Passive remediation of mine impacted water using selected treatment media containing-bioreactor

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Abstract. This study was carried out to develop a passive treatment method to treat contaminated water with heavy metals caused by mining activities using organic, industrial, quarry and mining waste itself. In particular, this study aims to evaluate the performance of selected treatment media in treating Acid Mine Drainage (AMD) (i.e. Spent mushroom compost (SMC), limestone (LS), steel slag (SS) and ochre). A series of tests were conducted to determine the effectiveness of the treatment media in single and mixed substrates treatment. For single substrate, both SMC and SS showed promising overall heavy metal removal efficiency of 94.6% and 96.7%, respectively. As for mixed substrates, R3 (composed of 40% SS, 30% SMC, 20% LS and 10% ochre) gave the best performance in overall heavy metal removal. This treatment ratio (4:3:2:1) was then used in column experiment where continuous flow of synthetic AMD water was supplied. After 30 days, results showed that heavy metals (i.e. Fe, Mn, Pb, Zn, and Al) were reduced significantly with 91–100% removal efficiencies except for Mn (61.15% efficiency). Therefore, this study has proven that the media chosen in passive treatment of AMD are efficient in the removal of selected heavy metals and in increasing the pH of AMD, which can be applied for real on-site treatment of such cases.

1. Introduction
In Malaysia, some surface water bodies in Lembah Kinta Perak, Bestari Jaya Selangor, Sungai Lembing Pahang and Mamut, Sabah ex-mining areas are impacted by metals-contaminated discharge primarily consist of iron, zinc, lead or cadmium (e.g. Ashraf et al., 2011; Ashraf et al., 2012). This drainage which originated from an abandoned and active metal mines are acute and pervasive form of aquatic pollution to both surface and groundwaters, and this contaminated water caused by the drainage is widely known as mine impacted water. Study by Madzin et al. (2015) has identified red discharges that have been released to the surface waters and produced acidic, heavy metal containing water which are characterised as Acid Mine Drainage (AMD). Apparently, this red discharge come from the bauxite mines located in Kuantan, Pahang which has been overexploited. Acid Mine Drainage (AMD) is an acidic water that has high metal content formed by the reaction between oxygen and water in sulphide bearing minerals (Roychowdury et al., 2015). Acidic waters that highly contain heavy metals are the end products of a variety of industrial operations which are mostly from mining activities. When the sulphur-rich rocks are removed from the mine and react with water and oxygen, it will be transformed into sulphuric acid. This acid is carried off to the streams by rainwater and other run off drainage hence creating environmental risk to the water source. Acid Mine Drainage has been a major issue affecting the environment and the economics of metal and coal mining...
operations throughout the world. Besides, the generation of AMD also possesses low pH and high metal content such as Zn, Fe, Mn, Cd, As, Co, Ni, Al, and Pb. These acidic waters carry along the metal content and increase the solubility of heavy metal in the affected region. Sulphide oxidation is an autocatalytic reaction and therefore, once AMD is generated, it can be very difficult to halt (Lottermoser, 2007). Heavy metal contaminations and the increased acidity caused by Acid Mine Drainage have a range of negative effects and can harm the environment if it is not well treated. These pollution effects are described as complex and include metal toxicity, sedimentation, acidity, salinity and salinisation. Additionally, according to Yesilnacar and Kadiragagil (2013), the leachates from mine wastes and tailings impoundments that flow and penetrate into water sources are not just acidic but contain high concentrations of dissolved metals that are harmful if consumed. These substances can severely contaminate surface and groundwater, as well as soils. The production of pyrite in AMD is the main cause of water pollution. Pyrite is a common mineral deposit in AMD as when it is exposed to the air, pyrite oxidises and changes into sulphuric acid when in contact with water. This acid mobilises heavy metals from mine activities, and hence bringing along dissolved salts and low water pH. Other than that, the economic issue on the mining operations is possibly to occur. The corrosive effects of acid water on the infrastructures and equipment will eventually take place as well as limitations on water reuse.

As mining industries keep on increasing over time, the need to solve problems regarding AMD also increase. Various treatment options were studied to overcome this issue. Generally, treatment technologies for AMD can be categorised as either active or passive, where both include physical, chemical and biological techniques. Active treatment systems require additional chemical reagents to function, regular maintenance and monitoring, while passive treatments require no reagents, active monitoring and mechanical devices (Lottermoser, 2007). These treatments have been discovered over the past 20 years for AMD treatment (Zagury, Kulnieks & Neculita, 2006), which give different advantages and disadvantages to the system. Improvements over the years has been done taken from the previous study in order to produce not just effective technology, but economical and require minimal maintenance to be applied in the mining sites. For example although the usage of ZVI (zero valent iron) as a media that act primarily as a metal reductant in most active remediation to treat heavy metals, however, the cost of ZVI is rather expensive and non-economical. Therefore, research has been done in order to identify other reactive materials that are similarly effective focusing on passive treatment method (Choudhary & Sheoran, 2012; Obiri-Nyarko, Grajales-Mesa, & Malina, 2014; Sheoran, Sheoran, & Choudhary, 2010; Wilkin et al., 2014; Zagury, Neculita, & Management, 2007; Zhou et al., 2014) because one of the important factors in designing a successful passive system is the selection of the reactive media (Madzin et al., 2016). Leticiariu (2015) reported that there are two types of potential substrates that have been studied which are cellulosic substrates (wood chips, sawdust, etc.) and organic substrates (manure, compost, slags, ochre and brewing wastes) that have improved AMD in long term experiments (Zagury et al., 2006). Organic wastes like spent mushroom compost, cow manure compost, activated sludge, woodchips, crab shell chitin, limestone, and steel slag or metallurgical slags were often used by researchers to test their capability for an effective AMD treatment (Muhammad et al., 2016; Muhammad et al., 2015; Zahar et al., 2015; Name and Sheridan, 2014; Choudary and Sheoran, 2012; Neculita et al., 2011). Spent mushroom compost, cut rice straw, wood chips, saw dust and cow manure have been characterised for their abilities to serve as the carbon source (food source) and energy for sulphate reducing bacteria (Neculita et al., 2011). Steel slag and limestone are popular for their highly alkaline properties and adsorption mechanism (Duan et al., 2014 and Zahar et al., 2015). Ochre or transformed red mud is proven to have the ability to remove Cd and Pb in aqueous solution (Sahoo et al., 2014).

Although there are numbers of economic and environmental factors in determining the treatment suitability in remediating AMD, passive treatment is often chosen as the ideal treatment option mostly because it is considered economical, maintenance requirements are low and the demand it needs for technical expertise is very little compared to active treatment (Johnson and Hallberg, 2005). Hence, much research in recent years have focused on the identification of low-cost, low maintenance passive
treatment options for the remediation of these polluting discharges namely AMD (Obiri-Nyarko et al., 2014; Liu et al., 2015; Vasquez et al., 2016; Kusin et al., 2016). For instance, the remediation of net-alkaline, iron-rich mine drainage has been regarded as proven technology especially in many European and American applications of passive treatment systems (e.g. wetland-type systems and bioreactors). However, the removal of zinc and manganese, which are prevalent in discharges from metal mines (and also is the case in Malaysian mine-impacted discharges), are more difficult to nearly impossible. Whilst iron is readily removed by the generation of oxyhydroxides in passive treatment, the hydroxide solubility products of zinc and other divalent metals are higher than that of iron, so that a higher target pH is required to remove these metals as hydroxides (Diaz et al., 1997). In contrast, the solubility product of sulphides of these metals are lower than that of iron, so organic substrates that contain sulphate-reducing bacteria (SRB) in treatment bioreactor may offer a more feasible approach to remove such metals at the pH values typically achievable in passive treatment systems (Mayes et al., 2011), and in timescales that result in reasonably sized systems. The development of bioreactors which harness bacterially mediated heavy metals reduction have been widely tested since the observations of Tuttle et al. (1969) on the effectiveness of acid-tolerant sulphate reducing bacteria in removing metals as solid monosulphides from Acid Mine Drainage. SRB perform the key terminal reductive step for metal removal which is rate-limited by the supply of carbonaceous organic matter to the SRB. For instance, a laboratory-scale sulphate reducing bioreactor or reducing and alkalinity producing systems (RAPS) have been developed to field-scale treating coal mine drainage where principal contaminants of concern include Fe, Al and SO$_4^{2-}$, i.e. some compost-based units around the UK (Mayes et al., 2011).

However, passive systems in which sulphate reduction will occur vigorously and consistently enough to affect the removal of metals to the low level sufficient for compliance with regulatory regulations for mining-related metal pollutants have not yet been developed. The removal of zinc is of interest as it is the most commonly encountered pollutant in rivers draining former metal mining districts in Malaysia (e.g. Ashraf et al., 2011, Ashraf et al., 2012). The use of bioreactor such as the RAPS were initially developed to overcome challenges and restrictions for anoxic limestone drainage (ALD) for low dissolved oxygen and heavy metals (Ordonez et al. 2012) and very successful in treating heavy metals (Taylor & Murphy 2005; Wang 2010). However, studies have shown that the restriction of this bioreactor treatment system is in terms of long term performance and the replenishment of the organic substrates (Wilkin et al. 2014; Obiri-Nyarko et al. 2014; Taylor et al. 2015). In many bioreactors and/or wetland-type system, the carbon source is initially present as labile cellulose-rich materials. This leaves more recalcitrant lignin-dominated material for later breakdown and limits supply of low-molecular weight carbonaceous material to the SRB communities (Hiibel et al., 2008). The necessity for replenishment of the carbon source in wetland-type system has long been acknowledged but it is something that can often be neglected in full-scale bioreactor operation. Thus, the addition of multiple organic substrates to assist the remediation process and sources of carbon are something to be discovered and taken into account.

As the impacts of Acid Mine Drainage can persist for decades and centuries, and even after the cessation of the mining activities, there is a need to develop inexpensive and sustainable remedial method to treat the contamination. Therefore, this study aims to develop a promising treatment technology for mine-impacted waters using passive treatment approach. A treatment bioreactor which is one of the passive AMD treatments was suggested in this study as it is low in cost, requires less maintenance and the substrates are abundantly available as organic and inorganic waste were used as the substrates. The waste-containing bioreactor has high potential in reducing heavy metals such as Mn, Fe, Al, Zn and Pb, and most importantly to produce alkalinity to neutralise the acidic water. This study provides a detailed investigation in the performance assessment of the passive treatment in removing heavy metals alongside with evaluation of each substrate chosen in this study, i.e. physicochemical characterisation of each substrate in treating the heavy metals as well as physicochemical parameter improvement and heavy metal removal after the treatment process. Therefore, the findings provided can be useful for on-site treatment if intended especially for application in such cases in Malaysia.
2. Method and Materials

2.1 Characterisation of treatment media
A total of four reactive media were selected and these were SMC, steel slag, limestone and ochre. The four types of treatment media were obtained from their respective places; mushroom farm in Puchong and Sungai Merab, Bangi, steel factory located in Banting, quarry in Teluk Intan and bauxite mine site in Kuantan, Pahang. All the treatment media were pre-treated where necessary for the use in the experiment.

Each treatment media was analysed for pH, redox potential (Eh), total dissolved solid (TDS), conductivity, salinity, alkalinity, total organic carbon (TOC), total volatile solid (TVS) and water content. The measurement of pH, Eh, TDS, conductivity, and salinity was done by using Myron 6P Ultrameter using distilled water based on solid to liquid ratio of 1:2. Alkalinity of media was measured using titration method of 10 mL sample with 0.16 N sulphuric acid and reagents (phenolphthalein indicator powder and Bromcresol Green-Methyl powder) and tested with HACH Alkalinity Test Kit (model:AL-AP). TOC was analysed using Shimadzu Total Organic Carbon Analyzer (TOC VCSN) following the EN 1484 standard guidelines for the determination of TOC. TVS is related to loss-of-ignition method where it gives rough estimation of the amount of organic matter present in the sample (Matthiessen et al., 2005). The water content of the treatment media was measured by subtracting the weight of a sample dried at 105 °C for 24 h from weight of sample before drying, while the total volatile solids (TVS) were determined by subtracting the weight of a sample dried at 550 °C from weight of sample at 105 °C.

2.2 Preparation of synthetic AMD
Synthetic Acid Mine Drainage water was prepared for both batch and column experiments. Synthetic AMD was used in the experiments because it was not possible to obtain the actual AMD and for the purpose of varying several treatment variables during the experiment. This was also to provide treatment consistency as well as to prevent any possible intrusion by conflicting pollutants (Cheong et al., 2010). The synthetic AMD in batch experiment were prepared based on two types of solution concentrations, i.e. high concentration and low concentration whereby the high concentration was imitated according to the average concentrations of metals found in the real effluent quality data of Mamut copper mine, Sabah (Jopony & Tongkul, 2009). The high concentration synthetic AMD was prepared to test whether or not the media can treat a relatively high concentration AMD. While low concentration solution was based on the case study of Kuantan bauxite mining area. The synthetic AMD was made up to contain primary metals of concern as in the case study (i.e. Mn, Al, Pb, Fe, and Zn). Whilst as for column experiment, low concentration synthetic AMD was infused as the influent. The synthetic AMD solution was simulated by dissolving the analytical laboratory salts by using distilled water in a 4 L volumetric flask. In order to lower down the pH, hydrochloric acid was added drop by drop until it reaches pH value of 6.4 and 3.5 for low and high concentration solutions, respectively. Table 1 shows the composition of synthetic AMD solutions used in the experiments.

| Component | Salt | Batch (mg/L) | Column (mg/L) |
|-----------|------|--------------|---------------|
|           |      | Low concentration | High concentration | Low concentration |
| Fe⁺       | FeSO₄.H₂O | 1.574 | 6.95 | 1.574 |
| Mn⁺       | MnSO₄.H₂O | 4.156 | 21.65 | 4.156 |
| Pb⁺       | Pb(NO₃)₂ | 0.578 | 83.40 | 0.578 |
| Zn⁺       | ZnSO₄.7H₂O | 0.204 | 18.19 | 0.204 |
| Al⁺       | Al(SO₄)₁₈H₂O | 0.856 | 26.95 | 0.856 |
| Ca⁺       | Ca(CH₃COO)₂H₂O | 44.35 | 83.2 | 44.35 |
2.3 Treatment of AMD

2.3.1 Batch experiment. A series of batch test is required in order to determine the performance of the reactive media in treating AMD water. Batch test was conducted for both individual (single media) and mixed media (where the substrates were mixed into five different ratios) to establish the potential use of the media. The batch test was undertaken for a period of 5 days and the best substrate with appropriate proportion mix was selected as the reactive media for column test. A 2 L beaker was used to be filled with its respective treatment media. 50 g of single treatment media which are spent mushroom compost (SMC), ochre, steel slag and limestone were each added in the beaker for single treatment media. A total of 8 beakers for treatment using single substrates were used; 4 beakers for low concentration synthetic AMD and another 4 were for high concentration synthetic AMD. 2 beakers were added with the same type and amount of treatment media, but with different concentrations of the synthetic AMD. On the other hand, another 8 beakers were used for treatment of synthetic AMD using mixed substrates; 4 beakers for low concentration and another 4 for high concentration of synthetic AMD. For the mixed substrates ratios, the substrates were added into the beaker according to the percentages ratio of; R1 (10% SMC, 20% ochre, 30% steel slag and 40% limestone), R2 (20% SMC, 30% ochre, 40% steel slag and 10% limestone), R3 (30% SMC, 10% ochre, 40% steel slag and 20% limestone) and R4 (40% SMC, 10% ochre, 20% steel slag and 30% limestone) (Table 2). An amount of 50 g of the mixtures were added (according to the table shown below) into 2 L beakers and was then filled with 1 L of synthetic AMD solution, then the beakers were tightly sealed with parafilm in room temperature in order to promote the anoxic condition while dissolved oxygen level was monitored at <1 mg/L. All of the water samples were taken at 0 h, 1 h, 3 h, 10 h, 24 h, 48 h and 120 h, respectively.

Table 2. Mixture percentage of media used in batch experiment

| Treatment media | SMC | Ochre | Steel Slag | Limestone | Ratio 1 (R1)* | Ratio 2 (R2)* | Ratio 3 (R3)* | Ratio 4 (R4)* |
|-----------------|-----|-------|------------|-----------|--------------|--------------|--------------|--------------|
| SMC             | 100 | 0     | 0          | 0         | 10           | 20           | 30           | 40           |
| Ochre           | 0   | 100   | 0          | 0         | 20           | 30           | 10           | 10           |
| Steel Slag      | 0   | 0     | 100        | 0         | 30           | 40           | 40           | 20           |
| Limestone       | 0   | 0     | 0          | 100       | 40           | 10           | 20           | 30           |

*Single media treatment
*Mixed media treatment (total mixture amount of 50 g)

2.3.2 Column experiment. A series of experimental treatment with two columns namely Column 1 (C1) and Column 2 (C2) filled with reactive media was conducted. The two columns were constructed using acrylic tubes (internal diameter of 6.5 cm and 50 cm height) and PVC caps at both ends. The bottom of the column contains a valve used as an influent port for synthetic AMD, and the top cap contains another valve, for effluent sampling and for continuous treatment connecting to the other column. The selected ratio of reactive media in the column test was determined from the batch test (ratio 3). 1.3 kg (1300 cm) of ratio 3 treatment media that gave the highest removal efficiency from batch test was inserted in both columns and synthetic mine water as the influent. Synthetic AMD in low concentration was pumped into C1 and C2 with an aeration tank in between both reactors. Then, the influent synthetic AMD water will pass through the columns and resulting in treated AMD in the effluent. The columns were packed, using the procedure described by Zagury et al. (2007). The continuous-flow column test was conducted for 30 days with an intermediate aeration tank to aid the degassing of carbon dioxide. An upward flow was applied to decline any preferential flow and system blocking as the direction of water rectify gravitational pull (Evans & Ko, 2013). Water from each
column was sampled on a daily basis. The experiment was conducted for a total of 30 days period in anoxic condition for both columns in order to observe a better removal efficiency of the heavy metals.

2.4 Assessment of AMD treatment performance

2.4.1 Physico-chemical analysis. Water samples from the batch and column tests were taken (triplicates) at specified time intervals (batch) and daily basis (column) to measure physico-chemical parameters. Measurements included pH, total dissolved solid (TDS), redox potential (Eh), and conductivity that were measured using a calibrated Myron 6P Ultrameter. Alkalinity was measured using a HACH alkalinity kit (AL-AP) by means of titration against sulfuric acid with phenolphthalein and brom cresol green-methyl red indicators. Dissolved oxygen was measured using YSI 52 Dissolved Oxygen Meter, and COD was measured by using HACH method (COD LR TNT 822 HACH) based on USEPA Reactor Digestion Method 8000 (Standard method 5220 D). All instruments were calibrated for each sampling period and were rinsed with deionised water upon used.

2.4.2 Heavy metal removal analysis. Water samples were analysed before and after batch and column tests were conducted for Fe, Mn, Al, Zn and Pb by using a Perkin Elmer Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES) Model Optima 8300. Cation calcium (Ca) was also analysed using ICP-OES. In batch experiment, all beakers were sampled using syringe and filtered using 0.2 µm Whatman membrane filter into 15 mL centrifuge tubes. For column experiment, the water samples were sampled from the effluent port in both columns in triplicates and were filtered into 15 mL centrifuge tubes. All samples were then acidified with 1% v/v nitric acid for sample preservation (APHA, 2008). All sampling and laboratory equipments were acid washed: rinsed three time with decon soap, soaked in 10% HCl for 24 hours, rinsed with warm water three times and rinsed with deionised water upon used (Evans & Ko 2013) to reduce any possibilities of interference in dissolved metals (Wang et al. 2012; Zhang et al. 2014; Praveena et al. 2016). Removal efficiency for the analysed metals were then calculated so that a significant difference before and after the treatment can be shown and the removal of heavy metals can be determined.

2.5 Statistical analysis
The statistical analysis of the water quality parameters was done by using Statistical Package for the Social Sciences (SPSS) version IBM SPSS statistics 22. The correlations among physico-chemical parameters and heavy metals were analysed by using Pearson’s correlation analysis to evaluate the significant correlation between the removals of specific metals as well as the changes in physico-chemical parameters of the synthetic AMD. The significance of each analysis was tested at 95% confidence level ($p = 0.05$). The statistical analysis will help strengthening discussion of the heavy metal removal and speciation of heavy metals in the subsequent discussion.

3. Results and Discussion

3.1 Treatment media characteristic
The characteristics of the treatment media are given in Table 3. SMC results has the highest TDS, electrical conductivity, alkalinity, TOC, TVS, and water content compared to the other three media. TVS is generally determined to indicate organic matter content (Neculita et al., 2008). Based on the TVS value, SMC consists of more than 58% of volatile solids and this is consistent with previous findings (e.g. Neculita et al., 2011). Similarly, SMC seems to have the highest amount of TOC which is the measure of total amount of organic carbon in the media. In addition, previous study has also stated that SMC has the highest amount of dissolved organic carbon, DOC (Song et al., 2012). DOC is the amount of available dissolved organic carbon released in the water for bacterial consumption. Remediation of AMD also depends on the activity of sulphate reducing bacteria (SRB) present in the media, and this activity is affected by the water content because SRB need moisture in order to
enhance their activity. Thus, lower moisture content can limit SRB activities because the bacteria are not able to spread on the entire media surface (Sani et al., 2016). Based on the water content of the media, SMC shows the highest percentage (more than 70%). The condition of SMC is more suitable for bacterial activity based on its water content. Furthermore, the pH of the treatment media shows that SMC, steel slag and limestone have an alkaline nature. Muhammad et al. (2016) found that the alkaline nature of SMC and limestone shows their potential as neutralising agents. This reflects the potential of steel slag to neutralise AMD due to its highly alkaline nature. The high TOC, TVS, water content, and the neutral pH of SMC suggest that SMC is the most potential substrate compared to others in treating AMD (Muhammad et al., 2015; Song et al., 2012; Neculita et al., 2011). However, limestone and ochre have high redox potential (Eh) where it influences most of microbial activity where organisms use oxygen as their source of energy (Kura et al. 2015). High in source of oxygen is crucial as the ability of water to transport metals is also controlled by Eh through reduction-oxidation potential reaction (Roychowdhury et al. 2015). Oxygenated water may oxidise the reduced, immobile metals condition and allows mobility and easily transports the metals from the AMD waters (Lottermoser, 2007).

| Table 3. Characteristics of reactive media |
|------------------------------------------|
|                           | Ochre | SMC  | Limestone | Steel slag |
|---------------------------|-------|------|-----------|------------|
| pH                        | 3.09  | 7.6  | 7.73      | 9.45       |
| Eh (mV)                   | 589   | 136  | 595       | 145        |
| TDS (ppm)                 | 224.2 | 998.9| 171.0     | 145        |
| EC (µS/cm)                | 349.1 | 1454 | 270.5     | 52.87      |
| Salinity (ppt)            | 0.1   | 0    | 0.1       | 0          |
| Alkalinity (mg/L as CaCO₃) | 10    | 260  | 20        | 60         |
| TOC (mg/L)                | 4.7   | 56.7 | 0.99      | 12.9       |
| TVS (% w/w)               | 16.6  | 58.92| 0.115     | 0.36       |
| Water content (%)         | 22    | 76.5 | 0.11      | 1.5        |

3.2 Treatment performance in term of physicochemical parameters

3.2.1 Physicochemical parameters of water sample in batch test. Increase of pH in all media was observed in both concentrations (i.e. low and high concentration). Steel slag (SS)-containing synthetic AMD showed the highest pH at 120h with an increase from 6.39 to 8.80 in low concentration and 3.5 to 8.39 in high concentration as shown in Figure 1. This can be reflected by the great increase of Ca concentration in SS-containing beaker (Figure 1) even though SS has the second highest Ca concentration at 120 h, while ochre yielded the highest Ca concentration at the end of the experiment. The high amount of Ca can be considered typical in SS treatment because the main component of steel slag is calcium oxide, and the Ca measured is caused by leaching of Ca into the synthetic AMD (Repo et al., 2014). The increase in Ca concentration reflected the potential of the media to buffer acidity and producing alkalinity thus increasing the pH of AMD (Choudhary and Sheoran, 2012; Song et al., 2012). Ca concentration is crucial in AMD treatment as it affects the pH, and the removal of heavy metals by means of precipitation or adsorption depends greatly on the pH. As mention by Muhammad et al. (2016), Ca could also help in providing negatively charged sites for ion exchange reactions to occur with heavy metals in the solution. The performance of steel slag in increasing the pH of the synthetic AMD was also reflected in the mixed substrates containing 40% of steel slag where R2 (ratio 2) and R3 (ratio 3) were almost similar in pH at 120 h. In R2 and R3, pH has increase above 8.0 for both concentration. This means that ratio 2 and ratio 3 were the best ratio in increasing the pH of the synthetic AMD. This suggest that SS can be used for pH control because of its high neutralisation capacity where study done by Kruse et al. (2012) has proven that SS is a good alkalinity source in treating AMD.
Furthermore, based on the redox potential (Eh) results, microbial activity was detected in SMC and Ochre media where the Eh value in high concentration AMD were reduced from 120 mV to 69 mV. These changes indicate that the activity of SRB was taking place (Gibert et al., 2003), and this can be explained by the consumption of oxygen causing the system to be in reduced condition. SMC and Ochre assist the SRB activities greatly in the mixed substrates when R2 (20% SMC, 30% ochre, 40% SS, 10% LS) had a notable decrease of Eh in high AMD concentration. While in R3-containing synthetic AMD (30% SMC, 10% ochre, 40% SS, 20% LS), Eh was reduced 62 mV in low concentration and to 50 mV in high concentration, thus indicating high SRB activities. On the contrary, the Eh increase towards the end of the experiment would suggest the gradual inactivation of SRB (Song et al., 2012). Meanwhile, SMC proved to experience SRB activities when it also shows a significant increase of conductivity in low and high concentration AMD. It reached up to 2155 mS/cm in low concentration, whereas in high concentration AMD, SMC and ochre have shown an increase with a similar value of 1092 mS/cm. It can be seen clearly in both concentrations that SMC has increased the conductivity way higher than the initial value. This shows that SMC has released a high amount of ionic components, and was experiencing active SRB activities in the beaker (Lyew and Sheppard, 2000). Similar in mixed substrates treatment, R4 (40% SMC, 10% ochre, 20% SS, 30% LS) which has the highest amount of SMC showed a rapid increase of conductivity in both low (139.1 µm/cm to 934.7 µm/cm) and high concentrations (520.2 µm/cm to 1654 µm/cm). R4 also yielded the highest TDS in both concentrations. Based on the observation, R1 that contain only 10% SMC yielded lower TDS (i.e. 373.4 mg/L and 512.5 in low and high concentration respectively) compared to R4 that has 40% of SMC. Hence, it is fair to say that the amount of SMC affects TDS and further affect the conductivity. This is proven statistically where TDS was found to correlate significantly with conductivity in all treatments for low and high concentrations. Single treatment media and mixed substrates in low concentration has a perfect positive correlations (r=1.000, p<0.01) while single treatment media and mixed substrates in high concentration showed strong positive correlation (r=0.863, p<0.01 and r=0.822, p<0.05, respectively) between conductivity and TDS. This indicates that conductivity and TDS are greatly related and the increase in both parameters is caused by concentration of metals that leached from the treatment materials. Both conductivity and TDS plots also showed a very similar pattern throughout the experiment, showing the close relationship between conductivity and TDS. On the other hand, although R3 did not experience much increase in conductivity like in R4, results have shown that conductivity still increase in both concentration (i.e. 139.1 µm/cm to 696 µm/cm and 520.2 µm/cm to 1435 µm/cm) as R3 contains 30% of SMC. This signify that SMC can greatly affect conductivity, which caused by the changing of the TDS value in the synthetic AMD and also caused by the increase of the SRB activities in the treatment beaker.

![Figure 1](image_url)

**Figure 1.** Graph of pH and Ca concentration in steel slag beaker within 120 hour.
3.2.2 Physicochemical parameters of water sample in column test. Column experiment were replicated, and each sample were taken in duplicate. The pH changes for both reactors were almost similar throughout the continuous experiment. During the initial acclimation period, pH value sharply increased from 2.71 to 7.54 in C1 and 7.64 in C2 reactors from day 1 to day 3 and remained almost constant from day 5 to day 14. The pH then fluctuated from day 15 to day 17 and increased back to circum-neutral condition until the end of experiment. Another observation found was that C2 had greater pH increase than C1. This might be due to that C1 has been fed with untreated AMD water whereas C2 received the influent from the treated effluent in C1. The pH increment was associated with increased alkalinity in both reactors from day 1 to day 3 before it started to decline until day 30 where it reached 55.00 mg/L in C1 and 30.00 mg/L in C2. Escalation in alkalinity mostly resulted from the high Ca content in SS and SMC in the reactive mixture (ratio 3) and also from dissolution of limestone that has occurred within the first several days (Vasquez et al., 2016a). Additionally, the increase was also attributed to the formation of carbonate species and oxidation of organic substrates developed by SRB which is generated by the SMC, as well as dissolution of the surface-bound hydroxyl ion from the reactive mixtures, which only occur under acidic condition (Neculita et al., 2011; Song et al., 2012). Hence, the alkalinity produced by the SMC has also contributed to acid neutralisation capacity for the AMD (Lefticariu et al., 2015).

In term of alkalinity, C2 showed higher alkalinity until day 27 but dropped until day 30 than in C1. The drop in alkalinity might cause by the limestone and metal sulphides precipitation that was formed through the experiment (Song et al. 2012; Lefticariu et al., 2015). These precipitations have restricted the dissolution of limestone and dropped the alkalinity level, which could occur after being exposed to AMD. Dvorak et al. (1992) stated that the fluctuation of alkalinity is due to the establishment of suitable biogeochemical environment in the substrates as occurred in both column where alkalinity fluctuate on day 3 until day 13. The most common carbonate material used in passive systems are SMC and limestone which are rich in calcite (CaCO₃) and they react with water to produce bicarbonate alkalinity and neutralise acid generation (Younger et al., 2002). Accordingly, the amount of Ca in C1 and C2 has increased rapidly in day 1 to day 3 and gradually increased until the end of experiment. This trend was almost similar to the pH trend and this may be due to the presence of bacterial sulphate reduction and dissolution of calcite by oxidation process. At pH greater than 5, the consumption of proton in neutralising acidity is rapid and is typically making the contact between water and calcite to reach equilibrium (Younger et al., 2002). Overall, by using R3 ratio which contains 40% steel slag, 30% SMC, 20% limestone and 10% ochre, the mixture has been effective for the pH generation, increment of alkalinity and Ca content in this test.

Moreover, reducing conditions were established at both reactors based on the redox potential (Eh) in both columns. C2 was in a better reduction phase than in C1. SRB needs an anaerobic and an anoxic reduced microenvironment to start generating the reactions as heterotrophs bacteria consumed energy as confirmed by the low Dissolved Oxygen (DO) and low Eh (Figure 2) (Choudhary and Sheoran, 2012). Eh value reduced was reflected by the TDS values; due the presence of organic matter and variety of organic compounds in the reactor system to enable SRB growth and hence established the anaerobic condition (Cheong et al., 2010). Additionally, the trend for TDS was similar to conductivity where they have a very strong relationship with average r=0.715, p<0.05. These conductivity and TDS were highly influenced by the concentrations of metals, sulphates and organic matter in the mixed substrates which showed very similar patterns. The high percentage of SMC in the mixed substrate has contributed to a higher ionic components into the solution, giving rise to the TDS concentration in C1 and C2 between day 19 to day 25 before it decreased back to the final reading in day 30 (Song et al., 2012).

Sulphate concentration experiences removal efficiency of 73% with a final reading of 46.70 mg/L. While in C2, removal of 90% occurred with final reading of 15.90 mg/L. This suggests that C2 gave a more efficient removal in sulphate than C1. The treated influent from C1 really helps in removing sulphate in the form of precipitation and adsorption in C2. Sulphate reduction in AMD treatment was initiated by SRB in SMC whereby the SRB is capable to degrade sulphates into hydrogen sulphide,
H₂S (Mayes et al., 2011), and also metal sulphides before gradually precipitates over time. Removal was also assisted through adsorption of sulphates on mineral and surfaces of organic compounds in mixed substrates (Lefticariu et al., 2015). The presence of SRB was observed by the black precipitates formed from the top to bottom layer in both column reactors throughout the experiment. Besides that, the bad odour generated in both effluents indicated the presence of H₂S in the column test. However, the sharp increase of sulphate in C2 compared to the AMD influent in day 2 was likely due to the leaching of organic substrates from SMC, yielding higher concentration of sulphate than in the influent, which was also reported in previous experiment done by Guo et al. (2001) and Vasquez et al. (2016) where the potential source was from gypsum in the SMC. Moreover, increased pH with decreased Eh have prompted the reduction of sulphate at which anaerobic condition that has been established, and that the SRB metabolism that took over the reduction mechanism thus reducing sulphates to sulphides (Jong and Parry, 2006; Cheong et al., 2010).

![Figure 2. Mean (a) dissolved oxygen (DO) and (b) conductivity (mV) parameters graphs of water samples in column test. The values are mean of triplicates and error bars represent standard deviations.](image)

### 3.3 Treatment performance in term of heavy metals removal for batch and column experiment

Removal efficiencies were calculated to interpret and determine performance effectiveness of the substrates. Table 4 shows the average contaminant removal efficiency of single and mixed substrates in low and high concentrations for batch and column test. For single substrate in low and high concentrations, SS showed the highest average contaminant removal (97%) compared to other substrates in the single batch experiment. SS showed great potential in removing heavy metals and sulphates and also has good capacity for alkalinity generation. Steel slag is a very good adsorbent agent and can perform hydration reaction, showing a good alkalinity generation, adsorption capacity and metal precipitation capacity (Duan and Su, 2014). SMC on the other hand showed the second highest contaminant removal capability with 76.8% efficiency. SMC exhibits good performance as an electron donor to other organic materials (Vasquez et al., 2016a), and composes variety of organic matter and abundant polysaccharide content in SMC that assist the growth of SRB (Chang et al., 2000); whereby SRB as the major carbon source contributor for sulphate reducers in treating AMD. Although it is reported that SMC is appropriate to be used as substrate in bioreactor in a long term treatment (Cheong et al., 2010), however, the exhaustion rate is faster than other treatment media due to the inhibition of SRB growth and from adsorption of metals during treatment, and hence it is dependent on other treatment media to supply dissolved organic carbon to boost the treatment rate (Cheong et al., 2010).

Additionally, LS can be an exceptional substrate for a bioreactor in low concentration but not in high concentration. Limestone is commonly known as a promising alkalinity generator through the dissolution of LS, creating instant increment in pH from acidic to neutral condition (Choudhary and Sheoran, 2012; Evans and Ko, 2013; Vasquez et al., 2016). However, from the batch and column results, LS is also capable of reducing metals through adsorption on their surface due to the surface of
LS that provides rough surface for chemisorption of metal ions in low concentration (Aziz et al., 2008). Although ochre had the least contaminant removal efficiencies (70.10% and 38.80% in low and high concentration respectively), due to abundant availability without much pre-treatment, removal of heavy metals by ochre is attracting more attention. Ochre from contaminated aqueous media has been studied earlier (Agrawal and Sahu, 2006; Feng et al., 2000; Hizal et al., 2009; and Romero-Gonzalez et al., 2005) and these iron oxy-hydro-sulphates have a large adsorption capacity due to their large surface area for adsorption of metal ions (Sahoo et al., 2014).

Therefore, the results from individual batch experiment have contributed to the evaluation of metal removals in the batch experiment using different mixed reactive ratios namely R1, R2, R3 and R4. Overall, all ratios have shown exquisite removal efficiencies giving more than 85% removal efficiencies in both concentrations. In low concentration, the highest to lowest removal efficiencies ratios are R3, followed by R1, R2, and R4 while in high concentration, R1 followed by R2, R3 and R4 with 98.1% in R1, 97.6% in R2, 97.1% in R3 and 95.9% in R4. Although R1 showed the highest percentage in contaminant removal, R1 has the lowest carbon source which could inhibit SRB growth and the removal mechanisms. R3 showed distinguished results in treating all tested heavy metals including sulphates and produced the highest carbon source, good Eh and pH. Therefore, R3 was chosen to be used in the column continuous flow treatment. The potential treatment of R3 in the batch experiment was generally reflected by the successful activity of SRB after feeding with SMC and performs metal precipitation and oxidation into soluble metal sulphides that support the accomplishment of treatment for the AMD waters.

Column experiment disclosed removal efficiencies of post treatment in C1 and C2 reactors with the average metal removal efficiency of 83.7% in C1 and 99.7% in C2 (table 4). All the treatment reactors performed generally well in removing all investigated metals for a total of 30 days in low concentration. In C1, Mn gave the lowest removal efficiency (61.15%) among all metals with a significance of r=0.416 p>0.01. Study done by Rose et al. (2013) stated that the competition for oxygen and the depletion of oxygen in the reactor can cause this to happen. Fe showed a very high removal efficiency in C1 (99.3%) while Zn was typically removed by co-precipitation and alongside with Fe with removal efficiency of 99.79%. Al and Pb removal efficiency are 99.4% and 98.4%, respectively. This shows that Zn has the highest removal efficiency followed by Al, Fe, Pb and lastly Mn. Overall, C1 was good in treating all heavy metals and sulphates except for Mn, as Mn was hard to immobilise and to treat in the presence of Fe and Zn. Whilst in C2, all heavy metals showed very high removal efficiencies with the average of 99.7%. C2 took the role in treating the untreated metal in C1 with a very high statistical significance of 1.00 with p>0.05 showing strong relationship between C1 and C2, thus resulting in a significantly clean effluent in the final treatment. This proves that R3 was a very good ratio of treatment media for the treatment of a given influent.

| Table 4. Removal efficiencies of batch experiment in low and high concentrations with column experiment |
|---|---|---|---|---|---|---|---|---|
| Conc. | SS | SMC | OC | LS | R1 | R2 | R3 | R4 | C1 | C2 |
| Low | 97.00 | 76.78 | 70.12 | 63.51 | 96.67 | 93.94 | 97.73 | 89.47 | 83.70 | 99.71 |
| High | 96.65 | 94.61 | 38.82 | 30.51 | 98.05 | 97.58 | 97.13 | 95.92 |   |   |

4. Conclusion
Findings showed that steel slag (96.7% overall removal efficiency) and SMC (94.5% efficiency) were the most effective media in removing heavy metals and governing increment of pH value in high concentration AMD. Ratio 3 (R3) showed distinguished results (97% overall removal efficiency) in
treating all tested heavy metals and produced the highest carbon sources, good Eh and pH. Therefore, R3 was chosen to be used in the column continuous flow treatment in the next phase using a treatment bioreactor.

In the column experiment, Fe, Mn, Pb, Zn, and Al were greatly removed (91–100% removal efficiencies) in both column 1 (C1) and column 2 (C2) except for Mn (61.15% efficiency) as Mn is hard to immobilise and to treat with the presence of Fe and Zn. Column experiment disclosed overall removal efficiencies of post treatment in C1 and C2 reactors with 83.7% in C1 and 99.7% in C2. Therefore, from this study, it can be concluded that the media chosen in this passive treatment of AMD are efficient in the removal of selected heavy metals and in increasing the pH of AMD.

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