The Effects of Aluminium- and Ferric-Based Chemical Phosphorus Removal on Activated Sludge Digestibility and Dewaterability

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Abstract: The uses of Al$^{3+}$ and Fe$^{3+}$ salts in chemical phosphorus removal (CPR) in activated sludge plants have increased considerably in recent years and their full impacts on downstream processes such as dewaterability and digestibility are not fully understood. In this research, the effects of CPR on sludge digestibility and dewaterability were investigated in laboratory-scale experiments using sludge samples from a full-scale wastewater treatment plant. The results of the digestibility tests showed a 21% and 36% reduction in the biogas volume generated during anaerobic digestion of surplus activated sludge at 0.1 g/L doses of Al$^{3+}$ and Fe$^{3+}$ salts, respectively. This demonstrates that Al$^{3+}$ dosing for CPR has less of a reduction effect compared with Fe$^{3+}$ salts on biogas generation during anaerobic digestion of sludge. The dewaterability tests showed that primary sludge dewaterability was improved by up to 25% by Fe$^{3+}$ and 16% by Al$^{3+}$, while that of surplus activated sludge was reduced by 64% and 73%, respectively, at a metal salt dose of 50 mg/L. Consequently, a pre-precipitation process during CPR where phosphorus is removed in the primary tank would, therefore, enhance sludge dewaterability.

Keywords: activated sludge; anaerobic digestion; biogas; metal salts; surplus activated sludge; capillary suction time

1. Introduction

The presence of nutrients, particularly phosphates, present a huge challenge in the treatment of wastewater both in municipal and industrial wastewater treatment plants (WWTPs). With the obligatory effluent discharge consent for phosphate removal becoming tighter under the EU Water Framework Directive, there is a growing demand for treatment plant upgrades to meet P consents in WWTP effluents. The activated sludge process (ASP) is the most widely used technique for municipal wastewater treatment and is able to achieve higher P removal to levels of less than 1 mg/L [1]. The two main processes for phosphorus removal are biological phosphorus removal (BPR) and chemical phosphorus removal (CPR). Both processes are used independently and, most times, in combination to achieve effluent consents for P. While BPR is considered the most environmentally friendly option, it has its limitations, particularly, the requirement for strong biological oxygen demand (BOD) in the influent wastewater. Consequently, most WWTPs in Europe use CPR to achieve their effluent P consents using mainly ferric (Fe$^{3+}$) and aluminium (Al$^{3+}$) salts for precipitation of phosphorus [2–4].

CPR has been reported to cause an increased volume of sludge between 37% and 97% [5]. Therefore, the CPR processes are to likely impact downstream processes due to the heavier load of metal salts used in the processes. The vital downstream processes include the anaerobic digestion (AD) and sludge dewatering processes [6]. The former is a well-known technology that biologically treats and degrades organic substrates in the absence of oxygen, the impact of which has been progressively increasing over
the last decade [7,8], while the latter is known to reduce the sludge volume by separating the water from the activated sludge (AS) solids [9]. The addition of coagulants (Al\(^{3+}\) and Fe\(^{3+}\)) can adversely impact the AD process and the dewaterability of the resultant sludges due to increased sludge production. Sludge treatment and disposal accounts for nearly 60% of the entire running cost of WWTPs [10] and, therefore, need to be further understood for the purpose of process optimisation and cost savings.

There have been various reports on the use of metal salts for the conditioning of sludge and their effects on sludge treatment processes [7–11]. Also, previous studies by Smith and Carliell-Marquet [12,13] have reported on the digestibility of Fe-dosed sludge, with a reduced biogas production rate as a result of Fe dosing. Research on the effects of Al\(^{3+}\) salt on the digestibility of activated sludge is limited in the literature. This study provides a comparative assessment of the effects of Fe\(^{3+}\) and Al\(^{3+}\) on the digestibility of surplus activated sludge (SAS).

Several factors have been reported to affect the dewaterability of activated sludge, including surface chemistry (zeta potential) [14]; yield stress, which explains the sludge rheological characteristics [15]; bound water content [16] and extracellular polymeric substances (EPS) content [17]. Several chemicals have been researched as conditioners for the improvement of sludge dewaterability including chemical coagulants such as aluminium sulphate, ferric chloride, calcium hydroxide, polyelectrolyte, surfactants and enzymes [18], acids and surfactants [19], Fenton’s reagent pretreatment [20], calcined aluminium salt and potassium ferrate [21]. While most of these studies focused on the effects of the use of these conditioners when used for conditioning during sludge treatment processes, there has been limited research on the effects of the chemicals used in the upstream activated sludge process for the precipitation of phosphorus on the downstream dewatering process. The second objective of this paper is to investigate the effects of CPR on the dewaterability of WWTP primary sludge and SAS.

2. Materials and Methods

2.1. Activated Sludge Digestibility and Dewaterability Sampling

Activated sludge samples were collected in three sampling campaigns between 2016 and 2017 from a WWTP in the West Midlands in the United Kingdom. The WWTP is an activated sludge plant with an average design flow of 450,000 m\(^3\)/d at full flow to treatment (FFT) of 1,070,000 m\(^3\)/d. The WWTP was chemically dosed at the end of the ASP and samples were collected upstream of the chemical dosing point. The SAS samples were collected in 32.5-L plastic containers from the distribution chambers and transferred to the laboratory-scale plant. The mixed liquor suspended solids (MLSS) concentration of the samples ranged from 2800 to 3500 mg/L, with the pH ranging from 6.5 to 7.5 and a phosphate concentration of 7–12 mg/L. All chemicals including aluminium sulphate and ferric chloride used were of analytical grade and purchased from Sigma Aldrich (Gillingham, UK). All experiments were commenced within 24 h of sampling, as findings have shown that longer storage times reduce biogas generation due to the degradability of the readily biodegradable carbon [12]. Al\(^{3+}\) and Fe\(^{3+}\) were used for the CPR process.

2.2. Digestibility Tests

Two quantities of 2-L flat round-bottom flasks were used as the laboratory digester for both the Fe\(^{3+}\) - and Al\(^{3+}\)-dosed samples alongside their respective controls. The two bioreactors (digesters) containing the SAS were made up of one as the test (chemical-dosed sludge) and the other as the control (Figure 1). As a control, 1500 mL of SAS was measured without chemical and transferred into the first flat round-bottom flask. To give it some organic carbon, 20.5 g of sucrose was added, which facilitated readily degradable carbon, and a magnetic stirrer was used to give it slow stirring to promote uniformity of the sample in the digesters. From the anaerobic sludge tank, 40 g of sludge was used for bioaugmentation to enhance and speed up the microbial activities. They were also flushed with nitrogen gas to ensure anaerobic conditions. The second flat round-bottom flask containing the same sample was then pretreated with 200 mL of 100 mg/L as Fe\(^{3+}\) solution. The experiments were also
repeated with 100 mg/L as Al$^{3+}$ solution. Initial jar tests showed that phosphorus levels were reduced to <0.5 mg/L between 50 and 100 mg/L doses of the metal salts. The maximum dose of 100 mg/L was then chosen for the digestion experiments. The test and control sludge samples were digested at mesophilic temperatures (35 °C) for 12 days until the biogas production subsided. The temperature of digestion was maintained at 35 °C throughout the experiment as most mesophiles grow best within the temperature range of 30–35 °C [22]. The experiments were repeated twice, and average data are reported. The digestibility of the test and control sludge was evaluated by measuring the biogas volume using a manometer (Dwyer flex-tube series 1222 U-tube manometer containing red gauge fluid, Michigan, USA).

**Figure 1.** Anaerobic digester setup for test and control samples.

### 2.3. Dewaterability Tests

For the dewaterability tests, a set of three laboratory-batch-scale experiments were carried out in 1000-mL beakers with a sludge sample of 500 mL. Al$^{3+}$ and Fe$^{3+}$ salts at volumes of 0, 10, 20, 25 and 50 mL were added to each beaker containing 500 mL of sludge. The homogeneity of the sludge mixture was ensured throughout the reaction by stirring at 2 rpm using an overhead stirrer. Then, 25 mL of the control and Al$^{3+}$ and Fe$^{3+}$-dosed samples (10, 20, 40, 50 and 100 mg/L) were collected and analysed using a standard Triton UK-Type 304B capillary suction time (CST) device (Essex, UK) [23], equipped with an 18-mm reservoir resting on standard Whatman No. 17 grade chromatography paper. The dewaterability of the sludge was monitored using the CST dewaterability parameter. Three replicates of each dewaterability condition were performed with the samples analysed in triplicates to ensure the reproducibility of the experimental test results, and the mean values of CST were then recorded and reported. The details of the experimental procedures have been previously described in detail by Scholz [24] and Sawalha and Scholz [25]. All the test results reported are the means and standard deviation of three independent samples.

The effects of the metal salts (Al$^{3+}$ and Fe$^{3+}$) were evaluated using Equation (1) for reduction percentage (%) of CST:

$$R\% = \frac{(CST_0 - CST_d)}{(CST_0)} \times 100\%$$

where $CST_0$ is the initial sludge CST, and $CST_d$ is the sludge CST after chemical dosing.
3. Results and Discussion

3.1. Effects of Aluminium and Ferric Dosing on Biogas Production

The sludge digestibility was investigated in a laboratory-scale anaerobic digester (Figure 1). All the test results reported in Table 1 and Figure 2 are the means and standard deviation of three independent samples. The results of the digestibility test showed that the mean cumulative biogas volumes produced for the undosed digested sludges after the first sludge age (12 days) were 31.56 ± 2.3 and 34.91 ± 1.3 mL, compared with the Al³⁺-dosed sludge of 24.85 ± 1.3 mL and Fe³⁺-dosed sludge of 22.46 ± 1.5 mL, respectively. This indicates a 21.3% and 35.7% reduction in the biogas volume as a result of CPR using 100 mg/L of Al³⁺ and Fe³⁺, respectively.

![Graph](image1)

(a)

![Graph](image2)

(b)

Figure 2. The effects of metal salt dosing for chemical phosphorus removal (CPR) on the cumulative biogas generation in an anaerobic digester. (a) Al³⁺-dosed surplus activated sludge (SAS) and (b) Fe³⁺-dosed SAS. Error bars represent the standard deviation (SD) of three independent replicates.
Reduced biogas production as a result of chemical phosphorus removal using ferric has been previously reported [13]. Biogas reductions of 20% [26,27], 21%–32% [28] and 32% [29] were previously reported for mixed sludges. The current study showed a 19.65% and 35.16% reduction in the biogas volumes after CPR treatment with 100 mg/L of Al\(^{3+}\) and Fe\(^{3+}\) salts, respectively. This is in agreement with the range of 20%–50% reduction previously reported by Ofverstrom et al. [30]. Although the previous studies were on mixed sludge, the current research provides data on SAS and compares the biogas reduction effects of alum and ferric salts. There was a clear indication that between the Al\(^{3+}\)- and Fe\(^{3+}\)-digested sludge, Fe\(^{3+}\) caused an estimated 15.51% further reduction in biogas production compared with Al\(^{3+}\). Therefore, for the purpose of CPR, Al\(^{3+}\)-dosed sludge yields about 15.51% more gas than Fe\(^{3+}\)-dosed activated sludge.

The reason for this high rate of biogas production in undosed sludge compared with the metal (Al\(^{3+}\) and Fe\(^{3+}\))-dosed sludges may be attributed to the increased availability of the substrate for metabolism and possibly due to the microbial community in the seeded sludge being more susceptible to breaking down undosed SAS compared with aluminium- and ferric-dosed SAS. The reduced biogas production for the Al\(^{3+}\)- and Fe\(^{3+}\)-dosed sludges can also be due to the substrates, such as proteins, that form the majority of the components in the sludge (SAS) being tightly bound to the surface of the Al\(^{3+}\)-dosed sludge precipitate and Fe\(^{3+}\)-dosed sludge being entangled within the sludge floc [28]. It has been suggested that the reduction in biogas volume of Al\(^{3+}\)-dosed sludge compared with undosed sludge may be due to the time length of producing and hydrolysing the substrate [31]. Further, the strong bond of proteins to aluminium may cause a reduction in the rate of biogas production [31]. It has also been inferred that the biogas reduction may be attributed to the reduced availability of microbial population to organics [26,28].

### 3.2. Effects of Aluminium and Ferric Dosing on Sludge Dewaterability

CST is the most widely used dewaterability parameter for monitoring sludge dewaterability. The CST test estimates the filtration rate in terms of time for free water to pass between two electrodes using a filter paper as the medium [32]. Longer CST indicates poor sludge dewaterability, while shorter CST indicates good dewaterability [9,33]. The results of the sludge dewaterability (mean CST) for Al\(^{3+}\)- and Fe\(^{3+}\)-dosed primary sludge and secondary sludges at concentrations of 0, 20, 30, 40 and 50 mg/L for the batch tests (1 and 2) using an 18-mm reservoir are summarised in Tables 2 and 3. All test results reported in Tables 2 and 3 are the means and standard deviation of three independent primary and secondary sludge samples. It was observed that the mean CST reduced with the increasing concentration of Al\(^{3+}\) and Fe\(^{3+}\) doses (20, 30, 40 and 50 mg/L) in primary sludge, while mean CST increased with the increasing concentration of Al\(^{3+}\) and Fe\(^{3+}\) doses (20, 30, 40 and 50 mg/L) in secondary sludge. Shorter CST indicates good dewaterability, while longer CST signifies poor dewaterability [10,27].

The chemically dosed primary sludges showed reduced CST (better dewaterability) compared with the undosed sludge. The CST decreased with increasing doses of Al\(^{3+}\) and Fe\(^{3+}\). As can be seen in Table 2, there was a 25.1% and 16.2% improvement in the rate of dewaterability of primary sludge at 50 mg/L CPR doses of Al\(^{3+}\) and Fe\(^{3+}\) salts, respectively. This indicates that CPR, by a pre-precipitation method where phosphorus is precipitated out in the primary sedimentation tank, would be more beneficial for enhancing sludge dewaterability. The observed CST reduction for the primary sludge following the CPR may be due to the ability of multivalent coagulants (Al\(^{3+}\) and Fe\(^{3+}\) salts) to interact with the microbial clusters and break the EPS structure bound with water [34]. This could also be

### Table 1. Cumulative biogas volume production after 12 days.

<table>
<thead>
<tr>
<th></th>
<th>Fe(^{3+})-Dosed SAS (Control)</th>
<th>Al(^{3+})-Dosed SAS (Control)</th>
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<tbody>
<tr>
<td>Cumulative biogas (mL)</td>
<td>22.46 ± 1.5 (34.91 ± 1.3)</td>
<td>24.85 ± 1.3 (31.56 ± 2.3)</td>
</tr>
<tr>
<td>% Biogas reduction</td>
<td>35.7%</td>
<td>21.3%</td>
</tr>
</tbody>
</table>
due to the neutralisation of the negative charge on the sludge floc since the EPS is negatively charged and responsible for an increased surface charge (zeta potential) of microbial aggregates which causes decreased settleability and flocculability of microbial clusters [35].

Table 2. Mean and standard deviation data of capillary suction time (CST) and CST reduction efficiency for undosed and dosed primary sludges.

<table>
<thead>
<tr>
<th>Coagulant Concentration (mg/L)</th>
<th>CST (s)</th>
<th>% CST Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe$^{3+}$</td>
<td>Al$^{3+}$</td>
</tr>
<tr>
<td>0</td>
<td>18.0 ± 3.04</td>
<td>18.0 ± 3.04</td>
</tr>
<tr>
<td>20</td>
<td>16.26 ± 2.22</td>
<td>16.83 ± 3.95</td>
</tr>
<tr>
<td>30</td>
<td>15.29 ± 1.77</td>
<td>16.24 ± 4.54</td>
</tr>
<tr>
<td>40</td>
<td>14.39 ± 1.84</td>
<td>15.66 ± 5.18</td>
</tr>
<tr>
<td>50</td>
<td>13.49 ± 2.18</td>
<td>15.07 ± 5.86</td>
</tr>
</tbody>
</table>

Table 3. Mean and standard deviation data of CST for undosed and dosed sludge surplus activated sludges.

<table>
<thead>
<tr>
<th>Coagulant Concentration (mg/L)</th>
<th>CST (s)</th>
<th>% CST Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe$^{3+}$</td>
<td>Al$^{3+}$</td>
</tr>
<tr>
<td>0</td>
<td>33.17 ± 2.04</td>
<td>33.17 ± 2.04</td>
</tr>
<tr>
<td>20</td>
<td>43.7 ± 1.76</td>
<td>47.97 ± 1.37</td>
</tr>
<tr>
<td>30</td>
<td>47.91 ± 2.77</td>
<td>52.49 ± 0.71</td>
</tr>
<tr>
<td>40</td>
<td>51.23 ± 4.87</td>
<td>55.57 ± 2.56</td>
</tr>
<tr>
<td>50</td>
<td>54.33 ± 4.87</td>
<td>57.37 ± 5.60</td>
</tr>
</tbody>
</table>

However, the neutralisation effect of increasing chemical dosing (Al$^{3+}$ and Fe$^{3+}$) on the primary sludge will improve dewaterability with a shorter CST value. This is due to reduced repulsive forces between the sludge flocs and release of bound water to the sludge floc matrix [36]. It was mentioned that surface charge chemistry and disruption of the EPS structure are responsible for shorter CST [37,38]. The observed shorter CST reported in the primary sludge could also be due to polymer bridging [39] resulting in the destabilisation of colloidal particles present in sludge floc. Therefore, in the current study, it can be concluded that the reduced CST, as a function of the impact of chemical dosing on the primary sludge, improved dewaterability due to the surface charge chemistry and disruption of the sturdy EPS structure bound with water.

In contrast, the results of the sludge dewaterability (mean CST) for Al$^{3+}$- and Fe$^{3+}$-dosed secondary sludge (SAS) at a concentration of 0, 20, 30, 40 and 50 mg/L using an 18-mm reservoir are presented in Table 3. From the results, it was observed that the mean CST increased with the increasing concentration of aluminum and ferric (20, 30, 40 and 50 mg/L). At 50 mg/L of Al$^{3+}$ and Fe$^{3+}$ CPR doses, 72.96% and 63.82% reductions in SAS dewaterability (increased CST values) were respectively observed, indicating that if CPR is applied by coprecipitation in activated sludge plants using these salts, there will be a significant reduction in the dewaterability rates of the resultant SAS. The observed behaviour may be due to the interaction between the multivalent coagulants (Al$^{3+}$ and Fe$^{3+}$) and higher EPS content, which has a tendency to limit the flocculating and settleability ability of microbial clusters. This limitation will further cause the water retention capacity and quantity of bound water in the EPS to rise and, hence, restricts the outflow of interstitial water from the sludge floc pore spaces [19,40]. Another probable reason may be due to the reduction and solubility of coagulants (Al$^{3+}$ and Fe$^{3+}$), causing protein to enter into the solution and a fragile connection between the protein structure and the sludge floc, which may limit dewaterability improvement [41]. Also, it may be due to increased resistance and binding from the sludge floc [42].
4. Conclusions

The effects of chemical phosphorus removal using Al\(^{3+}\) and Fe\(^{3+}\) salts on activated sludge digestibility in batch settling tests using a locally designed laboratory anaerobic digester and activated sludge dewaterability using a new CST type 304B suction device were investigated. The results demonstrated that the use of Al\(^{3+}\) and Fe\(^{3+}\) salts reduced the digestibility of surplus activated sludge, with Al\(^{3+}\) salt having up to 15% less reduction effect compared with Fe\(^{3+}\). Also, Al\(^{3+}\) and Fe\(^{3+}\) salts improved the dewaterability of primary sludge by 16% and 25% but significantly reduced the dewaterability of SAS by 73% and 64%, respectively. The results demonstrated that using Al\(^{3+}\) and Fe\(^{3+}\) salts in the CPR process will improve the dewaterability of primary sludge but decrease the dewaterability of SAS. It can therefore be inferred that for the purpose of optimising the dewaterability of activated sludge, a pre-precipitation process where phosphorus is removed in the primary tank would be more ideal during the CPR process.

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References


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