A parametric study of alum recovery from water treatment sludge
Mohamed Ayoub and Abdallah Abdelfattah

ABSTRACT
Alum recovery from water treatment sludge is a promising technique applied to decrease usage of fresh coagulants in the water treatment industry. In addition, alum recovery reduces sludge volume for easy handling. The undertaken work investigated the parametric conditions for alum recovery procedure by acidification. The results show that alum recovery reaches up to 69.03%, and the reduction of sludge volume reaches its highest level at 90%. Moreover, results of the parametric investigation reveal that the mixing time of 60 minutes and mixing intensity of 150 rpm are the optimum conditions of mixing for alum recovery from water treatment sludge. The optimum pH level is 1.50 for alum recovery as indicated by maximum aluminum releasing, maximum reduction of sludge volume, and reasonable dosages of added sulfuric acid.

Key words | acidification, alum recovery, sludge reduction, water treatment

INTRODUCTION
Water treatment sludge is produced from consecutive processes of water treatment including coagulation, flocculation, and sedimentation processes. All through the purification processes, alum is added to raw water for removal of colloids, color, suspended solids, and other contaminants. The formed sludge is lessened in volume in the sludge tank and afterward is disposed into watercourses. Aluminum species are harmful to aquatic life including benthic life forms (Evuti & Lawal 2011; Fungaro & Silva 2014; Allerdings et al. 2015; Roccaro et al. 2015).

Alum recovery from water treatment sludge for reuse is a key alternative to sludge disposal and would decrease the chemical usage in the water industry. Even though this concept is not novel, process financial aspects and recuperated item quality have restricted its implementation as a result of releasing other metals included in the sludge with aluminum, such as manganese, arsenic, and zinc. This would limit use of the recovered coagulants. Thus, it is suggested that the recovered coagulants be utilized in wastewater treatment processes (Chen et al. 2011). On the other hand, yields of coagulants and acid recovered (i.e. the procedure proficiency) are critical to process economics as would be expected. Higher alum recovery yields suggest reduced acid consumption per unit weight of coagulant, and in addition diminished waste and decreasing demand for supplementary fresh coagulants (Keeley et al. 2012; Abdel Azim et al. 2013).

Alum is finally converted into settled aluminum hydroxide [Al(OH)₃] after the consecutive processes of water treatment. Cheng et al. (2012) mentioned that around 120,000 tons of water treatment sludge results from water treatment plants (WTPs) yearly in Taiwan, and around 30% of this sludge contains aluminum hydroxide (Babatunde & Zhaoa 2011). In addition, Evuti & Lawal (2011) declared that water treatment sludge contains about 25% to 50% of aluminum (Boaventura et al. 2000; Parakash & SenGupta 2003). Furthermore, Zhao et al. (2013) affirmed that alum sludge contains 29.7 ± 13.3% of aluminum. On the other hand, Makris & O’Connor (2007) reported that aluminum concentration in the water treatment sludge has a wide variety that ranges between 15 and 300 g/kg of the sludge, and it has a neutral pH range of 5.0–8.2. Moreover, Abdo et al. (1993) showed that water treatment sludge contains 39% of total aluminum concentration by weight after coagulation, flocculation, and clarification processes in their study.

There are four approaches to recovering alum from water treatment sludge, to be used as a primary source of aluminum-based coagulant. These methods are acidification, basification, ion exchange, and membranes. The destabilized colloids are enmeshed through water treatment,
and acidification involves neutralizing these flocs of hydroxide to release aluminum coagulant recoveries in the solution including the release of some contaminants, heavy metals, etc. (Petruzelli et al. 1998; Vaedi & Batebi 2001; Stendahl et al. 2005; Xu et al. 2009; Evuti & Lawal 2011; Abdel Azim et al. 2013).

The acidification technique is less difficult than ion exchange and simple in operation (Evuti & Lawal 2011). Additionally, acidification is more economic than membranes (Keeley et al. 2012). Moreover, the acidification technique is more productive than the basification technique for aluminum recovery from water treatment sludge. In this manner, the aluminum recovery by acid extraction at pH range of 1.0–3.0 can achieve 70–90%, and also sludge volume is reduced for easier handling (Panswad & Chamnan 1992; Evuti & Lawal 2011). On the other hand, the size of the sludge particles and the disintegration temperature are imperative factors that impact the dissolution of metal ions. When the sludge particles are small, the ability to construct complex bonds between the sludge particles and the metal ions is weak. Such frail bonds may promote the dissolution rate of the sludge. Hence, the metal is effectively broken up at pH under 2.5 (Panswad & Chamnan 1992; Abdo et al. 1993; Li et al. 2005; Xu et al. 2009; Evuti & Lawal 2011; Abdel Azim et al. 2013).

Cheng et al. (2012) demonstrated that the aluminum dissolving viability in sulfuric acid (H₂SO₄)-acidified solution exceeded that in hydrochloric acid-acidified solution. Acidification with sulfuric acid occurs when sulfuric acid reacts with insoluble aluminum hydroxide to form alum solution, as represented in the following equation (Massides et al. 1988; SenGupta & Shi 1992; Xu et al. 2009; Huang et al. 2010; Evuti & Lawal 2011; Cheng et al. 2012):

\[2\text{Al(OH)}_3 + 3\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow \text{Al}_2(\text{SO}_4)_4 + 14\text{H}_2\text{O}\]

Abdel Azim et al. (2013) demonstrated that the recovered alum volume produced after the acidification process reaches between 94 and 98%, while the concentration of recovered alum ranges between 13.9 and 20.2%.

Chen et al. (2011) confirmed that alum recovery from water treatment sludge by acidification extends to somewhere around 4.6% and 72%. Furthermore, Chen et al. (2011) proved that the aluminum recovery efficiency by acidification is influenced by the sort of sediments in the water resource; more precisely, sludge from clay-based sludge has higher aluminum recovery efficiency than sludge from sand-based sediments using the acidification method.

Davis (2010) concluded that the recovered alum after the acidification method ranges from 60% to 80%. Davis (2010) deduced that 1 kg of recovered alum resulted from reaction of 1 kg of sulfuric acid with 0.50 kg of insoluble aluminum hydroxide.

Xu et al. (2009) reported that the optimum conditions and efficiency of the acidification method for alum recovery results in the highest level of 84.5%, and the reduction rate of sludge is 55.5%.

Massides et al. (1988) reported that more than 70% of alum recovery can be achieved by the acidification approach with pH of 2.0, mixing time of 30 minutes, and 300 rpm of mixing rotational speed. Moreover, acidification technique for alum recovery reduces sludge volume by 40–50% and decreases its disposal cost by 28% (SenGupta & Shi 1992).

The undertaken work aimed to investigated accurately the most appropriate conditions for alum recovery from water treatment sludge by acidification method and to investigate the influence of the selected alum recovery approach on the reduction of sludge volume.

MATERIALS AND METHODS

Collection of raw sludge samples

Water treatment sludge samples were collected from Japanese-El-Mahalla El-Koubra WTP, El-Santa WTP, and El-Melahaya–Tanta WTP. These WTPs are located in El-Gharbia Governorate, Egypt. Alum is used as coagulant and injected in the form of concentrated solution with raw water before rapid mixing, in the previously mentioned WTPs, with different doses according to characteristics of raw water influent to each WTP as shown in Table 1. The organic content in the sludge varied between 10% and 15% of total solids (TS). Furthermore, TS and aluminum content in raw sludge samples are presented in Table 1. Sludge samples were obtained from the clarifiers in the previously mentioned WTPs.

Experiments of sludge acidification for alum recovery

The sludge samples were acidified with sulfuric acid (H₂SO₄) with concentration of 98%. Sulfuric acid was added to 500 mL of raw sludge samples while the sludge samples were mixed simultaneously until pH of the solution reached a certain value (somewhere between
After that, the solids were allowed to settle for 15 minutes. Afterward, the adjusted sludge samples being mixed by jar test apparatus at a definite rotational speed (90, 150, and 200 rpm) for a particular time (15–90 minutes). All of these experiments were conducted at temperature of 25°C (Xu et al. 2009; Chen et al. 2011).

Aluminum detection

The aluminum content in the solid and liquid phases was analyzed after digestion by sulfuric acid using inductively coupled plasma optical emission spectroscopy (ICP-OES); model OPTIMA™ 7000 DV, USA (Xu et al. 2009; Chen et al. 2011).

Laboratory tests

Parameters, equipment, and the analyses conducted in the present study are presented in Table 2 on the basis of Standard Methods for the Examination of Water and Wastewater (APHA 1998). These experiments were conducted in Central Laboratory, Tanta University, as well as Sanitary Engineering Laboratory, Faculty of Engineering, Tanta University, Egypt.

### RESULTS AND DISCUSSION

**Determination of optimum mixing time**

Alum recovery percent from water treatment sludge and aluminum (Al) content in the recovered alum solution at Japanese-El-Mahalla El-Koubra WTP are shown in Figures 1 and 2 for a series of mixing times ranging between 15 minutes and 90 minutes. The mixing rotational speed was calibrated at 150 rpm and pH value was adjusted to 2.0 by adding sulfuric acid volume of 30 mL to digest the sludge sample.

It can be noticed that alum recovery percent and Al-content in the recovered alum solution slightly increase in the mixing time periods between 15 and 45 minutes and between 60 and 90 minutes. However, relatively significant increases in alum recovery from 9.75% to 11.48% and Al-content from 130.6 mg to 153.9 mg occur when the mixing time increased from 45 to 60 minutes. Therefore, the optimum mixing time for alum recovery from water treatment sludge as well as Al-content in the recovered alum solution.

**Table 1** | Characteristics of raw water and sludge samples in the different WTPs

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Japanese-El-Mahalla El-Koubra WTP</th>
<th>El-Santa WTP</th>
<th>El-Melaheya–Tanta WTP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Design discharge, m³/d</td>
<td>34,000</td>
<td>87,000</td>
<td>70,000</td>
</tr>
<tr>
<td>Raw water turbidity, NTU</td>
<td>18–22</td>
<td>12–13</td>
<td>8–9</td>
</tr>
<tr>
<td>Alum dose, mg/L</td>
<td>40–45</td>
<td>25–35</td>
<td>25–35</td>
</tr>
<tr>
<td>TS for water treatment sludge, g/L</td>
<td>32.85 ± 0.80</td>
<td>8.38 ± 0.30</td>
<td>39.00 ± 1.10</td>
</tr>
<tr>
<td>Aluminum content in raw sludge, mg/L</td>
<td>2,679.8 ± 108.3</td>
<td>1,124.34 ± 87.5</td>
<td>4,096.79 ± 163.9</td>
</tr>
</tbody>
</table>

**Table 2** | Parameters and equipment utilized in the laboratory tests

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Equipment and product information</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS, mg/L</td>
<td>Drying oven (BINDER®), analytical balance (OHAUS®), Germany</td>
</tr>
<tr>
<td>Aluminum, mg/L</td>
<td>ICP-OES; model OPTIMA™ 7000 DV, USA</td>
</tr>
<tr>
<td>Jar test apparatus</td>
<td>VELP® Scientifica, Italy, jar volume of 1 L, flat blade impeller</td>
</tr>
<tr>
<td>pH, Temperature</td>
<td>pH/C model CONSORT P400</td>
</tr>
</tbody>
</table>

**Figure 1** | Effect of mixing time on the alum recovery percent from water treatment sludge.
is selected to be 60 minutes. These results are compatible with that obtained by Chen et al. (2011).

**Determination of optimum mixing intensity**

Alum recovery percent from water treatment sludge and Al content in the recovered alum solution in Japanese-El-Mahalla El-Koubra WTP are shown in Figures 3 and 4 for three ascending values of mixing rotational speed (i.e. 90, 150 and 200 rpm). The mixing time was adjusted to 60 minutes and pH value was adjusted to 1.36 by adding sulfuric acid volume of 100 mL to acidify the sludge sample.

It can be noticed that alum recovery percent and Al-content in the recovered alum solution slightly increase with the increment of mixing rotational speed in general. However, it is noticed that relatively significant increases in alum recovery percent from 36.5% to 38.2% and Al-content from 520 mg to 562 mg occur when the rotational speed increases from 90 rpm to 150 rpm. On the other hand, increasing the mixing intensity from 150 rpm to 200 rpm results has little impact on enhancing the alum recovery percent, which increased from 38.2% to 38.8%, and Al-content in the recovered alum solution, which increased from 562 mg to 565 mg. In this manner, the optimum mixing rotational speed is selected to be 150 rpm. These results are compatible with those obtained by Xu et al. (2009), Evuti & Lawal (2011), Chen et al. (2011) and Abdel Azim et al. (2013).

**Impact of pH range on alum recovery**

Alum recovery percent from water treatment sludge was observed at a series of pH values ranging between 1.0 and 3.0 in order to determine the suitable pH value for alum recovery, as shown in Figure 5. The mixing rotational speed was calibrated at 150 rpm and the mixing time value was adjusted to 60 minutes. It can be noticed that the alum recovery percent increases with the decrease of pH values. Alum recovery percent reached up to 69.03% at El-Santa WTP as shown in Figure 5. These results are well-matched with that obtained by Xu et al. (2009) and Chen et al. (2011). In general, the alum recovery increases extensively when pH value is tapered from 2.0 to 1.25 for all WTPs. Therefore, the optimum pH range is 1.25–2.0 for alum recovery from water treatment sludge. On the other hand, the significant differences in alum recovery from various WTPs sludge can be interpreted as being due to variation in concentration of TS in raw sludge.
as well as difference in aluminum content in raw sludge, as presented in Table 1. Furthermore, the differences in alum recovery from various WTPs sludge may be influenced by nature of formation of different sludge types, e.g. surface area of sediments, sand content, silt content, and clay content, as reported in Cheng et al. (2012).

Relationship between pH value and added volume of sulfuric acid

Sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) with concentration of 98% was added to 500 mL of water treatment sludge samples. The added volume of sulfuric acid was observed at a series of pH values ranging between 1.0 and 3.0 as shown in Figure 6.

The mixing rotational speed was calibrated at 150 rpm and the mixing time value was adjusted to 60 minutes. The significant differences in doses of sulfuric acid from various WTPs sludge can be interpreted as being due to variation in concentration of TS in raw sludge as well as difference in aluminum content in raw sludge as mentioned before. All curves in Figure 6 can be divided into three stages, namely, first stage, intermediate stage, and ending stage. The first stage is the decrease of pH values from 3.0 to 2.0; this stage is distinguished by the slight increase in added volume of sulfuric acid which rapidly reduces pH values (from 3.0 to 2.0) as a result of reaction with alkaline carbonate. The intermediate stage is the decrease of pH values from 2.0 to 1.50; this stage is recognized by the significant increase in added volume of sulfuric acid, which reduces pH values to some extent from 2.0 to 1.50 as a result of reaction with aluminum and other metal hydroxide compounds in the sludge (Li et al. 2005; Huang et al. 2010; Cheng et al. 2012).

The ending stage in the decrease of pH values to less than 1.50; this stage is recognized by the multiplied increase in added volume of sulfuric acid (reached to 2–3 fold) because of stabilization of pH value and reaction finishing. The multiplied increase in added volume of sulfuric acid results in insignificant increase (i.e. less than 10%) in alum recovery percent as shown in Figure 5. In addition, pH range between 1.50 and 1.0 increases costs with multiplied increase in added volume of sulfuric acid, corrosion, and the associated risks of the alum recovery process. Therefore, the optimum pH range is between 1.50 and 2.0 from the viewpoint of added sulfuric acid.

Impact of pH range on alum releasing

Al-concentration in the recovered alum solution was detected at a series of pH values ranging between 1.0 and 3.0 in order to determine the optimum pH range for aluminum releasing as shown in Figure 7. The mixing rotational speed was calibrated at 150 rpm and the mixing time value was adjusted to 60 minutes. From Figure 7, it can be noticed that the maximum Al-concentration in the recovered alum solution is 1,114.5 mg/L for Japanese-El-Mahalla El-Koubra WTP and 576.6 mg/L for El-Santa WTP at pH level of 1.50, whilst the maximum Al-concentration in the recovered alum solution is 2,291 mg/L for El-Melaheya–Tanta WTP at pH level of 1.25. Hence, the optimum pH range is between 1.25 and 1.50 from the viewpoint of aluminum releasing. The recommended pH range is located within the scope of pH range for alum recovery in general (Xu et al. 2009; Chen et al. 2011; Evuti & Lawal 2011; Abdel Azim et al. 2013).
Impact of pH range on sludge reduction

The reduction of sludge volume was detected at a series of pH values ranging between 1.0 and 3.0 in order to determine the optimum pH value to get the maximum sludge reduction, as shown in Figure 8. The mixing rotational speed was calibrated at 150 rpm and the mixing time value was adjusted to 60 minutes. From Figure 8, it can be noticed that the reduction of sludge volume increases (from 87% to 90% for El-Santa WTP, from 53% to 66% for Japanese-El-Mahalla El-Koubra WTP, from 32% to 47% for El-Melaheya–Tanta WTP) with the decrease of pH values from 2.5 to 1.5 as a result of releasing of aluminum and other metals by acidification. These results are close to, or larger than in some cases, the results obtained by Xu et al. (2009) and SenGupta & Shi (1992). On the other hand, the reduction of sludge volume diminishes (from 54% to 53% for Japanese-El-Mahalla El-Koubra WTP, from 34% to 32% for El-Melaheya–Tanta WTP) with the decrease of pH values from 3.0 to 2.5 because of the acidification of alkaline carbonate. Likewise, the reduction of sludge volume decreases (from 90% to 84% for El-Santa WTP, from 66% to 63% for Japanese-El-Mahalla El-Koubra WTP, from 47% to 35% for El-Melaheya–Tanta WTP) with the reduction of pH values to under 1.50 because of stabilization of pH value until completion of aluminum release and accumulation of sediments into the digested sludge. Thus, the optimum pH value is 1.50 from the viewpoint of sludge reduction.

From the previous parametric analysis of results, it is recommended to apply the acidification procedure for alum recovery from water treatment sludge by selecting the mixing time of 60 minutes and mixing intensity of 150 rpm, in addition to pH level of 1.50.

Relationship between aluminum content and TS in raw sludge

Al-content and TS in raw sludge were measured for the different WTPs as already presented in Table 1, and outlined in Figure 9. A linear regression was applied for all results of Al-content and TS to predict the best-fit equations as shown in Figure 9. It can be noticed that the relationship between Al-content and TS is a strong correlation shown by R-squared value of 0.898 despite the contrast of the samples taken from different WTPs. Moreover, the TS contain 9.6% of aluminum concentration in water treatment sludge. These results are compatible with that acquired by Makris & O’Connor (2007).
Relationship between aluminum content in the recovered alum solution and raw sludge

Al-content in the recovered alum solution and Al-content in raw sludge were measured for the different WTPs as shown in Figure 10. The mixing rotational speed was calibrated at 150 rpm and the mixing time value was adjusted to 60 minutes in addition to maintaining pH level at 1.50. A linear regression was applied for all results of Al-content in the recovered alum solution as well as in raw sludge to predict the best-fit equations as shown in Figure 10. It can be noticed that the relationship between Al-content in the recovered alum solution versus Al-content in raw sludge is a very strong correlation shown by R-squared value of 0.96 despite the contrast of the samples taken from different WTPs. Furthermore, Al-content in the raw sludge is 48.5% of Al-content in the recovered alum solution. These results are higher than those attained by Abdel Azim et al. (2013).

CONCLUSIONS

Acidification is a promising technique for alum recovery and stabilization of water treatment sludge for easy handling and safe disposal. The results show that alum recovery reached up to 69.03%, and the reduction of sludge volume reached its highest level at 90%. Moreover, results of the parametric investigation reveal that the mixing time of 60 minutes and mixing intensity of 150 rpm are the optimum conditions of investigation reveal that the mixing time of 60 minutes and its highest level at 90%. Moreover, results of the parametric investigation reveal that the mixing time of 60 minutes and mixing intensity of 150 rpm are the optimum conditions of investigation reveal that the mixing time of 60 minutes and its highest level at 90%. Moreover, results of the parametric investigation reveal that the mixing time of 60 minutes and mixing intensity of 150 rpm are the optimum conditions of investigation reveal that the mixing time of 60 minutes and its highest level at 90%. Moreover, results of the parametric investigation reveal that the mixing time of 60 minutes and mixing intensity of 150 rpm are the optimum conditions of investigation reveal that the mixing time of 60 minutes and its highest level at 90%. Moreover, results of the parametric investigation reveal that the mixing time of 60 minutes and mixing intensity of 150 rpm are the optimum conditions of mixing for alum recovery from water treatment sludge. The optimum pH level is 1.50 for alum recovery as indicated by maximum aluminum releasing, maximum reduction of sludge volume, and reasonable dosages of added sulfuric acid. On the other hand, the TS contain 9.6% of aluminum concentration in water treatment sludge, even though aluminum content in the raw sludge is 48.5% of aluminum content in the recovered alum solution.

REFERENCES

Huang, S. H., Chen, J. L., Chiang, K. Y. & Wu, H. C. 2010 Effects of acidification on dewater ability and aluminum concentration...
of alum sludge. *Separation Science and Technology* **45** (8), 1165–1169.


