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Rui A.R. Boaventura¹, António A.S. Duarte³,
Manuel F. Almeida²

¹LSRE-Laboratory of Separation and Reaction Engineering

²LEPAE-Laboratory for Process, Environment and Energy Engineering
Faculty of Engineering, 4050-123 Porto, Portugal

³Department of Civil Engineering
University of Minho, Campus of Gualtar
4710-057 Braga, Portugal

ALUMINUM RECOVERY FROM WATER TREATMENT SLUDGES

Aluminum sulfate and polyaluminum chloride are widely used as coagulants in water treatment plants. A chemical sludge containing aluminium hydroxide, adsorbed organic matter and other water insoluble impurities is obtained after the flocculation-clarification process. In Portugal, an estimated amount of 66 000 ton/yr. (wet wt.) water treatment sludge is being disposed of on land or at municipal solid waste (MSW) landfills. Government restrictions to this practice as well as increasing deposition costs and the potential harmful impacts proceeding from the high aluminium content of the sludge have been leading to significant research efforts in order to evaluate different treatment alternatives, namely involving aluminium recovery and subsequent reuse. Despite membrane-based separation and liquid ion exchange processes have been studied for that purpose, the traditional acidic and alkaline extraction methods may be still explored to obtain a product susceptible of use as coagulant for industrial wastewater treatment purposes.

Centrifuged chemical sludge from a water treatment plant using polyaluminium chloride as coagulant was characterised in terms of humidity, volatile matter, Al, Fe, Mn, Cd, Cu, Cr, Pb, Ni and Zn. The dry sludge organic content is about 29% and the major elements determined are aluminium ($\approx 12.6\%$), iron ($\approx 2\%$) and manganese ($\approx 0.14\%$). The aluminium recovery was investigated both by acidic and alkaline leaching processes. Concentrated H_2SO_4 was selected as the acidic leaching medium and the process efficiency was evaluated at different operating conditions. The ratio dry sludge/sulphuric acid solution was varied between 0.5 and 2%, the pH ranged from 1.0 to 4.5, different stirring and settling times were established and the aluminium, iron and manganese dissolution was assessed. A similar study was performed at pH values between 10.0 and 13.6 using 2N/10N NaOH as the extracting solution and operating conditions as those of the acid extraction procedure. Whereas maximum aluminium recovery using H_2SO_4 was about 61% at pH=1.0, the alkaline extraction led to aluminium recoveries of about 71% at pH = 13.6 (2% dry sludge in suspension, 90 min stirring time and 45 min settling time). Decreasing the sludge dosage to 0.5%, aluminium extraction increased to 87.4% at pH=13. As expected, acid extraction led to a higher Fe (18.2%) and Mn (42.1%) dissolution as compared with alkaline extraction at pH=13.6 (Fe=2.1% and Mn=3.2%).

1. Introduction

Surface water treatment for domestic supply generally includes a coagulation/flocculation stage, often using aluminum sulfate as coagulant. Particulate, colloidal and soluble contaminants are entrapped or adsorbed on aluminum hydroxide flocs and further removed from the liquid phase by sedimentation. Since dried sludges have a high aluminum content, recycling this metal has become a significant environmental issue. Despite membrane-based separation¹ and liquid ion exchange processes² have been studied for that purpose, aluminum hydrox-

ide may be dissolved in strong acidic as well as alkaline media due to its amphoteric nature. So, the traditional acidic and alkaline extraction methods are still being explored³. According to Panswad and Chamnan⁴, the aluminum recovery by acid extraction (pH between 1.0 and 3.0) can reach 70-90%. Using the alkaline process, the highest removal efficiencies were found at the pH ranges 11.4-11.8 and 11.2-11.6, using NaOH and Ca(OH)₂, respectively⁵. The aim of this research work is to study the aluminium recovery from the chemical sludge produced at the Lever Water Treatment Plant (Oporto, Portugal) by acidic and alkaline extractions. The effect of some operating parameters such as pH, sludge dosage, stirring and settling time on the extraction efficiency is also investigated. As the sludge contains small amounts of Fe and Mn, the solubilization of these metals is also evaluated.

2. Materials and Methods

2.1 Water Treatment Chemical Sludge

The humidity of the raw sludge, as received at the laboratory, is 83.9%. Dry sludge was ground and sieved (RMU sieve shaker) and the analyses performed in the < 0.075 mm grain size fraction. The chemical composition (dry wt. basis), in terms of volatile matter and metal content is given in Table 1. Volatile matter was determined by calcinating the dry sludge at 500±50 °C and metals were measured by AAS (902 GBC spectrophotometer) after sludge acid digesting (2.5 g dry sludge + 12 ml conc. HCl + 4 ml conc. HNO₃) at 140 °C for 120 min.

Table 1. Main constituents of the Water Treatment Sludge (% dry wt.)

Constituent	% dry wt.	Constituent	% dry wt.
Volatile matter	28.86	Cr	0.001
Al	12.58	Cu	0.004
Fe	2.07	Ni	0.003
Mn	0.14	Pb	0.028
Cd	< 0.001	Zn	0.025

2.2 Solubilization Tests

Distilled water (100 ml) was added to 250-mL Erlenmeyer flasks containing weighted amounts of dry sludge. Suspensions were stirred using a multiple position magnetic stirring plate. The effect of pH, sludge dosage, stirring and settling times on Al extraction rate was investigated. The pH was adjusted either using concentrated H₂SO₄ to solubilize Al as Al³⁺ or 2N/10N NaOH to extract Al as

$\text{Al}(\text{OH})_4^-$. Sludge dosage varied between 0.5 and 2 %. Stirring time was selected as 90, 120 and 150 min and settling time as 15, 30 and 45 min. In addition to Al extraction, the solubilization of Fe and Mn was also assessed for different operating conditions. As other heavy metals, such as Cd, Cr, Cu, Ni, Pb and Zn, are present in the sludge in trace concentrations or below the detection level, their solubilization was not studied. Metals in solution were measured by AAS after filtering the suspensions through Whatman GF/C membranes.

3. Results and Discussion

Figure 1 presents Al extraction results using acid and alkaline solutions. In the acid range (pH between 1.0 and 4.5) the maximum extraction yield was 60.9% at pH=1.0, sludge dosage=2%, stirring time=90 min and settling time=45 min. A higher recovery rate (71.3%) was achieved in alkaline conditions (pH=13.6). The effect of the stirring time (90, 120 and 150 min) on Al extraction efficiency can be observed in Figure 2. Sludge dosage (2%) and settling time (45 min) were kept constant. The highest efficiency (75.7% Al recovery) was achieved at pH=13 and stirring time=120 min. In acid medium (pH=2), Al extraction was less affected by the stirring time, varying between 56.3 and 58.9%.

Fig. 1. Effect of pH on Al recovery

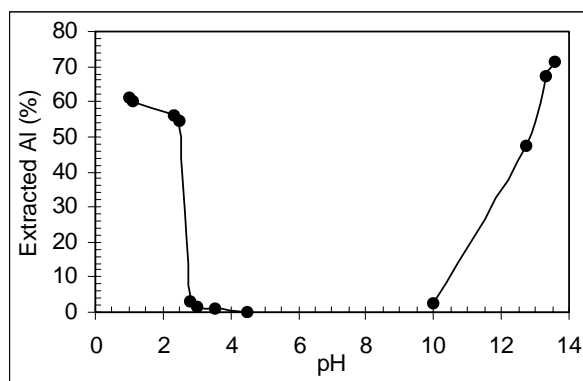
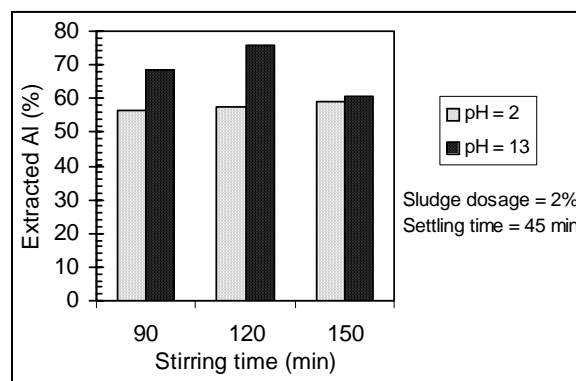


Fig. 2. Effect of stirring time on Al recovery

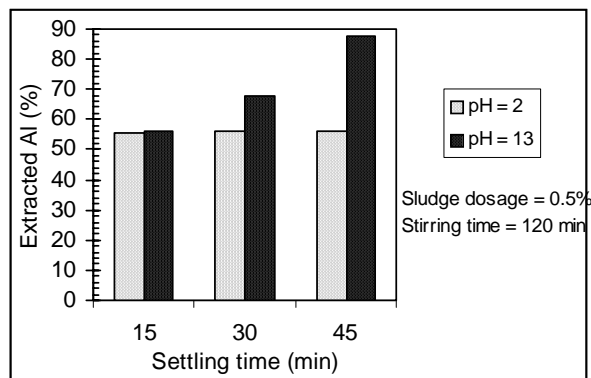
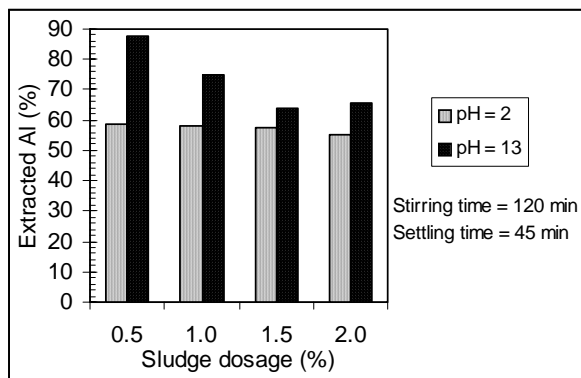


The results of Al recovery as a function of sludge dosage are presented in Figure 3. Stirring and settling periods were fixed at 120 and 45 min, respectively. Extraction increased as sludge dosage decreased, but a more marked effect was observed at pH=13. The highest Al extraction yields were found at 0.5% sludge dosage, both in acid (58.9%) and alkaline (87.4%) conditions. The effect of the post-reaction settling period on Al solubilization was studied for 0.5% sludge dosage and 120 min stirring time. In acid conditions extraction was unaffected by the settling time and averaged 56%. At pH=13, however, Al re-

covery increased with the settling time and the maximum extraction yield was 87.4% after 45 min settling.

Fig. 3. Effect of sludge dosage on Al recovery

Fig. 4. Effect of settling time on Al recovery



Acid extraction led to higher solubilization rates of iron and manganese. Dissolved Fe reached a maximum of 18.2% at pH=1.0 and Mn extraction averaged 42.1% in the pH range 1.0-3.6. Using the experimental conditions corresponding to the maximum Al recovery yield (pH=13; sludge dosage=0.5%; stirring time=120 min; settling time=45 min), Fe and Mn solubilization rates were 10.7% (11.1 mg/L) and 3.0% (0.20 mg/L), respectively.

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