1366.7 ± 57.8	1300.0 ± 0.0
200	75	1366.7 ± 57.8	1600.0 ± 0.0
300	75	1366.7 ± 57.8	1866.7 ± 115.5

3.5 Sulphur Content Before and After Treatment

Table 5a, 5b, 5c and 5d show the sulphur content of water sample before and after treatment with 50 g, 100 g, 200 g and 300 g organic material respectively. The result shows that the content of sulphur in water sample has decreased after treatment by using 50 g and 100 g organic material in all retention times. However by using 200 g organic material the content of sulphur has decreased only with retention times up to 30 minutes. After 30 minutes the sulphur content shows an increasing trend. Sulphur content decreased in water sample after treatment because sulphide ion

has reacted with metals to form precipitated sulphide metal that can be easily extracted from the solution [24,25]. Equation 3 and 4 show the reaction.

**Table 5a** Sulphur content in water sample before and after treatment with 50 g organic material

Weight of organic material (g)	Retention Time (min)	Sulphur content (mg/L)	
		Before	After
50	15	871.6 ± 12.5	607.4 ± 1.3
	30	871.6 ± 12.5	635.1 ± 4.8
	45	871.6 ± 12.5	687.2 ± 1.3
	60	871.6 ± 12.5	675.2 ± 11.5
	75	871.6 ± 12.5	664.0 ± 8.1

Table 5b Sulphur content in water sample before and after treatment with 100 g organic material

Weight of organic material (g)	Retention Time (min)	Sulphur content (mg/L)	
		Before	After
100	15	871.6 ± 12.5	651.0 ± 5.4
	30	871.6 ± 12.5	757.8 ± 6.7
	45	871.6 ± 12.5	728.0 ± 4.8
	60	871.6 ± 12.5	775.4 ± 9.3
	75	871.6 ± 12.5	834.2 ± 8.2

Table 5c Sulphur content in water sample before and after treatment with 200 g organic material

Weight of organic material (g)	Retention Time (min)	Sulphur content (mg/L)	
		Before	After
200	15	871.6 ± 12.5	799.6 ± 6.1
	30	871.6 ± 12.5	852.1 ± 14.3
	45	871.6 ± 12.5	886.5 ± 7.6
	60	871.6 ± 12.5	1052.0 ± 14.9
	75	871.6 ± 12.5	998.0 ± 9.8

Table 5d Sulphur content in water sample before and after treatment with 300 g organic material

Weight of organic material (g)	Retention Time (min)	Before	After
300	15	871.6 ± 12.5	890.7 ± 6.4
	30	871.6 ± 12.5	964.1 ± 6.8
	45	871.6 ± 12.5	1114.7 ± 7.8
	60	871.6 ± 12.5	1247.7 ± 17.8
	75	871.6 ± 12.5	1211.7 ± 5.7

4.0 CONCLUSION

Organic material can increase pH value of water sample from 2.4 to 7.2. The analysis shows that organic material with 50 g and 100 g weights can reduce sulphate content in water sample but the concentration value exceeds the international standard (WHO standard 500 mg/L ; Europe standard 250 mg/L) [26, 27]. Organic material with 50 g and 100 g weights can also reduce sulphur content in water sample. Similarly 200 g of organic material with retention times 15 and 30 minutes also can reduce sulphur content in water sample. However, retention time more than 30 minutes would increase the sulphur content after treatment. Based on all the results, the best parameter is 100 g organic material with retention time 75 minutes. The parameter has pH value 6.3 that comply with Environmental Quality Act 1974 including for effluent industry and effluent domestic [28]. Sulphate and sulphur contents of this parameter were 1300 mg/L and 834 mg/L respectively. The reducing of these two anions shows that the reaction has occurred between organic material and water sample.

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References

- [1] Anon (2003). Glossary of Environment and Waste Management Terms. 2003. *Handbook of Solid Waste Management and Waste Minimization Technologies*. 337-465.
- [2] Gibert, O., de Pablo, J., Cortina, J.L. and Ayora, C. 2004. Chemical Characterisation of Natural Organic Substrates for Biological Mitigation of Acid Mine Drainage. *Water Research*. 38: 4186–4196.
- [3] Jorgensen, B.B. 1982. Ecology of the Bacteria of the Sulphur Cycle with Special Reference to Anoxic-Oxic Interface Environments. *Philosophical Transaction of the Royal Society of London. Series B, Biological Sciences*. B 298: 543–561.
- [4] Masmann, G., Tichomirowa, M., Merzc, C. and Pekdeger, A. 2003. Sulfide Oxidation and Sulfate Reduction in a Shallow Groundwater System (Oderbruch Aquifer, Germany). *Journal of Hydrology*. 278: 231-243.
- [5] Mokone, T.P., van Hille, R.P. and Lewis, A.E. 2012. Metal Sulphides from Wastewater: Assessing the Impact of Supersaturation Control Strategies. *Water Research*. 46: 2088-2100.
- [6] Huismann, J.L., Schouten, G. and Schultz, C. 2006. Biologically Produced Sulphide for Purification of Process Streams, Effluent Treatment and Recovery of Metals in the Metal and Mining. *Hydrometallurgy*. 83: 106-113.
- [7] Zagury, G.J., Kulnieks, V.I. and G. and Neculita, C. M. 2006. Characterization and Reactivity Assessment of Organic Substrates for Sulphate-Reducing Bacteria in Acid Mine Drainage Treatment. *Chemosphere*. 64: 944–954.
- [8] Kakooei, S., Che Ismail, M. and Ariwahjoedi, B. 2012. Mechanisms of Microbiologically Influenced Corrosion: A Review. *World Applied Sciences Journal*. 17(4): 524-531.
- [9] Muyzer, G. and Stams, A.J.M. 2008. The Ecology and Biotechnology of Sulphate-Reducing Bacteria. *Nature Review Microbiology*. 6: 441-454.
- [10] Yuzwa, G.F. 1991. Corrosion by Sulphate Reducing Bacteria. *Alberta Public Work, Supply & Services Property Management Operations Division water Treatment Co-ordinators' Meeting No 14*. 16 October. Calgary, Alberta.
- [11] Sheoran, A. S., Sheoran, V. and Choudhary, R. P. 2010. Bioremediation of Acid-Rock Drainage by Sulphate-Reducing Prokaryotes: A Review. *Minerals Engineering*. 23: 1073–1100.
- [12] Hard, B., Friedrich, S. and Babel, W. 1997. Bioremediation of Acid Mine Water Using Facultative Methylophilic Metal-Tolerant Sulphate Reducing Bacteria. *Microbiology Research*. 152: 65–73.
- [13] Herrera, S.P., Uchiyama, H., Igarashi, T., Asakura, K., Ochi, Y., Ishizuka, F. and Kawada, S. 2007. Acid mine drainage treatment through a two-step neutralization ferrite-formation process in northern Japan: Physical and chemical characterization of the sludge. *Minerals Engineering*. 20:1309–1314.
- [14] Johnson, D.B. and Hallberg, K.B. 2005. Acid Mine Drainage Remediation Options: A Review. *Science of the Total Environment*. 338: 3-14.
- [15] Chun-bo, H., Hong-xun, Z., Zhi-hui, B., Qing, H. and Bao-guo, Z. 2007. Novel Acidophile Community Populating Waste Ore Deposits at an Acid Mine Drainage Site. *Journal of Environmental Sciences*. 19: 444-450.
- [16] Johnson, D.B. 1998. Biodiversity and Ecology of Acidophilic Microorganisms. *FEMS Microbiology Ecology*, 27: 307–317.
- [17] Ferguson, K.D. and Erickson, P.M. 1998. Pre-Mine Prediction of Acid Mine Drainage. In: Salamons, W. and Fortsner, U. ed. *Dredged Material and Mine Tailings*. Berlin: Springer-Verlag Berlin Heidelberg.
- [18] U.S. Environmental Protection Agency. 2004. Technical Document: Acid Mine Drainage Prediction. pp 1-48.
- [19] Pagnanelli, F., Luigi, M., Mainelli, S. and Toro, L. 2007. Use of Natural Materials for the Inhibition of Iron Oxidizing Bacteria Involved in the Generation of Acid Mine Drainage. *Hydrometallurgy*. 87: 27–35.
- [20] Doye, I. and Duchesne, J. 2003. Neutralisation of Acid Mine Drainage with Alkaline Industrial Residues: Laboratory Investigation Using Batch-Leaching Tests. *Applied Geochem*. 18:1197-1213.
- [21] Waybrant, K.R., Blowes, D.W. and Ptacek, C.J. 1998. Selection of Reactive Mixtures for Use in Permeable Reactive Walls for Treatment of Mine Drainage. *Environmental Science & Technology*. 32:1972–1979.

- [22] Cocos, I.A., Zagury, G.J., Clement, B. and Samson, R. 2002. Multiple Factor Design for Reactive Mixture Selection for Use in Reactive Walls in Acid Mine Drainage Treatment. *Water Research*. 36:167–177.
- [23] Sahinkaya, E. 2009. Microbial Sulfate Reduction at Low (8 °C) Temperature Using Waste Sludge as a Carbon and Seed Source. *International Biodeterioration & Biodegradation*. 63: 245–251.
- [24] Kikot, P., Viera, M., Mignone, C. and Donati, E. 2010. Study of the Effect of pH and Dissolved Heavy Metals on the Growth of Sulfate Reducing Bacteria by a Fractional Factorial Design. *Hydrometal*. 104:494–500.
- [25] Radhika, V., Subramanian, S. and Natarajan, K.A. 2006. Bioremediation of Zinc Using *Desulfotomaculum Nigrificans*: Bioprecipitation and Characterization Studies. *Water Research*. 40:3628–3636.
- [26] Al-Zuhair, S., H El-Naas, M. and Al-Hassani, H. 2008. Sulfate Inhibition Effect on Sulfate Reducing Bacteria. *Journal of Biochemistry Technology*. 1(2):39-44.
- [27] Visser, T. J. K., Modise, S. J., Krieg, H. M. and Keizer, K. 2001. The Removal of Acid Sulfate Pollution by Nanofiltration. *Desalination*. 140: 79-86.
- [28] Malaysia. 2012. *Akta Kualiti Alam Sekeliling 1974 (Akta 127), Peraturan-Peraturan & Perintah-Perintah*. P.U.(A) 271/10.