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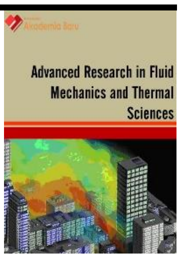

Removal of Selected Heavy Metals in Acid Mine Drainage using Chemical Precipitation Method

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ABSTRACT

The major problem confronting Acid Mine Drainage (AMD) in the mining industry is the remediation method. Active treatment used large amount of chemicals and normally require high cost to operate. Treatment causes other environmental problems such as the production of sludge. While long duration mechanism took from passive treatment is a disadvantage for industry. Although passive treatment is less costly compared to active treatment, it usually takes months or years to treat the AMD from mining and only applied at abandoned mining site. In addition, passive treatment requires greater space during the treatment processes. Insufficient land use and unsuitable topography nowadays makes passive treatment hard to apply. Due to that reason, batch tests have been conducted to study on the diffusion of alkaline in different length and concentration of modified ceramic membrane. The optimal surface area and alkaline concentration were identified in order to develop semi-passive treatment experiment. Column experiment had been conducted to study on the efficiency of semi-passive treatment for neutralization of AMD. Results shows that chemical diffusion increased with increased of alkaline concentration and different surface area also influenced rate of diffusion. A total alkalinity for 20g is highest compared to 5g at 40250 mg/l and 23750 mg/l, respectively. Larger surface area makes alkaline particles easily spread. Therefore, ceramic membrane with 8cm gives the largest surface area compared to 2cm ceramic membrane. Results from sampling and analysis of treated effluent on a daily basis over 4 months period show the efficiencies of column experiment for increasing pH and alkalinity, removing of $SO2^{4-}$ and selected heavy metals from effluent. As the time duration of semi-passive depends on the alkaline concentration in the column, thus it suffers limitations once the alkaline material is fully utilized. Column experiments showed a high percentage of heavy metals removal, with removal values of Cadmium, Ferum, Manganese and Zinc at 22.73%, 93.24%, 88.88% and 98.50%, respectively. Extensive research should be conducted thoroughly to obtain the optimum performance and characterization of semi-passive treatment for AMD by using different media as absorbents, such as polyurethane or activated carbon.

Keywords:
Acid Mine Drainage, Active Treatment, absorbents

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1. Introduction

The mining industry is one of the main contributions in countries such as Japan, Korea, USA and Malaysia. However, huge demand from these industries results in environmental problems encountered in mining application nowadays. Acid Mine Drainage (AMD) naturally occurs from the oxidation of sulphide minerals such as FeS_2 with presence of oxygen and water producing acidity, sulfate and iron. Even though it naturally occurs, the mining process accelerates AMD generation because mining will increase the exposure of sulphide minerals to water, air and microorganisms.

Based on previous study, the removal of heavy metals using chicken eggshells has the capacity of 1.57-387.51mg/g for Cd^{2+}, Pb^{2+} and Cu^{2+} [1]. The treatment of heavy metals was performed by precipitation using lime and sulphides, followed by ion exchange resulted purified water from acid mine that offered flexible and low cost [2]. Other than that, the total 100% removal of Iron, Lead and Cadmium with the improvement of pH by 1.6-fold at AMD using sandstone [3]. Furthermore, limestone of Vistea was successfully removed heavy metals of Fe, Cd, Zn and Cu using precipitations methods [4]. While MetX or specifically known as 1,3-benzenediamidoethanethiol dianion was discovered to remove more than 90% of problematic metals from AMD samples [5]. Substantial amounts of heavy metals like Fe, Cu, Zn and pyrite still contained in the tailings even after 40 years as it exposed to the environment [6]. There is also a technique called as *"Phytoremediation"* to remove heavy metals in the environment as reviewed by [7]. However, the efficiency of the technique will be affected by the temperature and climatic conditions.

Thus, there is an economic burden due to the high cost of maintenance and chemicals [8,9]. Alternatively, implementation of passive treatments such as wetland or bioremediation as a single permanent solution for AMD has much lower cost than active treatment. Mentioned by [10], the prevention of AMD generated can be done by analyzing the chemical reaction that produced and reaction by microbial that catalyzed the mentioned process. As compared to active chemical treatment, passive treatment normally required longer retention times and greater space, and thus will increase the long-term cost.

Thus, the aim of this study is to investigate the possibility of a semi- passive treatment to deal with the limitation of both active and passive treatment method. A system using a column method can reduce the requirement for continuous maintenance and alkaline chemical, requiring less energy consumption than active treatment and being more efficient than passive treatment. Thus, to achieve the objective of this study, several batch tests were conducted to study the diffusion of alkaline chemical with different surface areas and concentrations of Calcium Carbonate (H_2SO_4) to identify the optimal surface area and alkaline chemical concentration to be used in column experiments.

2. Methodology

2.1 Batch Test

Batch tests were conducted to study the diffusion alkaline chemical and to identify optimal surface area and porous media to be used in the column experiment. A commercial ceramic water filter was modified, filled with alkaline chemical, and covered with silicon caps on the top and bottom. This porous media was cut into desired lengths of 2cm, 4cm, 6cm and 8cm to study on the effects of surface area. For diffusion in the alkaline chemical study, each 4cm ceramic membrane was filled with 5g,10g, 15g and 20g of $CaCO_3$, respectively. Each ceramic membrane is soaked into acidic deionized water (pH=3) until the pH turn alkaline (pH=9). Initially, AMD was sampled every hour for the initial 6 hours and then continuously sampled every 6 hours. Total alkalinity for each sample was done at 0.5N HCl.

2.2 Experimental Set-up

Figure 1 shows the experimental set up consisting column experiments were conducted using the acrylic pipe 8.7cm diameter and column length of 15 cm. 50 litre containers functioned as a storage container for influent AMD fed against gravity to the column through Tygon tubing. Therefore, storage was placed in higher position than the column. Flows were controlled with peristaltic pumps at flow of 1 RPM as it is optimal for this experiment. At the beginning of the experiment, different RPMs were used in order to find the optimal speed used along the experiments. Columns were filled with modified ceramic membrane, gravels and a nylon mesh disk. The nylon mesh was used to prevent clogging at the influent and effluent ports. Rubber O rings were used in both top and bottom cover to prevent leaching. Two sizes of gravel were used; the small size was placed at the bottom of the column to minimize clogging at the inlet tube, while the large size gravel was placed in the middle and in between ceramic membrane and acrylic column in order to adjust void volume. The experiment ran for about 4 months until the effluent pH reached acidity or was equal to the influent.

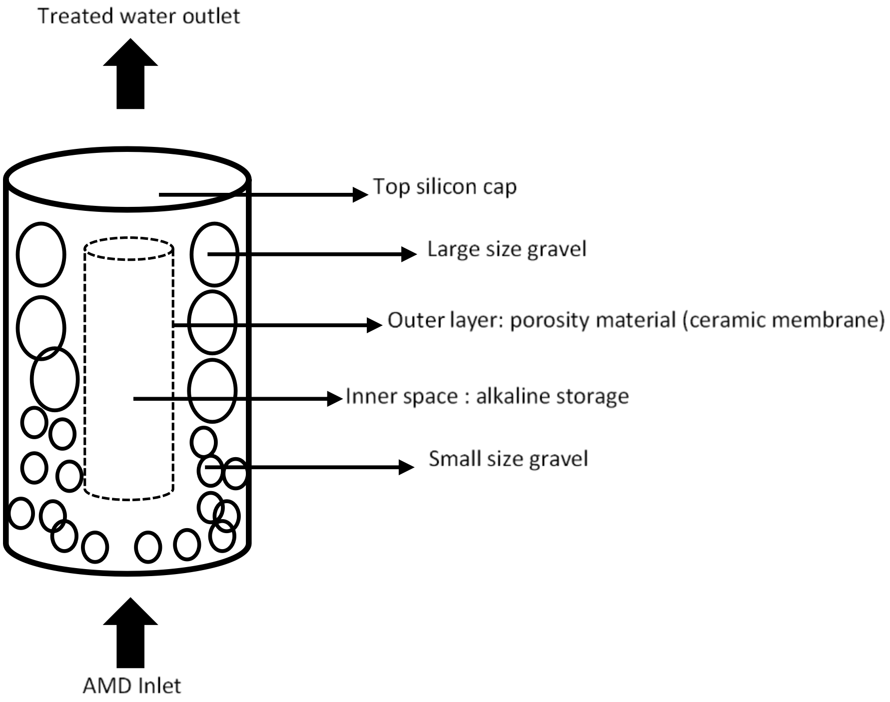


Fig. 1. Column test design

2.3 Synthetic of Artificial AMD

Artificial AMD was synthetized as per [11,12]. Initial pH of artificial AMD was adjusted to 3.0 for column experiment. pH was adjusted using 1 M H_2SO_4 solution. The composition of chemicals used for 10 L artificial AMD shown in Table 1 below. All chemicals were added in 1 L of deionized water and stirred in 24h for heavy metal dissolution.

Table 1
Composition of Synthetic of Artificial AMD

Component	Concentration (mg)	Source Formula
Fe^{2+}	3848.8	$FeSO_4.7H_2O$
Mn^{2+}	307.7	$MnSO_4.H_2O$
Al^{3+}	453.7	$Al_2(SO_4)_3.18H_2O$
Zn^{2+}	312.7	$ZnSO_4.7H_2O$

2.4 ICP-OES Analysis

The main objective of ICP-OES is to define the concentration of certain elements in the samples. The first step in ICP analysis is sample and standards preparation as an introduction to the ICP. In this experiment, 10 ml of AMD samples was filtered using a 0.45µm syringe filter before running the tests.

2.5 Material Analysis

The surface characterization will be performed using Fourier Transform Infrared (FTIR). The purpose is to identify the types of chemical bonds or functional groups present in a sample (gravel).

3. Results & Discussion

3.1 Batch Test

The alkaline chemical used in the test is $CaCO_3$ with different amounts for each 4cm modified ceramic membrane. From the experiment that had been carried out, chemical diffusion increased with the increase of concentration. According to the graph shown in Figure 2, 20 g of concentration has the highest total alkalinity at 40250 mg/l while the smallest is 5g concentration of $CaCO_3$ with 23750 mg/l. Based on the test conducted, $CaCO_3$ could increase pH from 3.0 to 9 in 6 days, as shown in Figure 2. Also, Figure 2 shows that the value of total alkalinity for 5g of $CaCO_3$ was higher than 10g of $CaCO_3$ by 1.4-fold as the surface area to volume ratio will influence the rate of molecules moving in and out of the ceramic, due to the length of the path that the molecules must take [13]. Consistent alkalinity-diffusion showed that a modified ceramic membrane and higher amount of $CaCO_3$ are suitable as alkaline materials to be used in the column test. This is because the differences in concentration influenced the rate of diffusion of molecules, and molecules will diffuse from high concentration to low concentration. This is because the differences in concentration influenced the rate of diffusion of molecules, and molecules will diffuse from high concentration to low concentration [14].

Based on the graph shown in Figure 3, the average value for total alkalinity levels of 6 cm and 8 cm were higher than 2 cm and 4 cm by 1.5-fold. This is because the surface areas of 8 cm and 6 cm ceramic membranes were higher; thus, more particles that are alkaline could spread easily as there was more area to travel by the alkaline materials. As reported by [13], the surface area to volume ratio will influence the rate of molecules moving in and out of the ceramic, due to the length of the path that the molecules must take. In this study easier get inside the ceramic membrane. Smaller masses have higher random velocity that is correspondent, 8cm has highest surface area compared to 2cm, 4cm and 6cm; thus, AMD molecules will to faster diffusion. Another factor leading to higher random velocity is ambient temperature, as a higher temperature will increase the random velocity.

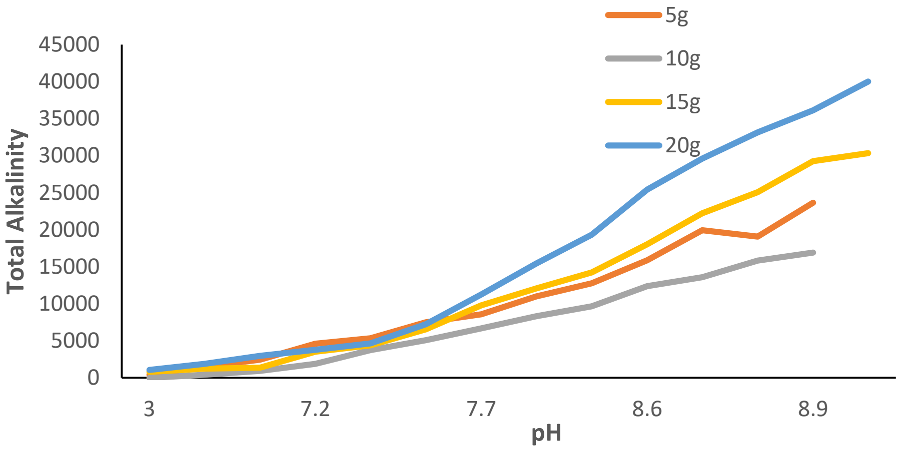


Fig. 2. Total alkalinity Vs pH for alkaline diffusion test

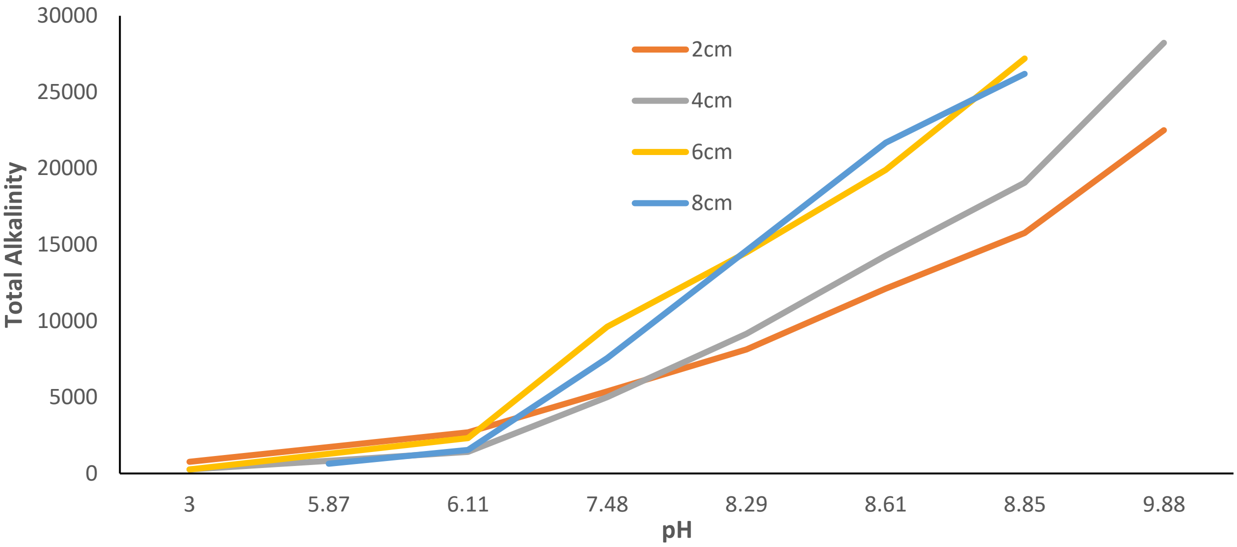


Fig. 3. Total alkalinity vs pH for effects of surface area

3.2 Column Test

Increasing pH is the main process for neutralization of AMD. Figure 4 shows the variation of the output pH along the experiments that had been carried out. Overall, it was observed that for each sampling column, the pH influent was lower. However, as AMD passed through the column, the value of pH was generally found to be increased rapidly. This would indicate that the alkaline material in the column was active and increased the pH value. Thus, the process generated the alkalinity and precipitation processes. According to Figure 4, the pH value for raw AMD was unstable due to AMD being added each time the volume in storage reached a minimum volume from 14 October 2017 until 26 October 2017. In addition, human error during the adjustment of pH for new AMD to pH 3 also gave influenced in the variance of pH. Once the errors were eliminated, it was observed that the variance of pH became more stable. As the AMD solution reacted with alkaline inside the column, the output pH appeared to increase slowly until it reached the end point. The test took almost four months for the AMD neutralization to reach the end point. As shown in the graph, the pH from treated AMD in each column increased to the alkaline level during the experiments. Each column had a variety of material as filter medias with gravel, activated carbon, polyurethane and polyurethane mixed with magnesium oxide used in column 1, column 2, column 3, and column 4, respectively.

Among all the columns, column 4 shows that even after four months of neutralization process, the pH still in alkaline state compared to other columns such as column one, two and three. For column one, two and three, the pH fluctuated and after two months of treatment, the pH changed drastically to an acidic state. These acidic conditions continuously occurred for column one, two and three and almost reach to the pH of raw AMD. This showed that the alkaline materials in those columns were completely utilized at that particular time. Thus, it is proved that AMD neutralization using semi-passive treatment has time limit and alkaline material used in the column should be changed after reached its end life. As the pH of AMD increased, those dissolved metals in AMD were precipitated. However, pH values for complete precipitation varied for each metal. The Fe^{2+} can be oxidized to Fe^{3+} through aeration in the presence of limestone as neutralizing agent in the range pH of 4.5 to 8.0, the Fe^{3+} were removed in the form of $Fe(OH)_3$.

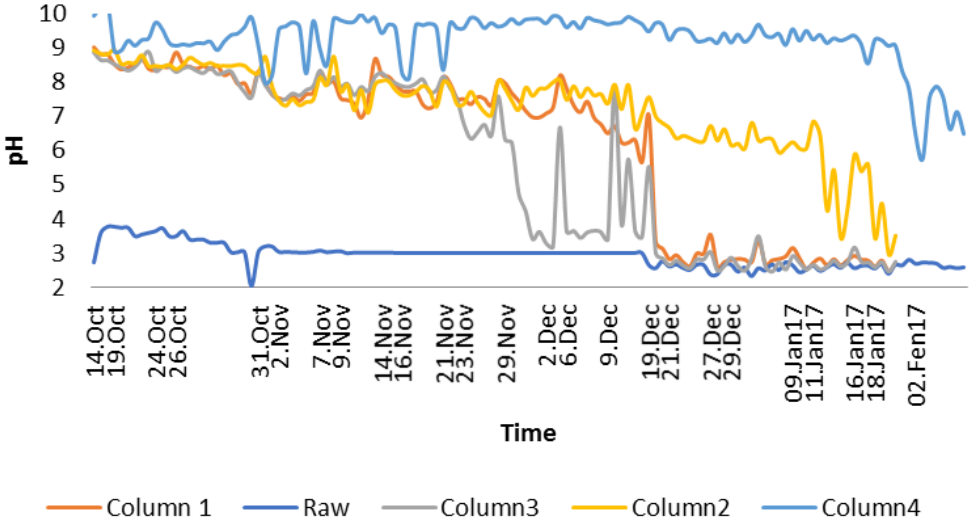
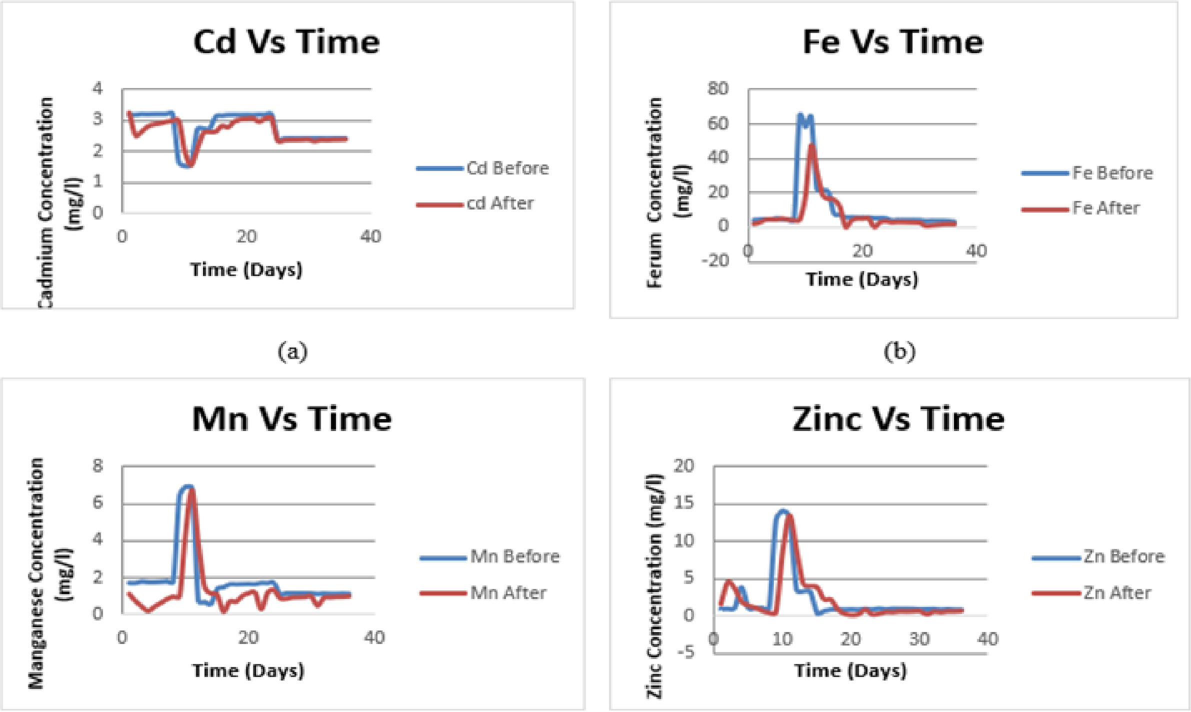


Fig. 4. Effects of pH for each column used

Figure 5 shows the trend reductions of selective heavy metals (Cd, Fe, Mn, Zn). Graph (a) refers to cadmium concentration before and after treatment. The maximum highest concentration before treatment for cadmium is 2.71mg/l, reduced to 2.10 mg/l after being treated. The percentage of heavy metals removal is about 4.96 mg/l and the concentration was reduced to 4.39 mg/l after the treated AMD flow through the modified ceramic membrane. Thus, the percentage of heavy metals removal for Fe was about 93.24%.22.72% at pH 2.73. Based on graph (b), initial concentration of heavy metals is higher before the treatment and became much likely the same in the end of the treatment. The highest concentration of Fe before the treatment was 64.96 mg/l and the concentration was reduced to 4.39 mg/l after the treated AMD flow through the modified ceramic membrane. Thus, the percentage of heavy metals removal for Fe was about 93.24%.

For manganese, highest concentration before treatment from ICP-OES is 3.19 mg/l. After treated, the concentration reduced to 0.20 mg/l and the percentage of removal reached about 88.88%. Highest zinc concentration before treatment is 3.17 mg/l then reduced to 0.01 mg/l after treated which give percentage of removal is 98.50%. Since the solubility of many metals can be described as amphoteric [15,2], the solubility for mixed metals differs based on pH. Manganese hydroxide and carbonate for example is generated at higher pH (>7.8) as reported by [9 and 16]. Fe3+ is removed as Fe (OH)3 within the pH range of 4.5 to 8.0 with Zinc precipitate at a minimum pH 8.4. The removals of selected metals such as Cd, Fe, Mn and Zinc in this study are at pH 2.73, 2.98, 2.81 and 2.82.

respectively. The removal achieved in this study was different from theory. Heavy metals concentrations might have been precipitated during pH adjustment due to the new AMD added each time the storage achieved its minimum volume. The situation also results in negative value for Zinc removal, as shown in Figure 6, due to lower Zinc concentrations in raw AMD. Zinc concentration lowered due to the additional of new AMD into the storage once it achieved minimum volume. pH adjustment after the additional new AMD also influenced the concentration of each heavy metal in the storage.



(a) (b)

(c) (d)

Fig. 5. Reduction trends of selective heavy metals

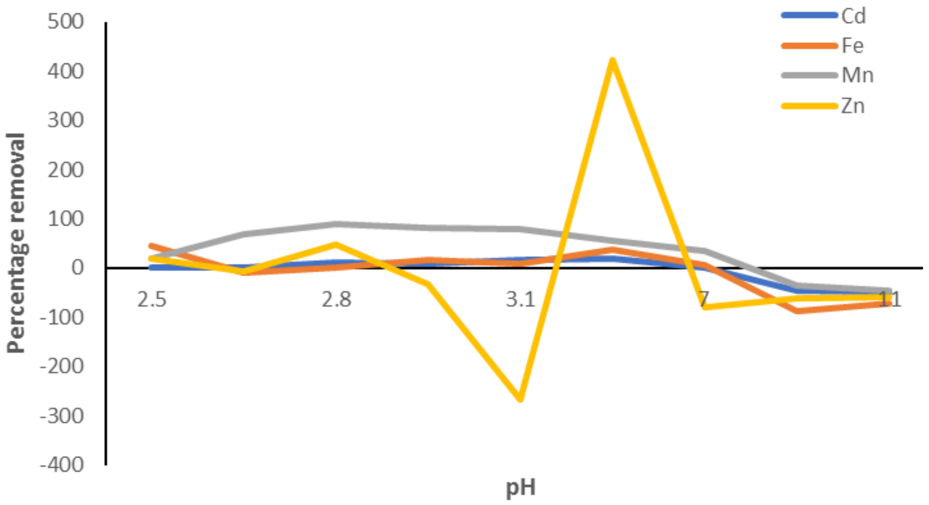


Fig. 6. Heavy Metal removal vs pH

FTIR analysis was conducted to find specific functional groups and chemical properties of the precipitants after the neutralization of AMD in a column test. FTIR developed using infrared (IR) radiation. IR radiation with less than 100 cm-1 frequency is absorbed and converted by an organic molecule into energy of molecular rotation. while IR radiation in the range from about 10,000 – 100 cm-1 is absorbed and converted by an organic molecule into energy of molecular vibration. Both absorptions are quantized but in different vibrational spectra. The vibrational spectra for IR radiation in range 10,000 – 100 cm-1 appear as bands rather than as lines such IR radiation for frequency less than 100cm-1 because of the single vibrational energy change in accompanied by a number of rotational energy changes. The vibrational–rotational bands occur between 4000 and 400 cm-1. The frequency or wavelength of absorption depend on the relative masses of the atoms, the force constants of the bonds, and the geometry of the atoms.

The two important areas for an examination of a spectrum are regions at high frequency portion, 4000- 1300 cm-1 and low frequency portion, 900- 650 cm-1. The high frequency portion, called the functional group region, has characteristics stretching frequency for important functional group such as OH, NH and C=0. The intermediate portion of spectrum, 1300 - 900 cm-1 is referred to as “finger-print” region. The absorption pattern is frequently complex, with bonds originating in interacting vibrational modes. Absorption in this intermediate region is unique for every molecular species. A nonaromatic structure is generally indicated at low region, 900- 650 cm-1 due to the lack of strong absorption bands.

The purpose of FTIR analysis was conducted in this study is to find the specific functional groups of the precipitants. For treated AMD, Figure 7 shows a comparison of IR radiation for each sampling point for column 1. The samples collected at three points are shown in Figure 7. Three different samples were selected in this analysis to study on the attachment of precipitant at three different locations of the column.

Fig. 7. Sampling point for column 1

Peaks in the range of 350– 3850 cm-1 bands were observed and show three main common absorptions as shown in Figure 8. At point (a), the wavelength was between 350 – 850 cm-1. This means that at this point it is a nonaromatic structure. The Nonaromatic is generally indicated at low region, 900- 650 cm-1 due to lack of strong absorption bands. The point (b), the peak is 1350 cm-1, which is recognized as C-H. While at point (c), the wavelength has very distinct strong and broad shape located between 3570- 3200 cm-1. When there are elongated “U-shaped around this region, there is an alcohol group, O-H . Bands at point (c) attributed to a combination of OH stretching from hydrogen bonding and free Si-OH. Any critical peak could not have been found at sampling point 1, which means that gravel at the point compound does not involve any reaction with carbon groups.

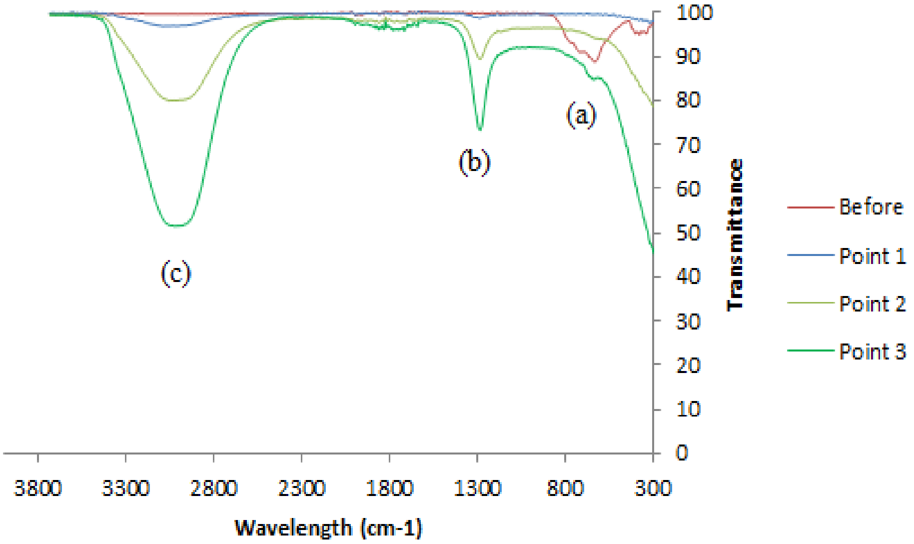


Fig. 8. FT-IR spectra for Column 1 before treatment and after treatment

4. Conclusion

Based on the findings as discussed above, the semi-passive method is suitable and efficient for AMD remediation since this method offers less energy consumption, is cheaper and only needs a minimum maintenance compared to active treatment method. In addition, semi-passive is also effective in AMD neutralization in terms of non-electric condition and its ability to change the pH value from acidic to alkaline of AMD and has high potential in heavy metal removal (~98%).

The time duration of semi-passive treatment depends on the alkaline concentration in the column. Therefore, each time the column has reached its limitation, the alkaline material in the column must be changed. It is recommended that a further study be conducted for the column experiment with different media used as an absorbent in order to obtain the optimum performance and characterization of semi-passive treatment for AMD by using different media as absorbent such as polyurethane or activated carbon. To reduce the effects due to the technical problems and human error occurred during the study, it is advised to use appropriate and consistent methods to evaluate the effectiveness of metal removal by chemical precipitation. As for recommendation for future research, more characterization to support on removal of selected heavy metals contained in AMD using chemical precipitation method.

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