Alum recovery and wastewater sludge stabilization with sulfuric acid: Mixing aspects

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Abstract: Coagulation-flocculation is used to remove helminth ova from wastewater intended for agricultural reuse. Nevertheless, it has the drawback of producing a large amount of sludge which together with the chemicals used to treat wastewater increases the operating cost. This can be overcome by recovering and recycling the aluminum contained in the sludge. This paper presents how an acid recovery process was applied to an Advanced Primary Treatment (APT) sludge to partially treat it and to reduce its quantity. This is a method applied several decades ago in water sludge that has not been used in secondary wastewater sludge to recover aluminum and to inactivate microorganisms. By adding sulfuric acid to a 6% TS sludge, more than 70% of the aluminum added during the coagulation flocculation process was recovered when a pH of 2 was maintained for a duration of 30 minutes and at 300 rpm of mixing conditions. Mixing at high TS content can become a critical parameter needing optimization. Alum acid recovery reduced sludge volume by 45% and mass by 63%, inactivating 5 logs of fecal coliforms and 68% of helminth ova. Due to the lower alum consumption, the operating cost of the APT is reduced by 3.78 US$/1000 m^3.

Keywords: Aluminum recovery, Coagulation-flocculation, Helminth ova, sludge reduction, Wastewater

INTRODUCTION

Coagulation-flocculation is a process used to remove suspended solids from wastewater. New applications are helminth ova and phosphorus removal for agricultural reuse or environmental protection. A technology used for one of these purposes is known as APT (Advanced Primary treatment), which basically is a low dose coagulation-flocculation process coupled with a high rate settler (Odegaard, 1998; Harleman and Murcott, 1999; Jiménez and Chavez, 1997). In Mexico, APT has been used since 1997. Thanks to its affordability, ten wastewater treatment plants have been built around the country with a total capacity of 10.7 m^3/s and producing treated wastewater to irrigate 70,000 hectares. Alum is the coagulant used in all cases and it is estimated that the wastewater treatment plants produce around 103,000 dry tons/yr of sludge. The purpose of this research was to study the effect of applying an acid extraction method to: (a) recover alum to be used again as a coagulant, (b) reduce the amount of sludge produced; and (c) inactivate helminth ova in the sludge formed to reduce its treatment cost.

BACKGROUND

APT is a coagulation-flocculation process used to remove helminth ova but which produces a large amount of sludge (around 148 kg TS/10^3 m^3, Jimenez and Chavez, 1997). This sludge is partly formed by the coagulant used and contains a high content of microorganisms. A way to reduce the amount of sludge is by recovering the coagulant. And, because in APT the coagulant used is aluminum, this recovery can be performed with an acid extraction method that can inactivate microorganisms and helminth ova.

The acid aluminum recovery method has been applied in sludge produced during water treatment with an efficiency rate of more than 70%, reducing the operating cost of the coagulation flocculation method used to treat wastewater by 50-60% due to savings on chemicals (Massides et al., 1988). Furthermore, acid recovery
reduces sludge volume by 40-50% and decreases its disposal cost by 28% (Sengupta, 1994). The acid recovery method is based on the solubilization of aluminum hydroxides. Experience in water treatment plants obtained several years ago shows that:

(a) Although stoichiometrically \(5.44 \text{ g of H}_2\text{SO}_4/\text{g Al}^{3+}\) are needed, in practice values of up to 7.3 g/g must be added because of the sludge buffering capacity (Fulton, 1974; Bishop et al., 1987);

(b) Along with the aluminum, other metals that may interfere with its coagulating capacity or pollute the wastewater to be treated are solubilized, and

(c) Recovery must be performed in sludge with 2% TS, at a pH of 2 and with a 15 minute contact time (Fulton, 1974; Cornwell and Susan, 1979).

Little experience is available on the application of an acid recovery method to wastewater sludge. Only Cornwell and Zoltek (1977) reported the use of a selective acid method in a tertiary thickened sludge. Adding acid to a pH of 2 (7.3 g acid/g Al\(^{3+}\)) and with a contact time of 15 minutes they recovered 80-93% of the aluminum after settling and metal extraction with phosphoric acid. The mixing conditions, the final biological quality of the sludge as well as the recommended TS content were not reported from this experiment. Massides et al., (1988) also achieved a recovery efficiency of 96% using an optimal pH of 2.5 with tertiary sludge formed in a phosphorus removal process. Experiences concerning the application of the acid recovery method to a secondary sludge have not been reported and neither has the effect of the acid on the biological content of the sludge.

The biological content of the sludge places limitations on its revalorization or disposal. In literature, it has been reported that microorganisms and helminth ova can be inactivated by adding strong acids. Barrios (2003), for instance, using sulfuric acid at a 1.5-3 pH and a 30 minute contact time, reported 60% inactivation of helminth ova and 3-5 fecal coliforms log reduction in a secondary high polluted sludge.

METHODS

Over a period of 15 months, sludge was taken from a 35 L/s wastewater treatment plant serving 15,200 inhabitants from a low income area of Mexico City. The plant has an APT process using around 115 mg/L of \(\text{Al}(\text{SO}_4)\cdot 14\text{H}_2\text{O}\) and 1 mg/L of an anionic high molecular weight and high density charge polymer. The effluent produced has \(<1 \text{ HO/L and } <1000 \text{ MPN/100 mL of fecal coliforms and was used for agricultural irrigation. The sludge produced during treatment was only thickened to a 4-7% TS content but not treated. For the study, sludge was characterized both prior to and after acid treatment using the parameters presented in Table 1.}

Aluminum recovery

To evaluate the effect of the acid/aluminum mass ratio (5, 7 and 9 g/g), the contact time (15, 30 and 45 minutes), the TS content (1.8-6.9%) and the mixing conditions (100, 200 and 300 rpm) on the aluminum recovery a factorial design of \(3^3\) was used.

Mixing conditions

To study the effect of different mixing conditions, two types of paddles were used (a rectangular-flat one and a helical one), in a 2-L circular beaker. Mixing intensity for the rectangular-flat paddle was 200, 400, 600 and 800 rpm and for the helical one it was 600, 800, 1200 and 1500 rpm. The acid/AI\(^{3+}\) ratio varied between 3.4, 10 and 13.7 gH\(_2\)SO\(_4/g\) Al while the contact time was held constant at 30 minutes. To study the TS effect, thickened sludge was diluted with the wastewater treatment plant effluent to obtain values close to 2, 4, 6 and 7%. Each experiment was repeated three times.

Aluminum balance

In order to determine the origin of the aluminum extracted, 1250 L of raw wastewater were treated with 59 mg/L of alum and 1 mg/L of anionic polymer. Rapid mixing was performed for 30 seconds at 300 rpm and slow mixing at 84 rpm for 5 minutes (Jimenez and Chavez, 1997). Fifty liters of sludge at 0.5% TS were recovered.
Six sludge samples were acidified. The Al\(^{3+}\) content was measured in raw wastewater, raw sludge, acid sludge, the supernatant and the treated wastewater.

### Table 1 Parameters and analytical methods used

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Analytical Method*</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4500-H'B</td>
</tr>
<tr>
<td>TS, %</td>
<td>Gravimetric 2540 G</td>
</tr>
<tr>
<td>Fecal coliforms, MPN/gTS</td>
<td>9221E</td>
</tr>
<tr>
<td>Total and viable helminth ova, Ova/gTS</td>
<td>US EPA, 1992</td>
</tr>
<tr>
<td>Aluminum, mg/L and mg/gTS</td>
<td>3500-Atomic absorption</td>
</tr>
<tr>
<td>Specific resistant to filtration, mg/kg</td>
<td>WPCF, 1988;</td>
</tr>
<tr>
<td>As, Ca, Cd, Cr, Fe, Mg, Ni, Hg, Pb and Zn, mg/L</td>
<td>3500-Atomic absorption with SW 846-3051 to measure the total content</td>
</tr>
<tr>
<td>Fecal coliforms, MPN/100mL</td>
<td>Membrane filter technique, 9222A</td>
</tr>
<tr>
<td>Helminth ova, ova/L</td>
<td>US-EPA, 1992</td>
</tr>
<tr>
<td>Turbidity, NTU</td>
<td>2130</td>
</tr>
<tr>
<td>Total Phosphorus, mgP/L</td>
<td>4500-P</td>
</tr>
<tr>
<td>Total Nitrogen, mgN-NTK/L</td>
<td>4500-N</td>
</tr>
<tr>
<td>Chemical oxygen demand, mg/L</td>
<td>5220D</td>
</tr>
</tbody>
</table>

*APHA, AWWA and WEF, 1995 unless indicated

**Successive extractions**

To define the quality of the coagulant recycled several times, five successive acid extractions were performed per triplicate in a sludge produced at the laboratory treating wastewater as described in Aluminum balance. Sludge was then acidified to recover the aluminum. Centrifuged sludge was re-suspended and the acidification process repeated.

**Coagulation efficiency of the recovered aluminum**

To evaluate the efficiency of the aluminum recovered, ten liters of wastewater were treated with acid. The aluminum content was measured in the supernatant and then used as a coagulant, adding fresh alum to meet the optimal dose of around 30%. The recycling procedure was repeated five times, measuring the TS, turbidity, conductivity, metal, total phosphorus, total nitrogen and the COD content in both the raw and treated wastewater.

**RESULTS**

**Wastewater and sludge characterization**

Sludge was characterized (Table 2) by a much higher helminth ova content than the one reported in Metcalf and Eddy (2003) of <10 HO/gTS due to the notably lower health conditions in developed and developing countries. Additionally, TSS and COD in wastewater were considerably higher because the main activity in the area is the production of typical Mexican food. As expected, the aluminum content in the APT sludge (40±16 mg Al/gTS) was higher than the one reported for a sludge coming from an activated sludge treatment plant (19.7–26.3 mg/gTS, Umita et al., 1999) obviously due to the alum added during the treatment process but also, and not so evident, to the natural presence of aluminum in the suspended solids originally contained in wastewater, as will be later shown. The aluminum concentration in sludge turned out to be highly variable (24-61 mgAl/gTS) due to differences in alum dosification at the wastewater treatment plant and the content in the wastewater. This situation had an effect on the variability of the results observed.
Table 2 Wastewater and sludge characteristics at the wastewater treatment plant during the study

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mean</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total suspended solids, mg/L</td>
<td>485±17</td>
<td>4±3</td>
</tr>
<tr>
<td>Turbidity, NTU</td>
<td>662±13</td>
<td>72±3</td>
</tr>
<tr>
<td>Chemical oxygen demand (total), mg/L</td>
<td>1547±51</td>
<td>5.16±0.6</td>
</tr>
<tr>
<td>Chemical oxygen demand (soluble), mg/L</td>
<td>760±40</td>
<td>10^1 ±10^4</td>
</tr>
<tr>
<td>Fecal Coliforms, MPN/100 mL</td>
<td>4.2x10^6</td>
<td>106±55</td>
</tr>
<tr>
<td>Aluminum (mg/gTS)</td>
<td>40±16</td>
<td></td>
</tr>
</tbody>
</table>

Aluminum recovery

**pH and H2SO4/Al3+ ratio.** Aluminum recovery efficiency varied along with pH and the TS content (Figure 1). As cited in literature, aluminum solubilization began at a pH of 4 and reached maximum values of between 1-3 (Chen et al., 1976). Because of this, and following recommendations from Fulton, (1974) and Cornwell and Susan (1979), a pH of 2 was used during the rest of the study. Greater efficiencies (70%) were obtained with sludge having a TS content of 4.9-5.9%. Lower ones (20 to 30%) were obtained from sludge with 6.7-7.2% TS. This suggested that Al solubilization was affected by the TS content.

![Figure 1](image)

**Figure 1** Aluminum extraction efficiency at different pHs and different sludge samples.

Tests performed with different acid/aluminum ratios (5, 7 and 9g of acid/g Al^3+^) did not show any significant difference in the amount of Al^3+^ solubilized in the supernatant (1326±5%). This was unexpected because it was thought that in contrast to water treatment sludge, wastewater treatment sludge would need a greater acid/Al^3+^ ratio than the one reported in drinking water plants (5.4-7.3 gH2SO4/gAl^3+^ (Bishop et al., 1987, and Cornwell and Susan, 1979) due to a higher alkalinity content in wastewater (Culp et al., 1978) as well as to the presence of a wide variety of metals in greater concentrations. The lower acid demand was explained by the fact that the APT sludge had an acid pH (of ~5), and so there was no need to neutralize the buffering capacity.

**Contact time**

It was found that 30 minutes were needed to reach the maximum Al^3+^ solubilization (Figure 2), instead of the 15 minutes recommended for water treatment plant sludge (Fulton, 1974; Cornwell and Zolteck, 1977). This longer contact time also proved useful to disinfecting sludge (Barrios, 2003).
Figure 2  Soluble aluminum content in the supernatant at different contact times for two sludge samples.

**TS content**

Using prepared sludge samples with 1.8, 4.2, 5.8 and 6.9% TS content under the same extraction conditions (pH≤2, 300 rpm, 30 minutes and a 51 mg Al/g TS sludge) a greater quantity of aluminum was extracted, as the TS content was increased (Figure 3a). Nevertheless, this increase was not proportional to the TS increase, because in more concentrated sludge mass transportation phenomena and mixing conditions became a critical factor. These results also suggest that floc size may play an important role during aluminum extraction. The surface curve obtained after adjusting data (Figure 3b) shows that as the TS (in %) and the aluminum content in the sludge (AC in mg Al/gTS) increased, the aluminum concentration in the supernatant also increased.

Mixing conditions

The mixing intensity effect is shown in Figure 4a using a rectangular-flat paddle and two types of sludge (2.9% TS with 26.15 g Al/gTS and 6.71% TS with 61.38 mg Al/gTS). In both cases, efficiency increased by around 10% as the mixing intensity increased from 200 to 800 rpm. However, energy consumption also increased by 13.5 times meaning that from an economic point of view this may not be worth it. Figure 4b shows aluminum recovery efficiency using two types of paddles (a rectangular-flat paddle and a helical one with three vanes) and two sludges (4.93% TS with 21.1 mg Al/gTS and 6.71% TS with 61.4 mg Al/gTS). For the 6.71% TS sludge, efficiencies with the rectangular-flat paddle (20.7%±4) and with the helical one (13.1±2%) were similar at different mixing rates and the difference using one or other paddle was 7.6%. The greater efficiency obtained with the rectangular-flat paddle was due to its larger area (1.7 times greater) producing a higher mixing gradient. Results with the 4.9% TS sludge showed a similar behavior, although in this case the efficiency difference between paddles was smaller (1.5%), indicating than in less concentrated sludge mixing conditions are less critical.

![Figure 2](image-url)  Soluble aluminum content in the supernatant at different contact times for two sludge samples.

![Figure 3](image-url)  Aluminum content in the supernatant as function of (a) the TS content and (b) The TS and the Al content in sludge.

![Figure 4](image-url)  Mixing conditions
Successive extractions
In five successive acid extractions using a 3.4% TS sludge containing 32 mg Al/gTS, during the first cycle 77±2% of the aluminum was solubilized increasing to 91.6±1% in the second and going from 96.5%±0.2 to around 100% in the other three. Given that going from the first to the second cycle resulted in a net cost in chemicals of -0.35 US$/1000m^3, it is recommended that only one extraction cycle be performed.

Aluminum balance
The mass balance performed made it possible to determine that the quantity of aluminum contained in the sludge was almost twice the amount of the aluminum added as coagulant; therefore, a large quantity came from the solids removed. In relation to the total amount of aluminum entering the wastewater treatment process, 88% went to sludge.

Efficiency as coagulant
In Table 3, it can be observed that the coagulant capacity of the fresh and the recycled aluminum is almost the same. This Table also contains the metal content limits in the Mexican standard for agricultural reuse that are similar to US-EPA criteria for the same purpose. It is observed that raw wastewater initially meets the standard, and after recycling the coagulant five times, the metal content does not significantly increase. In fact, only zinc showed a large increase (41%), but the value in the effluent was still well below the standard. Because acidification dissolves other metals (Cornwell and Lemunyon, 1980; Sengupta and Shi, 1992) the amount of Fe, Ca and Mg extracted were measured resulting in 0.12±0.015, 0.75±0.02 and 0.10±0.014 mg per mg Al, respectively. These values were higher than those reported by Bishop et al. (1987) for water treatment sludge and equal to 0.146 for iron, 0.001 for calcium and 0.003 for magnesium mg/mg Al. The amount of iron in the supernatant was 158 mg/L and certainly contributed to enhancing the coagulation capacity of the recycled coagulant.

Final sludge characteristics
The initial content of fecal coliforms in sludge varied from 1.5x10^6 to 2.3x10^7 MPN/gTS. As expected, a correlation between the pH in the sludge and fecal coliform inactivation was observed. At a pH of 4, only 1 log of FC was inactivated while at a pH of 2, more than 6 logs were reduced, thus meeting the US-EPA criteria and the Mexican standard (10^3 MPN/gTS).

Figure 4. Effect of (a) mixing intensity on the aluminum recovery efficiency for two types of sludge; and (b) using different paddles.
Table 3 Wastewater and effluent quality using recycled aluminum for a selected cycle, in mg/L

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Parameter, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw wastewater</td>
<td>COD</td>
</tr>
<tr>
<td>0</td>
<td>1547±141</td>
</tr>
<tr>
<td>1</td>
<td>800±11</td>
</tr>
<tr>
<td>2</td>
<td>872±6</td>
</tr>
<tr>
<td>4</td>
<td>808±12</td>
</tr>
<tr>
<td>5</td>
<td>867±16</td>
</tr>
<tr>
<td>Norm</td>
<td>NL</td>
</tr>
</tbody>
</table>

<BL Below the detection limit
NL: No limit

At a pH of 2 and a 30 minute contact time, 68% of the helminth ova were inactivated. But because 42±27 ova/g TS remained in the sludge, this inactivation was not enough to meet the Mexican criteria for biosolids class A or B. To further reduce the helminth ova content another method such as lime stabilization could be applied. Alternatively, the possibility of using a greater contact time than the one used here (30 minutes) to improve the final quality of sludge could be explored.

Thanks to the aluminum extraction, the final amount of sludge produced was reduced by 63±4% in mass and 45±6% in volume, which is between the values presented in the background for water treatment sludge.

Specific resistance to filtration (SRF) was increased during acid treatment from 98x10¹² m/kg for raw sludge (a value slightly lower than the one reported for a primary sludge of 1.5-5x10¹⁴ m/kg) to 139x10¹² m/kg. This result contrasted with the one reported by Bishop et al. (1987) and Chen et al. (1976) for a water treatment sludge, who found that dewaterability was improved by adding acid. The reason for this is that water treatment sludge mainly contains large amounts of aluminum hydroxide, which is a gelatinous compound that tends to remain in a semi-fluid stage, while in wastewater sludge many other compounds are present. To reduce the SRF in the acidified sludge, the addition of an appropriate polymer was needed. It was found that with 4.5 kg/ton TS of an anionic polymer, the SRF was reduced to 0.4x10¹² m/kg, a value that is below the threshold value for economically dewatering sludge (1x10¹² m/kg, Christensen and Dick, 1985).

Costs

In this study, the savings from reducing alum consumption was 3.78 US$/1000 m³, a value greater than the one reported for a water treatment sludge of 1.21 US$/1000 m³ by Fulton (1974) but less than the one of 6.39 US$/1000 m³ reported for a wastewater treatment sludge by Cornwell and Zoltek (1977). Considering the reduction in mass in sludge production, the operating cost can still be reduced by 60% if a lime stabilization process is selected (WEF and ASCE, 1998).

CONCLUSIONS

The addition of sulphuric acid to an APT sludge produced the extraction of 70% of the aluminum in a 30 minute contact time at a pH of 2, an acid/Al ratio of 5.44g/g. TS <6% and 300 rpm. Unlike water treatment sludge, the contact time was higher and efficiency was shown to be dependent on the TS content. However, optimal mixing conditions should seek to balance energy consumption and recovery alum efficiency. Additionally, it would be interesting to investigate the effect of the floc's size on the amount of aluminum solubilized under the same operating conditions. Mixing conditions turned out to be important, as sludge has greater TS content than wastewater treatment sludge and should be optimized. Besides extracting aluminum, the operating conditions selected reduced 5 logs of faecal coliforms and inactivated 68% of the helminth ova content. Longer contact times may further increase helminth ova inactivation. Finally, savings of 3.78 US$/1000m³ may be obtained by recovering alum and the treatment cost may be reduced by 60% if a lime stabilization process is selected.
ACKNOWLEDGEMENTS

CYDSA Group provided the economical support for this research project and our thanks go to Catalina Maya and Paulina Aguilar for assisting in the collection of data.

REFERENCES


