Peat Soil for Synthetic Acid Mine Drainage Treatment: Characteristic Study

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Abstract. Acid Mine Drainage (AMD) is an untreated outflow of acidic water from metal or coal mines. Improper treatment of the harmful effluent causes major environmental concern and remains as an unsolved problem for mining operators worldwide. The untreated AMD contains high concentration of several heavy metals despite low pH level. Iron (Fe) is most dominant element of heavy metal spotted in the AMD water and must be filtered and treated before being released to open water bodies. Current practises by the industries adopted two categories of AMD treatment methods, namely active and passive treatments. Passive treatment method was adopted into this study by using successive alkalinity producing system (SAPS) to reduce Fe concentration in the AMD. Strict regulations by mine operators to acquire on-site AMD, led to use of synthetic AMD. Peat soil was introduced as organic substrate treatment media, as compared to common materials used such as mushroom spent, wood shaving and animal manure. In this research the peat soil was characterized and its effectiveness to filter the Fe content was assessed using laboratory scale studies. Prior to the test, the natural peat soil was analyzed via Scanning Electron Microscopy (SEM) analysis, Energy Dispersive X-Ray (EDX) analysis and carbon-hydrogen-nitrogen-sulphur (CHNS) element analysis. After going through laboratory tests, the peat soil residues were assessed through SEM-EDX analysis to determine the trapped Fe content. The natural peat soil does not contain any Fe substance. However, the analyzed peat soil residues showed that, approximately one to four percent of the Fe were found in the peat soil residues. The use of the peat soil for the AMD treatment in SAPS method is applicable and can be used as alternative organic substrate for treatment media.

1. Introduction
Acid Mine Drainage (AMD) is one of the biggest environmental problems associated with the mine industry. In Malaysia, untreated AMD is one of the largest impairments of surface water. The AMD produces iron (Fe) that will precipitate into ground water aquifer or move through streams and end up...
in the larger water bodies. In addition to increased Fe, AMD also very acidic as sulfuric acid (H$_2$SO$_4$) is generated in the abandoned mines. Thus, AMD must be treated properly, efficient and the process is continuous [1]. Current practices by the industries adopted two categories of AMD treatment methods, namely active and passive treatments. Active treatment reliance on additional chemicals introducing into AMD while passive treatment reliance on biological and geochemical. The passive treatment was explained by Zipper et al. [1] in their study to treat AMD. Similarly, this research explores more on the passive treatment to reduce Fe content in the treated AMD.

Alkalinity Producing System (SAPS), a passive treatments process was explored to treat AMD. In SAPS, selection of organic substrate is essential as the system requires high carbon content. The carbon source reduces sulphate (SO$_4^{2-}$) to hydrogen sulphate (H$_2$S) which reacts with dissolved metals to form metal sulphates [2]. The organic substrate serves as the substrate of sulphate reduction bacteria (SRB) [3]. The SRB generates alkalinity and sequester metal as sulphide [1]. However, study indicates that much of the precipitate is associated with organic matter rather than precipitated as metal sulphide [4]. According to RoyChowdhury et al. [3] in their previous study on anaerobic wetlands which much similar mechanism to SAPS, about 50 to 80 percent (%) of metal removal from AMD inside the anaerobic wetlands system take place due to sorption of metals onto organic surface.

The objective of this research is to quantify the effectiveness of peat soil for AMD treatment. This research looks further into the application of the organic based material as a treatment media. The peat soil was selected as an alternative treatment media for mushroom spent, wood shaving and animal manure that are commonly used to treat AMD. Previous study indicated that the peat soil was not extensively used as major treatment media [4]. The peat soil has been used as alternative organic substrate in this research due to abundance of the material locally and available at a lower cost.

Due to difficulty to conduct the tests using the actual AMD from site, the synthetic AMD with high Fe concentration and low pH level was formulated and used in the research. Most of the researches worldwide used synthetic AMD for their [5, 6, 7].

2. Experimental

Figure 1 shows overall research methodology associated with this research. The successive alkalinity producing system (SAPS) polypropylene tank was fabricated for testing purposes. The Scanning Electron Microscopy (SEM) analysis, Energy Dispersive X-Ray (EDX) was included as part of the analysis process. The peat soil sample, and synthetic AMD are simultaneously prepared, and the volume of the synthetic AMD depends on the design of experiments. General description on the selected materials is included in the following section. The descriptions on the peat soil and synthetic AMD preparation are also available, while brief information on laboratory test set up and analysis are included as well.

2.1. Material

The peat soil sample is obtained from a local nursery located in district of Nibong Tebal, Penang, Malaysia. The peat soil content nutrient-rich humus compound, red burnt soil, charcoal and some river sand. The Carbon, Hydrogen, Nitrogen and Sulphur (CHNS) analysis and SEM-EDX analysis were conducted to characterize basic compositions of the peat soil.
2.2. Sample preparation

2.2.1. Peat soil. The peat soil was stored at ambient temperature. Prior to the analysis, the peat soil was dried under direct sunlight to partially remove moisture content. Then, the peat soil was subjected to cone and quartering process (figure 2a) and subsequently splitting process to ensure homogenous and unsegregated materials. Subsequently, the peat soil sample was pulverized using ring mill. The pulverized sample was sieved into five different sieve sizes at 425 Micron (µm), 300 µm, 225 µm, 150 µm and 75 µm, respectively. However, only sample passing sieve size 75 µm (fine powder) selected for further analysis. The pulverized samples passing 75 µm were tested through CHNS analysis and SEM-EDX analysis to determine basic composition of the material. Ensure no re-use of the same peat soil for subsequent laboratory test. Next, the peat soil residues (figure 2b) were gathered and sun dried accordingly. Then the residues were pulverized and sieved. The fine powder was then tested for Fe content using SEM-EDX.
2.2.2. Synthetic AMD Preparation. Synthetic AMD is a solution that represents the actual AMD at site which contains high acidity with the pH lower than five, high concentration of Fe and $SO_4^{2-}$. Distilled water was used due to its purity and less contaminant as compared to tap water. The distilled water was contained inside a 60 Liter (L) container. Then, approximately 2.3 milliliter (ml) of $H_2SO_4$ was added by using a pipette. The solution was stirred thoroughly to ensure the acid was well dissolved. Consequently, the pH was measured by using pH meter and the reading of pH was supposed to be at range of pH three to four.

Then, to prepare concentration of Fe as heavy metal in the synthetic AMD, Iron Sulphate ($FeSO_4$) powder was used. Equation (1) was used to calculate required volume of $FeSO_4$ to prepare synthetic AMD with 50 part per million (ppm), 75 ppm and 100 ppm.

$$\% Fe = \left(\frac{\text{Molar mass Fe}}{\text{Molar mass } FeSO_4}\right) \times 100$$

(1)

The molar masses of 55.845 gram per mol (g/mol) and 151.908 g/mol were used for Fe and $FeSO_4$, respectively. Thus, it was computed that one ppm of $FeSO_4$ contained 0.368 ppm of Fe. Then, proportion formula was used to determine the weight of $FeSO_4$ required to prepare synthetic AMD in mg/L. The $FeSO_4$ was weighed accordingly using the analytical balance using a 50 ml beaker and quantitatively transferred into the 60 L acidic solution and stirred thoroughly to make up the solution with 50 ppm, 75 ppm and 100 ppm of Fe, respectively.

2.3. Laboratory Set Up

A transparent polypropylene tank was fabricated to store the synthetic AMD solution during the laboratory scale test. The limestone aggregate was laid as the bottom layer. The material was carefully laid and covered the effluent pipe outlet. The peat soil was placed on top of the limestone aggregate layer as illustrated in figure 3. As a precautionary step, the packed peat soil and limestone are not compact and physical disturbance to prevent creation of zones of preferential vertical flow, that will ‘short circuit’ the system and decrease treatment effectiveness as suggested by [1].
The depth of the synthetic AMD in the experiment tank was initially kept at a constant five cm depth. The synthetic AMD solution was supplied from solution tank through influent pipe at the top of the tank. Then the synthetic AMD infiltrated downward through the peat soil, followed by the limestone layer.

Table 1 shows the design of experiment that relates experiment numbers, Fe concentration in ppm, peat soil thickness in cm, and retention times in hours. This experimental set up was generated by design of experiment using Minitab software. The initial Fe concentrations range from 50 to 100 ppm. The limestone aggregate and the peat soil vary from 5 to 10 cm. The maximum thickness for both materials is 15 cm. For instance, if the thickness of the peat soil is 5 cm, the limestone thickness will be 10 cm and vice versa. Eventually, the treated solution was collected at effluent pipe for every 6 hours interval of the stated 30 to 48 hours retention time. The effluent was tested for pH and 15 ml of the effluent was collected to measure the Fe concentration by using ultraviolet–visible spectrophotometry (UV-Vis spectrophotometry).

Table 1. Design of experiment.

| Experiments | Initial Fe concentration (ppm) | Peat soil thickness (cm) | Retention time (hour) |
|-------------|--------------------------------|--------------------------|-----------------------|
| 1           | 50                             | 5.0                      | 48                    |
| 2           | 50                             | 10.0                     | 48                    |
| 3           | 75                             | 7.5                      | 30                    |
| 4           | 75                             | 7.5                      | 30                    |
| 5           | 100                            | 5.0                      | 48                    |
| 6           | 100                            | 10.0                     | 48                    |

3. Results and Discussions

Peat soil characterization analysis was performed to identify the chemical composition and physical properties via CHNS and SEM-EDX. In general, the main composition of the peat soil is organic content which is carbon. The characterization needs to be done to identify the percentage of the carbon content and other element that exist in the peat soil sample. The SEM-EDX was conducted to support the finding from the CHNS analysis and to provide the physical structure of the peat soil.

3.1. SEM-EDX analysis
Figure 4 shows image of the pulverized peat soil under 500 times magnifications by microscopy analysis of the SEM. Porous structure on the peat soil surfaces are clearly visible. The precipitation and absorption of Fe onto the peat soil surfaces are possible due to the porous structure and irregular surfaces. The irregular surfaces enhance the chances to capture the tiny Fe component. It was unclear whether the pores within the particle itself is inter-connected or not. Nonetheless, previous study by Syafalni et al. [9] showed that it is highly possible that the closed “honey comb” pore tunnels with straight path within the peat soil particle enhance the porosity of the material.

Figure 5 shows the result of EDX analysis of the peat soil before the synthetic AMD flowing through. Half of the volume in the peat soil sample is Calcium (Ca) (50%), followed by Silica (Si) (25.8%), and Aluminium (Al) (14.0%). A higher Ca composition helps to increase the alkalinity of the AMD to stabilize pH level. Presence of Al and Si elements in the peat soil sample are due sand or soil that formed naturally in the peat soil. This is the reason why most of researchers utilize pure organic substrate to avoid or reduce presence of heavy metal elements in organic substrate layer in their studies. The presence of a high heavy metal element in organic substrate might increase the heavy metal concentration in AMD during treatment process. Meanwhile, the carbon content obtained from EDX analysis is 6.24 %. It is noted that there is no Fe element in the natural condition.

Figure 4. SEM-EDX Analysis: Image of peat soil under 500 times magnifications.
3.2. CHNS analysis

CHNS analysis was conducted by using carbon analyzer. The elements that can be traced by this equipment other than carbon are hydrogen and nitrogen contents. Table 2 shows result obtained for the peat soil sample, where carbon content is 10.7% while hydrogen and nitrogen are 1.2% and 0.17%, respectively. The peat soil sample can be classified as low carbon content compared to other organic substrates. The percentage of carbon content obtained from CHNS and EDX are slightly different due to the random selection of sample for EDX analysis. The higher carbon content of organic substrate is desired, to increase the effectiveness of SRB to reduce Fe concentration via precipitation as iron sulphide (FeS). The peat soil was selected in this study due to geological formation in Malaysia, where the peat soil is locally available at a low price.

Table 2. Result of CHNS analysis of peat soil.

| Element | Weight (%) |
|---------|------------|
| Carbon  | 6.24       |
| Na      | 1.64       |
| Ca      | 50.01      |
| Al      | 14.02      |
| Si      | 25.81      |
| S       | 1.28       |

3.3. Residues analysis

Residues analysis of the peat soil are conducted to determine Fe content retain in the peat soil. Based on figure 6 graph, there are around one to four percent of the Fe exist within the residue samples. The highest value of Fe content is 4.08% from Experiment 6. While the lowest value is 1.09% obtained from experiment 3. The average value is 2.4% of Fe content. The results show that the iron content precipitated on the peat soil is influenced by the amount of the peat soil and the retention time. For instance, Experiment 2 and Experiment 6 was conducted by applying the highest amount of peat soil and the longest retention time. The use of the least amount of peat soil in Experiment 1 and Experiment 5 led to saturation and exhaustion due to the reduction of the available surface of the peat soil. While Experiment 3 and Experiment 4 was applying a moderate amount of the peat soil but conducted in the shortest retention time. The results for both experiments are recorded among the lowest value of Fe content.

The results prove the effectiveness and ability of the peat soil to absorb or allow the iron to precipitate onto its porous surface. As compared to the composition of natural peat soil with no traces of Fe content. More sustainable iron removal by absorption mechanism was achieved when the amount of the peat soil increased and less amount was prone to the exhaustion problem over a long period.
8

Exp. 1
Exp. 2
Exp. 3
Exp. 4
Exp. 5
Exp. 6
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Fe
Fe (Mass %)
Experiment

Figure 6. Result of percent Fe in peat soil residues.

4. Conclusions
It is characterized that the peat soil formed with porous structures. Carbon element exists and its composition helps to increase the alkalinity of the AMD to stabilize pH level and precipitate iron as FeS. The amount of peat soil and retention time affects the Fe content trapped in the peat soil residue. The use of the peat soil for AMD treatment in the SAPS method is applicable and can be used as an alternative organic substrate. However, the favorable outcome of the treatment is reliant on the amount of the peat soil and the retention time. The characteristic of the peat soil is essential to understand its grain structure and absorption ability.

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