



UNIVERSITI PUTRA MALAYSIA

***PASSIVE REMEDIATION OF METAL AND SULFATE-RICH ACID MINE
DRAINAGE USING A SULFATE REDUCING BIOREACTOR***

SITI NURJALIAH BINTI MUHAMMAD

FPAS 2016 12



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By

SITI NURJALIAH BINTI MUHAMMAD

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in
Fulfilment of the Requirements for the Degree of Master of Science**

December 2016

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

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December 2016

Chairperson: Faradiella Mohd Kusin, PhD
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Acid mine drainage (AMD) is an environmental pollution that needs to be treated for sustainable environment in the future. Sulfate reducing bioreactor is one of the promising AMD treatments which can improve the health and conditions of mine water in an economical and sustainable way. The characterization of the treatment media used for AMD remediation was done for spent mushroom compost (SMC), limestone, and activated sludge. The SMC greatly assisted the removals of sulfate and metals and also acted as an essential carbon source for bacterial sulfate reduction (BSR). A column experiment was conducted to evaluate the performance of sulfate-reducing bioreactor in a continuous flow system in anoxic condition. The treatment media that composed of 40% crushed limestone, 30% SMC, 20% activated sludge and 10% woodchips were used in the column experiment. Generally, Fe, Pb, Cu, Zn, and Al were effectively removed in the treatment with 87 to 100% removals. However, Mn was not successfully removed from the treatment at the end of experiment despite initial Mn reduction during the early phase of the experiment. It was found from the column experiment that the first 15 days of treatment was an essential phase for the removal of most metals where contaminants were primarily removed by the BSR in reducing condition, in addition to calcite dissolution function. The treatment condition was favored by the availability of sufficient carbon source from the organic materials to enable bacterial sulfate reduction to occur effectively. The importance of bacterial sulfate reduction mechanism in the presence of organic materials was also supported by the metal accumulation analysis in the treatment substrates that primary metal accumulation occurs mainly through metal adsorption onto the organic matter and Fe/Mn oxides fractions.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Sarjana Sains

**PEMULIHAN PASIF BAGI SALIRAN LOMBONG BERASID YANG KAYA
DENGAN LOGAM DAN SULFAT MENGGUNAKAN BIOREAKTOR
PENGURANGAN SULFAT**

Oleh

SITI NURJALIAH MUHAMMAD

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Fakulti: Pengajian Alam Sekitar

Saliran lombong berasid (AMD) adalah pencemaran alam sekitar yang perlu dirawat untuk alam sekitar yang mampan pada masa hadapan. Bioreaktor pengurangan sulfat adalah salah satu rawatan AMD menjanjikan yang boleh meningkatkan kesihatan dan keadaan air lombong dengan cara yang menjimatkan dan mampan. Pencirian media rawatan yang digunakan untuk pemulihan AMD telah dilakukan untuk kompos sisa cendawan (SMC), batu kapur, dan enapcemar diaktifkan. SMC banyak membantu penyingkiran sulfat dan logam dan juga bertindak sebagai sumber karbon penting untuk bakteria pengurangan sulfat (BSR). Eksperimen kolum telah dijalankan untuk menilai prestasi bioreaktor pengurangan sulfat dalam sistem aliran berterusan berkeadaan anoksik. Media rawatan yang terdiri daripada 40% batu kapur yang dipecah, 30% SMC, 20% enapcemar diaktifkan dan 10% sisa kayu telah digunakan dalam eksperimen kolum. Secara umumnya, Fe, Pb, Cu, Zn, dan Al telah berkesan disingkirkan dalam rawatan dengan 87 ke 100% penyingkiran. Walau bagaimanapun, Mn tidak berjaya disingkirkan dari rawatan pada akhir eksperimen di sebalik penurunan Mn awal semasa fasa awal eksperimen. Ia didapati daripada eksperimen kolum bahawa 15 hari pertama rawatan adalah tahap yang penting untuk penyingkiran bagi kebanyakan logam di mana terutamanya bahan cemar telah disingkirkan oleh BSR dalam keadaan pengurangan, di samping fungsi pembubaran calcite. Keadaan rawatan telah menjadi pilihan oleh adanya sumber karbon yang mencukupi dari bahan-bahan organik untuk membolehkan pengurangan sulfat bakteria berlaku dengan berkesan. Kepentingan mekanisme pengurangan sulfat bakteria dalam kehadiran bahan organik juga disokong oleh analisis pengumpulan logam dalam substrat rawatan yang pengumpulan logam utama berlaku terutamanya melalui penjerapan logam ke bahan organik dan pecahan Fe/Mn oksida.

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I certify that a Thesis Examination Committee has met on 20th December 2016 to conduct the final examination of Siti Nurjaliah Muhammad on her thesis entitled “Passive Remediation of Metal and Sulfate-Rich Acid Mine Drainage Using A Sulfate Reducing Bioreactor” in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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LIST OF ABBREVIATIONS

ALD	Anoxic Limestone Drainage
AMD	Acid mine drainage
ARD	Acid Rock Drainage
AS	Activated Sludge
BET	Brenauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
BSR	Bacterial Sulfate Reduction
CEC	Cation Exchange Capacity
CLS	Crushed Limestone
EDX	Energy Dispersive X-ray
FeS ₂	Iron sulfide
HRT	Hydraulic Retention Time
LOI	Loss-On-Ignition
RAPS	Reducing and Alkalinity Producing System
SAPS	Successive Alkalinity Producing System
SEM	Scanning Electron Microscopy
SET	Sequential Extraction Technique
SIM	Sulfate, Indole, Motility
SMC	Spent Mushroom Compost
SRB	Sulfate-reducing bacteria
USEPA	United States Environmental and Protection Agency
WC	Woodchips



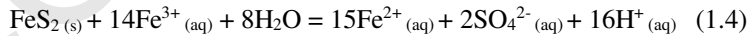
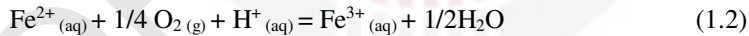
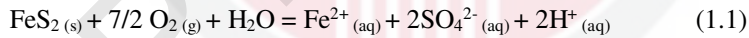
CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Acid mine drainage (AMD) is typically known as a serious environmental problem resulting from active and abandoned mining activities, causing undesirable impacts on the environment such as on the aquatic life, groundwater, streams, and humans (Akcil and Koldas, 2006; Diz *et al.*, 2006; Lottermoser, 2007; Kruse *et al.*, 2012). High acidity and concentrations of heavy metals and sulfate are often observed in most AMDs. The toxic metals that received most attention in AMD include As, Ag, Cd, Cr, Cu, Fe, Hg, Mn, Pb, and Zn. AMD may cause severe impacts on biological systems and the problem may persist in the environment for many decades to thousands of years (Luptakova and Macingova, 2012). Acid generation and metals dissolution in coal or non-coal mining are resulted when pyrite (FeS_2) is oxidized and exposed to oxygen and water. This results in the release of hydrogen ion that increases acidity, sulfate ions, and soluble metal cations (Costello, 2003).

Specifically, AMD is formed by the weathering of minerals i.e. iron sulfide (FeS_2), often known as pyrite. The production of acidic water is due to oxidation of pyrite in the presence of water and oxygen, in which pyrite can dissolve heavy metals to be transported into the streams and oceans (Motsi, 2010). The processes of pyrite oxidation are explained in these following equations:



As in the equation 1.1, FeS_2 is oxidized, thereby releasing ferrous iron which is the reduced form of iron, sulfate, and acid. Ferrous iron can be oxidized to form ferric iron in the equation 1.2. Equation 1.3 shows that ferric iron can then be hydrolyzed and form ferrous hydroxide and acidity H^+ or it can act as a catalyst in generating much greater amounts of ferrous iron, sulfate, and acidity shown in equation 1.4.

AMD has been encountered around the world such as in South Africa (Vadapalli *et al.*, 2012), Ontario, Canada (Kwong *et al.*, 2007), Utah, USA (Mayo *et al.*, 2000), Makum

Coalfiled, India (Equeenuddin *et al.*, 2010) and many more. The examples of former mining areas in Malaysia include former tin mining sites in Bestari Jaya, Selangor (Ashraf *et al.*, 2012), iron ore mines in Sungai Lembing, Pahang (Alshaebi *et al.*, 2009; Yaacob *et al.*, 2009), tin mining district in Kinta Valley, Perak (Ahmad and Jones, 2013), and copper mining area in Mamut, Sabah (Jopony and Tongkul, 2009). In terms of environmental degradation, the Mamut former mining area has been reported to cause severe water pollution in nearby water bodies. The site was known to have contaminated a river several kilometers away from the source. The mining area was known as the only copper mine located in Sabah. The mining activities started in 1975 and came to an end after 24 years of mining operation. It was known as an abandoned toxic legacy of residual pollution in the nearby waterways and was the worst AMD scenario that had given catastrophic impact to the environment (Choe, 2014). The mining area had suffered severe environmental degradation with AMD known as notable pollution for the post-mining stage (Daily Express, 2014). Nevertheless, this environmental issue of AMD is uncommon in Malaysia.

There are various methods that can be applied in treating AMD including active and passive treatment technologies. Active biotic treatment is the improvement of water quality that requires continuous inputs of artificial energy and/or biochemical reagents while passive biotic treatment is more cost effective and the system is low in maintenance such that it does not need any chemicals addition. The common examples of passive remediation for AMD include aerobic wetlands, compost bioreactors or wetlands, permeable reactive barriers, and packed bed iron-oxidation bioreactors (Younger *et al.*, 2002; Johnson and Hallberg, 2005).

In this study, the treatment concept using a compost-based bioreactor was applied; utilizing organic materials and limestone as treatment substrates. It is a sulfate-reducing bioreactor with the concept that resembles those of the reducing- and alkalinity-producing system (RAPS) or successive alkalinity producing system (SAPS) commonly used for acidic and sulfate-rich mine water (Younger *et al.*, 2002; PIRAMID, 2003). It is a long-term AMD treatment, which offers economical and low maintenance alternatives (Burns *et al.*, 2012), although treatment longevity issue of compost wetlands e.g. replenishment of carbon sources in such reactor has been reported (Kleinmann, 1990; Kim *et al.*, 2014). Nonetheless, RAPS or SAPS has been successfully used for the treatment of acidic and sulfate-containing mine water in many applications in the UK, US and Europe (Younger *et al.*, 2002; PIRAMID, 2003). However, none of the applications has been developed in Malaysia when given similar nature of contaminated mine water.

1.2 Overview of Passive Treatment of AMD using Sulfate-Reducing Bioreactor

Passive bioremediation of AMD incorporating sulfate-reducing bacteria (SRB) is the key treatment mechanism applied in this study. Sulfate-reducing bioreactors have been used for the treatment of mine drainages where heavy metals and sulfates are the primary contaminants of concern (e.g. Mayes *et al.*, 2011; Das *et al.*, 2012). SRB utilizes low-carbon number compounds, most commonly acetate, which is in turn produced by the

hydrolysis of lignocellulosic materials (Younger *et al.*, 2002). Incorporating SRB for passive AMD remediation requires certain pH range and sufficient source of carbon and nutrient and a solid matrix on which the SRB can sustain their growth (Cheong *et al.*, 2010; Mayes *et al.*, 2011). It has been reported that sulfate reduction in systems receiving acidic water will vigorously occur as long as calcite dissolution can maintain high pH for the neutrophile SRB to thrive (Younger *et al.*, 2002).

Simple organic carbon sources such as ethanol and lactate have been successfully used in laboratory-scale bioreactors although the materials are very expensive for full-scale deployment (Neculita and Zagury, 2008; Cheong *et al.*, 2010). However, higher sulfate reduction can be achieved in mixture of easily biodegradable organic carbon sources (Neculita and Zagury, 2008). The carbon source can be obtained from the usage of carbonaceous material, e.g. spent mushroom compost (SMC) which can minimize the plugging of bioreactor due to its large pore spaces, low surface area and small void volume (Cheong *et al.*, 2010). SMC has shown good performance as an electron donor for SRB and contains various organic matters including lignin, cellulose and hemicelluloses (Jordan *et al.*, 2008). In fact, the carbon source for SRB remediation in many bioreactors is present as labile cellulose-rich materials for later breakdown to sustain the bacterial activity. The SMC is also easily obtainable and is typically regarded as a waste material. Additionally, limestone has also been used as a substrate in sulfate-reducing bioreactor as an alkalinity generator to increase the acidic pH of water, which in turn facilitates the conditions for metal removal (Genty *et al.*, 2011; Kusin *et al.*, 2014).

1.3 Problem Statement

Acid mine drainage (AMD) persists as a toxic repercussion of overabundant contaminants to accessible waterways affecting the quality of water environment. Pollution generated from AMD that contains high concentration of heavy metals and sulfates with extremely low pH will cause serious threat to environment and aquatic organisms. In Malaysia, the occurrence of AMD has been reported as an aftermath of copper contamination at Mamut Copper Mine in Sabah. The copper mines in this country began to churn out in 1975 until its cessation in 1999 and had been known to have left behind a toxic legacy of residual pollution to nearby waterways. Human exposure to toxic heavy metal can be through ingestion, inhalation and dermal contact. The ingestion effect of heavy metals over a long run is carcinogenic and can increase the rate of mortality due to many chronic diseases related to heavy metal exposure, such as arsenic, chromium, copper and lead (Choe, 2014).

It has been reported that some huge area of wasteland where the copper mine was in operation had been deteriorated and become a serious environmental degradation where AMD emerges as the most impactful pollution in the phase of post-mining. Continuous monitoring by the Department of Environment (DOE) and Mineral and Geoscience Department (JMG) revealed that the water in the mine pit has a constantly high acidity of between pH 2 and 3 (Daily Express, 2014). The abandoned copper mine was also

associated with potential impact of mining overflow such as in the case of flooding or earthquake that can bring catastrophic effect to people living surrounding the area.

Even though AMD has been known as a significant environmental issue, the cost for rehabilitating the mine-impacted area has become an impediment to develop an appropriate remediation technology. Therefore, instead of using active AMD treatment that is usually expensive and high in maintenance, it has been suggested that passive treatment is used, which is more economical, uses naturally available materials, and requires low system maintenance. In this study, sulfate-reducing bioreactor is used as to study the performance of passive treatment for AMD that is high in concentrations of heavy metals and sulfates with extremely low pH resembling the Mamut AMD water.

1.4 Scope of Work

This study focuses on the development of laboratory-scale sulfate-reducing bioreactor for passive treatment of metal- and sulfate-rich AMD. A series of experimental column study was conducted to evaluate treatment performance of the continuous flow bioreactor system. The treatment media used (i.e. limestone, spent mushroom compost, and activated sludge) were characterized for their physico-chemical characteristics, surface morphological structure, elemental components and bacterial composition. Performance of the bioreactor system was evaluated according to treatment efficiency using synthetic AMD prepared similar to the range of the concentrations of heavy metals and sulfates of Mamut former mining pond and with some modifications on the concentrations. This is because it is not possible to obtain the actual mine water from the Mamut mining site, and the difficulty in making the concentrations to be exactly similar with the original concentration.

1.5 Significance of the Study

Acid mine drainage needs to be appropriately treated before being released into the environment as to avoid the contamination due to heavy metals into the surface and groundwater. The concept of passive AMD treatment was used in this study because the treatment is relatively low in cost, the materials are easily available and it does not require frequent maintenance. A sulfate-reducing bioreactor has the potential of removing metals and sulfates as well as neutralizing acidic water, which is essential for the remediation of AMD. This study provides detailed information on the treatment performance and the characteristics of each substrate used for the removal of heavy metals such as Mn, Fe, Cu, Pb, Zn, and Al as well as sulfate removal mechanisms from the AMD. The experimental findings would be useful for the design of potential on-site treatment application for such AMD cases. Therefore, performance of the sulfate-reducing bioreactor will be sufficiently evaluated as to reflect the treatment concept using a Reducing and Alkalinity Producing System. This passive treatment technique can also be regarded as a green technology for securing environmental sustainability in terms of the protection of our water environments.

1.6 Research Objectives

The main objective of this study is to evaluate the performance of a passive remediation for acid mine drainage (AMD) using a sulfate-reducing bioreactor for reduction of acidity and concentrations of heavy metals and sulfates. The specific aims of this study are:

1. To characterize the treatment media (i.e. limestone, spent mushroom compost and activated sludge) used for the treatment of metal- and sulfate-rich AMD
2. To assess treatment performance in a continuous flow sulfate-reducing bioreactor for alkalinity generation and removal of sulfate and heavy metals (column study)

1.7 Thesis Organization

Following this chapter, the remaining chapters of the thesis are outlined below:

Chapter 2 details on the topics covered throughout the study which consists the overview of the development of mining activities in Malaysia, the fundamentals and occurrence of acid mine drainage (AMD) and related processes, treatment options for AMD, mechanisms of metal removal in AMD treatment and potential substrates for AMD remediation.

Chapter 3 presents the research design for this study. This includes the characterization of treatment media used in the treatment of AMD, experimental design and methods, measurement technique of the analyzed experimental parameters/variables, and data analysis.

Chapter 4 discusses the results of the laboratory batch test and column experiments of the AMD treatment. The findings presented are the comparison between different substrates and mode of treatment for remediating AMD in terms of physico-chemical parameter improvement and removal efficiency of heavy metal and sulfate in mine water and their accumulation in the substrates. Bacterial identification in the treatment media used is also presented.

Chapter 5 summarizes the major findings of the study in the fulfillment of the research objectives. Recommendations for future studies in this field are also included.

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