Aluminium recovery from water treatment sludge under different dosage of sulphuric acid

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Abstract. Aluminium sulphate Al\(_2\)(SO\(_4\))\(_3\) known as alum is commonly added chemical in coagulation-flocculation process in water treatment plants. Despite of its effectiveness in treating the water, it produces high volume of residual alum sludge to be discarded to sludge lagoon. Therefore, sludge disposal is one of the main drawbacks in water treatment plants as it requires large footprints to store the residual sludge before being dumped at landfills. The sludge still contains high concentrations of aluminium that can be recovered for further use. Acidification process using sulphuric acid is investigated in this study to recover the aluminium from sludge. Different dosage of sulphuric acid ranges at 0.45 – 1.80M at constant weight of alum sludge at 300g were analysed to obtain the maximum percentages of aluminium recovery. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to analyse the recovered aluminium concentration. Besides the element of aluminium, other elements such as Ferum (Fe), Calcium (Ca) and Potassium (K) were also recovered through the acidification process. It was found that element of aluminium shows the highest concentration. The optimum recovery of aluminium was attained at alum sludge 300g and dosage of 1.35M sulphuric acid in which the recovery ratio at up to 98%. This shows that the aluminium present at high concentration in the sludge and if the sludge is dumped at landfills, the remaining aluminium will affect the environment. Furthermore, it is recommended that the recovered aluminium from water treatment sludge has the potential to be an alternative coagulant element in water treatment process.

1. Introduction
Aluminium has been used for essential pre-treatment by water industries around the world including Malaysia in water purification processes [1]. Aluminium (Al) salts sheets are used as Aluminium Sulphate (Alum) as the primary coagulating-flocculating agents [2,3,4]. It is to make sure that water sent for domestic use is free of solid particles.

Aluminium Sulphate, Al\(_2\)(SO\(_4\))\(_3\) coagulates with solids particles forming alum sludge. Alum sludge is a by-product of the water treatment plants specifically generated from the coagulation-flocculation processes and settles at the bottom of water treatment plants together with the solid particles. In
Malaysia, more than two million tonnes of alum sludge are produced annually from water treatment plants [5] and usually disposed to landfill or stored in the sludge lagoon at the treatment plant as residuals. As the production of alum sludge will continuously increase in the future, hence, more land area is required to dump the alum sludge. Nonetheless, due to the additional cost in providing larger footprint for storage of sludge in the treatment plant and finding new landfill, researchers are now looking for alternative ways to convert the residuals into useful resources. The study was intended to discover capabilities of residuals alum sludge to be an added value product and reduce pollution. Therefore, replacement of these unwanted wastes into a recycle resources can provide alternatives solution from depending on raw resources to obtain aluminium [6].

Recovery of aluminium in water treatment plant can be a significant approach towards sustainability development. Aluminium can be recovered to enhance the utilization of using recycle Aluminium Sulphate Al2(SO4)3 in the industry especially in the coagulation of the water treatment. According to Dassanayake [1], many studies have been conducted to determine the possibilities of aluminium recovery and their effectiveness which is an environmentally sustainable manner remains a significant social and environmental concern. Therefore, recovery of aluminium will decrease the usage of fresh coagulant in the water treatment industry. In addition, alum sludge recovery reduces sludge volume by-product of water treatment process for easy handling [2,4].

Acidification is one of the processes applied to the alum sludge to recover and extract the aluminium [7,8]. Sulphuric Acid, (H2SO4) used as the acidification agent in the recovering of the aluminium and the process also will extract other chemical contaminants and heavy metals. Acidification plays a significant role in neutralizing alum flocs by leaching the aluminium concentration to the supernatant solution [8,9]. A few researchers assert that the effectiveness of acidification process to concentrate alum salt from sludge is high when pH is low [7,10,11]. Besides the types of extractant (acid) and its dosage, there are some other factors that affect the recovery of aluminium at the optimum point. Stirring speed and centrifugal time will have an effect on the precipitation period, aluminium recovery and percentage of recovery efficiency [8]. Other researchers found that the time for acidification reaction towards alum sludge is between 30 to 60 minutes [15]. The time interval also allows the sludge to settle down instead of reaction time of the sulphuric acid to react with alum sludge. Lin [15,16] found that in order to do an acidification process, the alum sludge can also be used to remove phosphate in treatment plants. The acidification process has a high potential in removing the phosphate contain in alum sludge [17].

In terms of sludge weight, Cheng [8] used different sludge amounts between 60 – 300 g/l. When the aluminium concentration is increased, the ammonium removal effectiveness increases and ammonium alum creation is upgraded. For the most part, when the sludge focus is 300 g/L, an ammonium removal efficiency of 69% can be accomplished. Based on this removal efficiency, this study adopted the 300 g of sludge as the constant weight.

This study is to investigate the effect of acidification towards recovery rate of aluminium with different dosage of sulphuric acid. Hence, the gap of the study is using a constant weight of alum sludge and to determine the optimum aluminium recovery under a ranges of acidification process. There is variation can be compare with the other research on supporting the capacities of acidification processes. Further explanation on the method and materials are discussed in the next section.

2. Materials and method
2.1. Sludge sampling and preparation
The sludge sample was taken from Syarikat Air Darul Aman (SADA), Kulim, Kedah. Aluminium based coagulant was used in the primary treatment process at the water treatment plant (WTP). The WTP was designed for 400,000 populations equivalent (PE) which provides water demand from the residential and industrial areas in Kulim, Kedah. The sludge sample was transported to the laboratory. It was dried in an oven (Model: Binder ED720) at 105°C for 24 hours to remove the moisture content present in the sludge until a constant weight was obtained. Then, the dried sludge was sieved through a 2 mm wire mesh pan to remove debris and stones. Following that, the dried sludge was crushed and
sieved again using wire 16-mesh sieve pan. The sieve sludge was kept in a clean and dry container until usage. In this study, only particles of sludge that passed through the 16-mesh sieve was used as adopted by others[8]. Then, the dried sludge was weighed by using electronic weighting balance which is 300g for six samples. All the samples were mixed with 1000mL of distilled water for each sample. Samples were mixed using magnetic stirrer at 30 rpm for 30 minutes until it become homogenous.

2.2. Extraction and acidification process

| PHASE 1 | Sludge Sampling (Alum Sludge) From Syarikat Air Darul Aman (SADA) |
|---------|--------------------------------------------------|
| PHASE 2 | Dewatering Process The sludge was dried at 105°C for 24 hours |
|         | Extraction Process Mixed the constant weight of dried sludge with 1000mL of pure water using jar test apparatus |
|         | Optimum Acidification Process Sample mixed with various molarity (M) of H₂SO₄ |
|         | Mixing Process Mixed the sample by using stirrer at 30 rpm for 30 minutes |
|         | Filtration Process Extract the sample at supernatant layer and filtrate using suction pump |
|         | Final Aluminium Concentration The determination of final aluminium concentration using ICP-OES |

**Figure 1.** Framework of the study

In this study, distilled water was used as solvent to dissolve dried sludge to form sludge in liquid mixture. Sulphuric acid (H₂SO₄) was used as the acidification agent with several specific molarity between 0.45M – 1.80M. The efficiency of these solvent and extractant in the acidification process were evaluated at a constant amount of sludge weight. Figure 1 illustrates the overall framework of the study which involved four phases of laboratory work. The first phase involves sludge sampling and preparation. The second phase is the extraction and acidification processes while the third phase is the separation process by filtration. The final phase involves the determination of concentration extracted aluminium using Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) (Model:PerkinElmer® OptimaTM 7300 DV, Inc. Shelton, CT, USA) machine. ICP-OES was equipped with WinLab32™ for ICP, Version 4.0 software for simultaneous measurement of all analyte wavelengths of interest [18].
The acidification process is to leach out the aluminium from the sludge [7,8]. The time for acidification reaction towards alum sludge is between 30 to 60 minutes. The time interval also allows the sludge to settle down instead of reaction time of the sulphuric acid to react with alum sludge [15]. In this study, each sample was mixed for 30 minutes at 30 rpm. The temperature of the magnetic stirrer was adjusted to 10°C [15,16].

After the reaction process, the samples were filtered with 16 μm of filter paper by using filter funnel and conical flask. After using 16 μm size of filter paper, the sample was filtered again with 12 μm size of filter paper by using suction pump. The filtration process was repeated two times to ensure the sample is clean from any particles that can affect the reading of aluminium concentration. Fifty (50)mL of sample was added into the tube and preserved at 10°C. Then, the preserved sample was set at room temperature at about 27°C – 30°C prior to determine the aluminium concentration using ICP-OES. The ICP-OES machine can only read the samples if the samples are at their certain temperature [19]. Room temperature is the best temperature to get an accurate result from ICP-OES.

ICP-OES is an instrument in which a procedure to determine the composition of elements in water dissolved samples by using plasma and a spectrometer. The instruments provide a technique which are reliability, multi-element options and high throughput. A 23-element standard (V23, PerkinElmer, Shelton, CT, USA) for ICP-OES was used as the stock solution for preparing sample standards. The samples were transferred in ICP-OES vials and were prepared by standard dilution process. Then, the concentration of elements was controlled by the calibration curve. The accuracy of the calibration curve was confirmed by calibrating with a V23. The calibration curve was linear across the entire range with a correlation coefficient of at least 0.999 for all elements [18]. There are 23 elements concentration were obtained as the results from the ICP-OES. The results were transferred and tabulated in excel template.

Apart from that, the results of the experiment are the effects of the temperature, mixing rate, mixing time and pH value. The effective temperature towards recovery rate of aluminium is 10°C [15,16]. Moreover, 30rpm of mixing rate with 30 minutes of mixing time is one of the best mixing rate and mixing time [15]. The temperature, pH, mixing rate, mixing time, amount of distilled water and amount of sulphuric acid, \(\text{H}_2\text{SO}_4\) are controlled after considering the results of previous research. The initial pH of sample (alum sludge and sulphuric acid) was pH 3.3. It was takes about 30 minutes for sulphuric acid to react with the alum sludge and leach out the aluminium in the sludge. In addition, during mixed the sludge with the acid, the mixture supernatant was turned to dark brown murky coloured liquid and lathered. Those reaction was indicated the acidification process was leached out the aluminium from the alum sludge.

3. Results and discussion

Table 1 shows that the reading of aluminium concentration in sludge sample with various molarity of \(\text{H}_2\text{SO}_4\). In order to determine the optimum dosage of \(\text{H}_2\text{SO}_4\), the weight of alum sludge should be fixed. In this experiment, the weight of sludge used was 300g and the molarity of \(\text{H}_2\text{SO}_4\) was varied from 0.45M, 0.90M, 1.35M and 1.80M. The initial reading of aluminium concentration is the same due to the same weight of sludge which is 4.093 mg/L. From the results obtained, the range of final aluminium concentration is between 61.530 – 256.639 mg/L.

In order to recover the aluminium in sludge, the acidification process is able to leach out several elements. With ICP-OES technique, there are 23 elements that are obtained from the acidification processes. The four significant elements recovered from the acidification process were aluminium (Al), Ferum (Fe), Calcium (Ca) and Sodium (Na). Al has the highest concentration in the sludge. Figure 2 shows the concentration of Al, Fe, Ca and Na recovered from the acidification process.
Table 1. Aluminium concentration with fixed weight (300g) of sludge and various molarity of H$_2$SO$_4$.

| Weight of Alum Sludge, (g) | pH | Mixing Rate, (rpm) | Mixing Time, (min) | Distilled water, (mL) | Molarity of H$_2$SO$_4$ (M) | Initial Aluminium Conc. (mg/L) | Final Aluminium Conc. (mg/L) | Ferum Conc. (mg/L) | Calcium Conc. (mg/L) | Sodium Conc. (mg/L) |
|---------------------------|----|-------------------|-------------------|-----------------------|----------------------------|-------------------------------|-------------------------------|-------------------|-------------------|-------------------|
| 300                       | 3.4 | 30                | 30                | 1000                  | 0.45                       | 4.093                         | 176.540                       | 109.024           | 39.555            | 11.185            |
| 300                       | 3.3 | 30                | 30                | 1000                  | 0.90                       | 4.093                         | 189.540                       | 119.814           | 37.474            | 8.356             |
| 300                       | 3.3 | 30                | 30                | 1000                  | 1.35                       | 4.093                         | 256.639                       | 172.731           | 40.788            | 8.911             |
| 300                       | 3.2 | 30                | 30                | 1000                  | 1.80                       | 4.093                         | 61.530                        | 49.798            | 32.126            | 10.023            |

Figure 2. Recovery of other significance chemical elements from different dosage of acidification process.

Based on figure 2, at 0.45M amount of H$_2$SO$_4$, the acidification process also recovered ferum concentration which is 109.024 mg/L, calcium concentration which is 39.555 mg/L and sodium concentration which is 11.185 mg/L. Apart from that, at 0.90M amount of H$_2$SO$_4$ the ferum, calcium and sodium concentration is 119.814 mg/L, 37.474 mg/L and 8.356 mg/L respectively. Furthermore, for 1.35M amount of H$_2$SO$_4$, ferum, calcium and sodium concentration are 172.731 mg/L, 40.788 mg/L, and 8.911 mg/L respectively. Lastly, for 1.80M of H$_2$SO$_4$, the ferum, calcium and sodium concentration is 49.798 mg/L, 32.126 mg/L and 10.023 mg/L respectively.

During the acidification process of alum sludge, other elements in the sludge were leached out, hence a significant reduction of the sludge volume is expected. Most of the elements dissolved during the acidification process are minerals, and the reduction of sludge should be closed in order to recover the coagulant [7]. Therefore, the elements recovered from the sludge also contains high concentration of ferum, calcium, and sodium. There are several contaminants other than Al, Fe, Ca and Na have been leach out from the process, but the recovered of those heavy metal elements concentration is not significant. It is because the concentration obtained is low compared with Al, Fe, Ca and Na.

The results show, the molarity of H$_2$SO$_4$ yield dissimilar amount of recovered aluminium. Higher or lower H$_2$SO$_4$ molarity were not contribute towards increasing proportion of recovered aluminium. Based on the results, even though with the highest H$_2$SO$_4$ molarity, the recovered aluminium does not achieve the highest recovered aluminium. There are two factors affecting the high level of minerals recovered which are; the sludge sample may contain existing natural minerals and the H$_2$SO$_4$ in the sample are strong absorbent. Moreover, as the cycles of recovery increases, the efficiency of recovered
coagulant to remove the colour declines slightly [7]. This is because when the H$_2$SO$_4$ reacts with the alum sludge, the colour of the sample will turn to dark brown.

Table 2. Results of aluminium recovery rate with fixed weight of sludge.

| Weight of Alum Sludge, (g) | Molarity of H$_2$SO$_4$, (M) | Final Aluminium concentration, (mg/L) | Recovery Rate, (Based on Initial Aluminium concentration) (%) | Recovery Rate, (Based on Element Ratio in Recovered Sample) (%) |
|---------------------------|-------------------------------|--------------------------------------|-----------------------------------------------------------|-------------------------------------------------------------|
| 300                       | 0.40                          | 176.540                              | 97.68                                                     | 48.41                                                        |
| 300                       | 0.90                          | 189.541                              | 97.84                                                     | 49.84                                                        |
| 300                       | 1.35                          | 256.639                              | 98.41                                                     | 50.36                                                        |
| 300                       | 1.80                          | 61.530                               | 93.35                                                     | 35.41                                                        |

Table 2 shows the final aluminium concentration and aluminium recovery rate for the selected molarity of H$_2$SO$_4$. It can be seen that, the weight of sludge and the ion of H$^+$ in H$_2$SO$_4$ affect the recovery rate of alum sludge. During the acidification process, the aluminium dissolved in water sample is proportional to the quantity of the sludge. Therefore, the amount of aluminium that leach out from the sludge is also increased. The molarity of H$_2$SO$_4$ consumed in the sludge varies with the amount of sludge sample. Because of the aluminium sulphate in the sludge consume H$^+$ to dissolved with aluminium ions, the H$_2$SO$_4$ consumption rate is proportional to the sludge concentration even after adding the same amount of H$_2$SO$_4$. According to Cheng [8], the analytical result of the study confirms that 100mL of H$_2$SO$_4$ added with 1000mL of dewatering process enough to dissolve the aluminium contamination in the sludge. The recovery rate of the aluminium nearly reaches 100 % which is the highest recovery rate at 98% for 300g of alum sludge and 1.35M of sulphuric acid.

As mentioned before, there are 23 identified elements that have been leached out from the sludge. The recovery of aluminium based on ratio from 23 elements found in the sample is 50.36%. It is the highest concentration of recovered element in the sample.

4. Conclusion

Acidification process can affect the recovery rate of aluminium from the sludge. The results show that the aluminium can be leached out from the sludge after the acidification process. In this research, the minimum recovery rate of aluminium is 93% and the maximum recovery rate is 98%. The optimum molarity of sulphuric acid is 1.35M, which able to leach out the highest aluminium concentration. The highest concentration of recovered aluminium is 256.639 mg/L. Based on these findings, acidification is able to leach out aluminium from the alum sludge. Producing alternative method for extracting aluminium will promote green approach on reducing and recycling raw material usage in the industries. A lot of benefits can be derived including economic, social and environmental concerns where the usage of recovered aluminium can encourage sustainable operation especially in the water treatment industry.

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