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Passive Treatment of Metal and Sulphate-Rich Acid Mine Drainage (AMD) Using Mixed Limestone, Spent Mushroom Compost and Activated Sludge

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ABSTRACT

Acid mine drainage (AMD) is a major environmental problem as it involves the release of acidic, sulphate- and metal-containing water into the environment. It usually has low pH which is acidic and contains toxic and non-biodegradable pollutants such as heavy metals, e.g. lead (Pb), aluminium (Al), copper (Cu), iron (Fe) and zinc (Zn). Passive treatment has been regarded as a reliable means for treating AMD and was assessed in this study using multiple substrates. This study aims to provide an evaluation of passive treatment of metal- and sulphate-rich AMD incorporating limestone, spent mushroom compost and activated sludge (mixed substrates). Batch experiment was conducted using different mixture of treatment media over 120 hours. Synthetic mine water was used in the batch experiment. Samples were analysed for pH and alkalinity increase, sulphate reduction and heavy metal removals. Spent mushroom compost was found to be effective in producing the highest increase in pH and alkalinity as well as the greatest sulphate removal among other single media. The mixed substrates (40% limestone, 30% spent mushroom compost, 20% activated sludge, and 10% woodchips) were effective for the removal of most heavy metals studied.

Keywords: Acid Mine Drainage, Passive Treatment, Limestone, Spent Mushroom Compost, Activated Sludge

I. INTRODUCTION

Acid mine drainage (AMD) is generated through a combination of chemical and biological processes by which metal sulphides (e.g. pyrite) are converted to sulphates and metal hydroxides when exposed to fresh water and oxygen [1, 2, 3]. Moreover, acid mine drainage formation is further amplified when the reactions are catalyzed by aerobic bacteria such as *Acidithiobacillus ferrooxidan* [4].

Acid mine drainage can be a major environmental problem as it involves the release of acidic, sulphate- and metal-containing water into the environment, particularly into watercourses. It usually has low pH which is acidic and contains toxic and non-biodegradable pollutants, i.e. heavy metals such as lead (Pb), aluminium (Al), copper (Cu), iron (Fe) and zinc (Zn). The impacts of acid mine drainage pollution on biological systems are mostly severe and the problem may persist from many decades to thousands of years and pollute many water resources [5, 6, 7]. Most streams that have been affected or polluted may have pH as low as 2 which are definitely undesirable to a healthy stream environment.

There are several technologies that can be used to treat heavy metals in water through various treatment mechanisms such as adsorption, precipitation, ion exchange, cementation, coagulation-flocculation or membrane separation [8, 9, 10, 11]. However, these technologies are usually energy and cost-intensive [12, 13]. There have been many researches on the identification of low cost and low maintenance treatment systems to treat acid mine drainage. Most of the compliant restoration action plans develop acidity neutralization and metal removal in chemical reactors by the use of limestone as alkaline reagent, which enhances precipitation of hydroxides of metals such as iron (Fe) and aluminium (Al) [14].

The development of bioreactors which mobilize bacterially arbitrated sulphate reduction have been greatly assessed, and has been recently seen and expanding as an attractive solution to treat acid mine drainage [15, 16]. Sulphate reducing bacteria are a category of anaerobic bacteria, proficient of reducing sulphate and oxidizing organic substrates concurrently. It commonly enrols a mixture of alkaline material, usually limestone or other carbonates to increase and maintain neutral water (pH) and an organic substrate which acts as carbon initiator for the bacterial metabolism to rectify acid mine drainage. Sulphate is then microbially reduced to hydrogen sulphide which precipitated with heavy metals [17].

This study proposes a passive treatment of AMD to remove sulphate and heavy metals in mine water as well as to observe the conditions under which pH is increased and metals are removed in the water. In this study, we adopt the concept of a sulphate reducing bioreactor to treat the mine water containing high concentration of heavy metals and sulphate. Mixed substrates were used, i.e., incorporating limestone (alkalinity-producing agent), spent mushroom compost (carbon source), activated sludge (source of microbes) and woodchips (porous media) [18]. Treatment efficiency was evaluated through batch experiments using synthetic AMD treated by single and mixed substrates.

II. MATERIALS AND METHODS

A. Preparation of limestone, activated sludge (AS) and spent mushroom compost (SMC)

Limestone was obtained from a quary, Imerys Mineral Sdn. Bhd at Simpang Pulai, Perak Darul Ridzuan, of 1 cm and 2 cm in size. Then, the limestone was soaked in acidic water for 24 hours (70% concentrated nitric acid). Activated sludge was obtained from Indah Water Konsortium (IWK) treatment plant, Bangi and spent mushroom compost was taken from Kapar, Selangor.

B. Preparation of Synthetic Acid Mine Drainage

Synthetic acid mine drainage was prepared based on the actual data of Mamut former mining area, taking into consideration the worst case scenario (Table I). Each salt was weighed and mixed homogenously with the distilled water. 37% concentrated hydrochloric acid was added drop by drop to obtain the initial pH of 3.1.

TABLE I

CHARACTERISTICS OF SYNTHETIC ACID MINE DRAINAGE

Parameters		Conc.(mg/L)	Salt	Mass(mg)of salt for 17L	Mass
pH		3.1	HCl/NaOH(1N)		
Temperature(°C)					
Conductivity(µs)		2300			
TDS(mg/L)		1190			
Eh/ORP(mV)		1.95			
Alkalinity(mg/L)					
DOC(mg/L)					
Heavy Metals(mg/L)	Al	25.7	Al2(SO4)3.18H2O	436.9	0.4369
	Mn	20.7	MnSO4.H2O	351.9	0.3519
	Fe	7	FeSO4.7H2O	119	0.119
	Cu	5.7	CuSO4.5H2O	96.9	0.0969
	Pb	0.8	Pb(NO3)2	13.6	0.0136
	Zn	1.4	ZnSO4.7H2O	23.8	0.0238
Cations(mg/L)	Mg	42	MgSO4.7H20	714	0.714
	Ca	29	Ca(CH3OO)2.H2O	493	0.493
	Na	0.1		1.7	0.0017
	K	3.5	K2HPO4	59.5	0.0595
Anions(mg/L)	SO4	1466.7(1500)	Na2SO4.10H20	24933.9	24.9339
	Cl-	18.3	NaCl	311.1	0.3111

C. Batch Test

TABLE II

SUBSTRATE MIX IN BATCH EXPERIMENT

Beaker	Description
1 (control)	1500mL acid mine drainage and 450.0g spent mushroom compost
2 (control)	1500mL acid mine drainage and 450.0g activated sludge
3 (control)	1500mL acid mine drainage and 450.0g crushed limestone
4 (Ratio 1)	1500mL acid mine drainage, 225.07g crushed limestone, 90.0g spent mushroom compost, 90.0g activated sludge, and 45.0g woodchips

5 (Ratio 2)	1500mL acid mine drainage, 180.6g crushed limestone, 135.0g spent mushroom compost, 90.0g activated sludge, and 45.0g woodchips

Batch test was conducted to identify the suitable media for bioreactor treatment. The condition was anoxic which required the presence of very limited oxygen [19]. 5 beakers of 2000 mL were used. Each beaker was filled with different materials and ratios (Table II).

D. Measured Parameters

Physico-chemical parameters were measured in-situ in the lab. Ultrameter II 6P was used to measure pH, conductivity, total dissolved solids (TDS) and Eh (redox potential). Alkalinity was determined using HACH Alkalinity Test Kit with Phenolphthalein and Bromocresol Green-Methyl Red Indicator powder pillow added, titrated with sulphuric acid until the sample colour changed.

Cations (Ca, Mg, Na, K) and heavy metal contents (Al, Mn, fe, Cu, Pb, Zn) were analysed using ICP-OES. Anion (Cl) was analysed using titration method and SO_4 was determined using turbidimetric method by HACH meter using SulfaVer 4 Sulphate Reagent Powder Pillow. Dissolved organic carbon (DOC) was analysed using Shimadzu 5000 Total Organic Carbon (TOC) Analyzer.

III. RESULTS AND DISCUSSION

A. pH and Alkalinity Increase

From Figure 1, it can be seen that all treatment media and both mixture ratios show an increase in pH. The pH was increased from initially 3.1 to circum-neutral range (6.5-7.5).

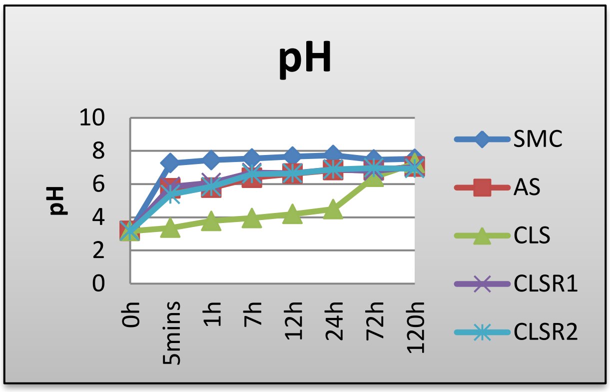

Figure 1: pH Increase

The results agree with the findings from [20]. Rapid pH increase was seen during the first 5 minutes of reaction, whereby the spent mushroom compost indicated the highest pH rise to > 7. The crushed limestone showed the slowest pH rise but still reached pH > 7 at the end of experiment. Both the mixed substrates showed gradual increase in pH and reached pH > 7 after 24 hours.

As seen in Figure 2, all treatment media and both mixture ratios show an increase in alkalinity, which corresponds to the pH increase indicating the neutralisation of the acid mine drainage [21]. As for pH increase, the mushroom compost indicated a rapid alkalinity increase up to 800 mg/L as $CaCO_3$. Slowest alkalinity was produced by the crushed limestone compared to other media. Comparing the mixed substrates, ratio 2 gave a higher alkalinity increase towards the end of experiment (alkalinity ~ 500 mg/L as $CaCO_3$).

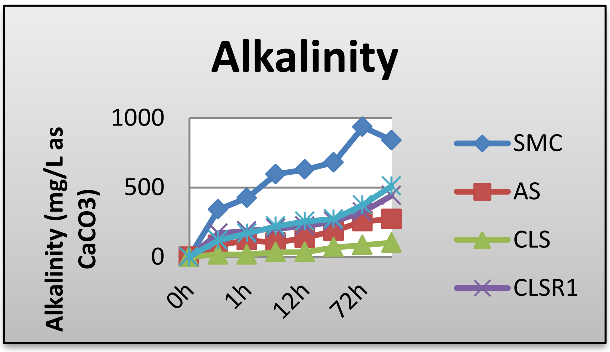

Figure 2: Alkalinity Increase

B. Sulphate Reduction

Sulphate is the main element to be removed in this study. The sulphide produced in the first step is oxidised to elemental sulphur. The concentration reading shown by all treatment media and both mixtures are mostly fluctuated (Figure 3).

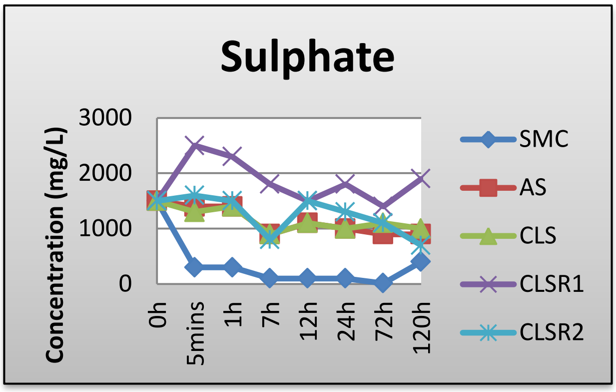

Figure 3: Sulphate Reduction

Spent mushroom compost seems to be the most effective media compared to others as the pattern does not fluctuate much, and the fact that the sulphate concentration was reduced greatly. Mixed substrates (ratio 2) showed decreasing concentration of sulphate towards the end of experiment despite fluctuating results over the duration. Overall sulphate was removed up to73%. Sulphate removal efficiency using some of the media was also found in [22, 23].

C. Heavy Metal Removal

From Figure 4, it can be seen that at the early observations (below 7 hours), the manganese concentration shows fluctuating trends. It is believed that manganese is one of the toughest elements to be removed from mine water, and the presence of other metals may also influence its removal. In some instances, to effectively remove manganese from mine water, Fe concentration must be < 2 mg/L. The most effective media is spent mushroom compost (97 % removal) compared to other media as it showed steady decrease in manganese over the experiment. Despite initial fluctuating concentration, manganese was removed in both mixed substrates.

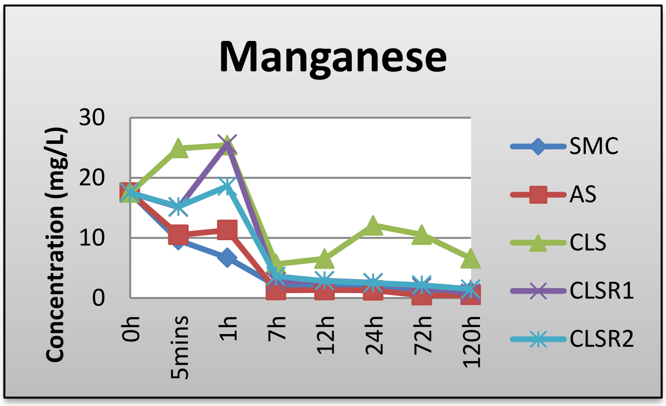

Figure 4: Manganese Removal

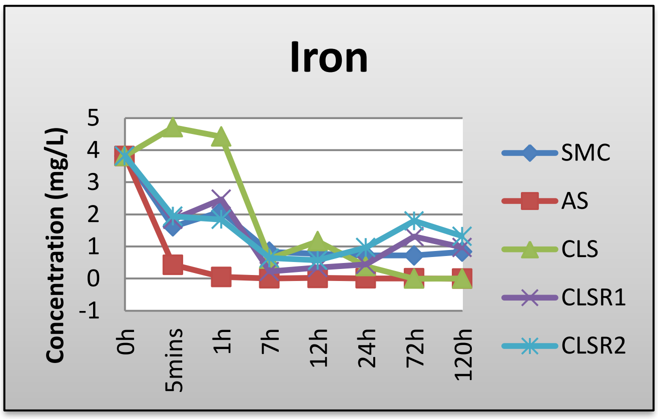

Figure 5: Iron Removal

The readings of iron concentration given by all treatment media and both ratio mix are also unstable (Figure 5). It is understood that removal of iron can be difficult in the presence of manganese, as iron removal requires two ingredients also needed for manganese removal which are hydroxide and oxygen. Iron were removed between 65 – 99 %.

The concentration of copper decreases rapidly at the early observations of the experiment (Figure 6). All treatment media show their effectiveness in removing copper. Below 1 hour, most treatment media showed a little fluctuation in copper concentration. Activated sludge indicated a rapid decrease in copper at 5 minutes and steadily reduced to a lower concentration. Comparing the two mixed ratios, ratio 2 gave a greater decrease in copper concentration over the experiment (99 % removal).

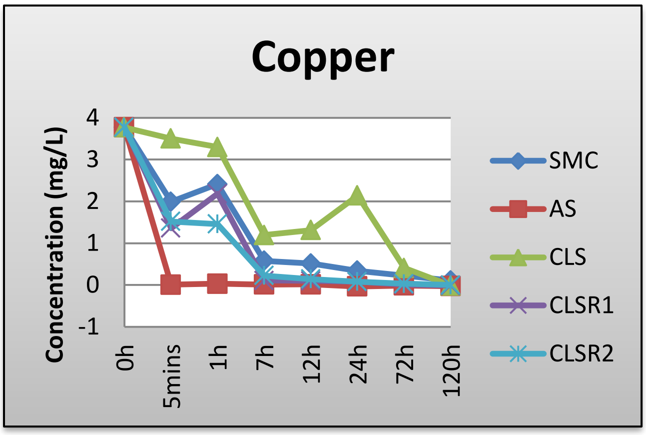

Figure 6: Copper Removal

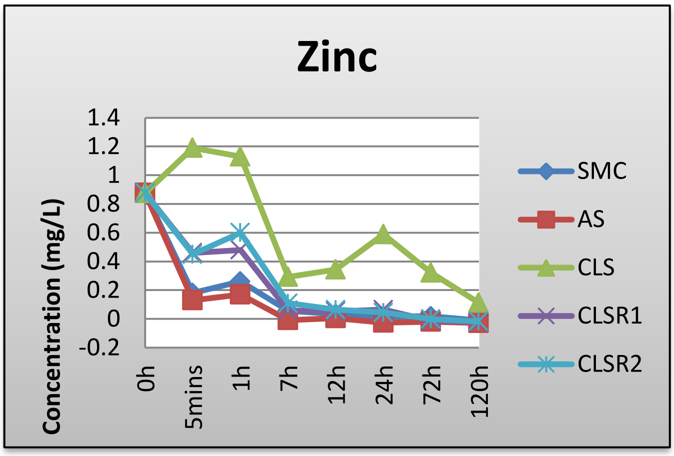

Figure 8: Zinc removal

Lead was removed from all the treatment media (Figure 7). Rapid decrease of Pb was found at 5 minutes of reaction for most media except for crushed limestone. This is not surprising because limestone is added as an alkalinity producing agent mainly for removing acidity and increasing pH. Both mixed substrates showed almost the same pattern of Pb removal in the mine water (~98 % removal).

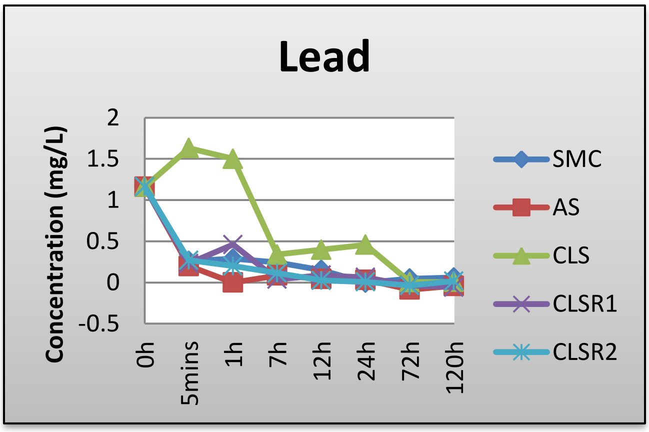

Figure7: Lead Removal

As can be seen in Figure 8, spent mushroom compost and activated sludge are the most effective media in removing zinc from acid mine drainage. Despite this, both mixed substrates also showed promising results in zinc removal. The crushed limestone also demonstrated zinc removal although at a rate slower than other media.

IV. CONCLUSION

This study evaluates the potential use of several treatment media that would be used in a sulphate reducing bioreactor, adopting the so-called passive treatment of acid mine drainage. Results showed that all treatment media which are spent mushroom compost, activated sludge, and crushed limestone are effective in removing sulphate alongside other heavy metals in the acid mine drainage. The most effective media is spent mushroom compost as it gives greater removal efficiency of most contaminants compared to other treatment media. As anticipated, crushed limestone alone produces a rather slow removal because the material is meant for alkalinity production while at the same time may help in contaminant removal. Two mixed ratios of substrates had also been assessed and the results showed that ratio 2 is more effective than ratio 1 (up to 99% removal of contaminants). Ratio 2 substrates contain 40% limestone, 30% spent mushroom compost, 20% activated sludge, and 10% woodchips. From this study, it can be concluded that these treatment media can be used in sulphate reducing bioreactor for efficient removal of sulphate and selected heavy metals in acid mine drainage. Further evaluation will be assessed in the following column experiment.

V. ACKNOWLEDGEMENT

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