Impact of Al$^{3+}$ on sludge granulation in UASB reactor

Tasneem Abbasi, R Sanjeevi, J Anuradha and S A Abbasi*
Center for Pollution Control and Environmental Engineering, Pondicherry University
Puducherry 605 014, India

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Impact of trivalent aluminium (Al$^{3+}$) ion, added to the feed of upflow anaerobic sludge blanket (UASB) reactor, was assessed on the granulation of the reactor sludge. The impact on the reactor efficiency in treating chemical oxygen demand (COD) and generating biogas was also simultaneously assessed. It was seen that, at all the three Al$^{3+}$ concentrations (100, 200 & 300 mg/L) studied, the metal ion facilitated formation of larger-sized granules in greater proportions than the control reactor; the effect was most pronounced at 300 mg/L Al$^{3+}$ concentration. The metal fortification did not, however, influence the reactor efficiency.

Keywords: Calcium, COD, granulation, trace metals, UASB, wastewater treatment

Introduction

The upflow anaerobic sludge blanket (UASB) reactor was invented in the early 1970’s after Lettinga and van Velsen had observed the presence of biomass aggregates suspended in the interstitial voids of filter media in a clarigester. This led them to realize the presence of ‘biomass aggregates’ (since called ‘granules’) in wastewater treatment systems and the role they seemed to play in wastewater degradation. They felt that granules may be adequate for biomass retention in the anaerobic reactor and that inert carrier material of the type necessary in anaerobic filter may not be essential for that purpose. UASB was subsequently developed and has since become the most widely used of all high-rate anaerobic reactors, ahead of anaerobic filter, anaerobic baffled reactor, down flow fixed film systems, expanded/fluidized bed anaerobic reactors, etc. Close to 90% of all anaerobic wastewater treatment in the world is being done with conventional UASB reactors or its variants/hybrids UASB technology.

Very early in the development of UASB technology, it was realized that granular sludge of appropriate particle size, particle density and microfilm characteristics enhances the reactor efficiency in terms of the rate as well as the extent of wastewater treatment. From then onwards, efforts have been made by scientists across the world to understand the factors which shape the granules and the manner in which the granules contribute to wastewater treatment. Among the attempts to speed-up granule formation and enhance their efficacy, the use of metals has been explored.

Trivalent aluminium (Al$^{3+}$) is one of the metal ions reported to have beneficial effect on the granulation of anaerobic sludge in UASB reactors. Yu et al, who studied UASB reactors with and without supplementing the feed with 300 mg/L of Al$^{3+}$, found that granules began to appear earlier and grew faster in aluminium-spiked reactors. Al$^{3+}$ also seemed to improve biomass retention and enabled higher rate of chemical oxygen demand (COD) removal. However, beyond an organic loading rate (OLR) of 5.3 g COD/L.d, the specific methanogenic activity (SMA) in the Al$^{3+}$-spiked reactors dropped slightly, while the SMA in the control reactor continued to increase. Evidently the larger granule size in the former began to hinder mass transfer from the granule surface towards the inner bacterial layers; the mass transfer in this case being driven predominantly by diffusion.

The difference in the extent of sludge granulation among the two reactors was significant only at the initial stages (d 1-60). At the final stage (d 130-146), the control reactor behaved very similarly to the Al$^{3+}$-spiked reactor; the former had a little less biomass concentration but a slightly higher SMA than the latter, resulting in COD removals and effluent volatile...
suspended solid (VSS) levels very similar to the Al$^{3+}$-spiked reactor. Hence, in the study of Yu et al.$^{10}$, the addition of AlCl$_3$ was seen to play an important role only in the initial stage of granulation and its effect was seen to diminish after the development of mature granules.

A significantly different conclusion was reached by Boonsawang et al.$^{13}$ in their study of the impact of Al$^{3+}$ supplementation at 300 mg/L on the performance of UASB reactor. They found that the reactor with Al$^{3+}$ supplementation could provide a large granule size (0.8 mm) within 35 d, whereas granules of this size in the reactor without Al$^{3+}$-supplement became visible only after 63 d. Moreover, the Al$^{3+}$-spiked reactor could reach steady state within 45 d, 10 d earlier than the control reactor did.

Considering that Al$^{3+}$ is an easily available and inexpensive entity, it is important to determine whether its use in UASB is beneficial, as was found by Boonsawang et al.$^{13}$, or is it really inconsequential as reported by Yu et al.$^{10}$. Hence, in the present work, the role of 300 mg/L of Al$^{3+}$ has been reassessed to see whether it enables endorsement of the findings of Yu et al.$^{10}$ or Boonsawang et al.$^{13}$. In addition, the role of 200 and 100 mg/L of Al$^{3+}$ has also been studied.

**Materials and Methods**

**Operation of UASB Reactors**

Glass-made UASB reactors of 1000 mL working volume (Fig. 1) were employed. Four sets of reactors, in duplicate, were seeded with equivalent amounts (150 mL) of sludge obtained from a mature UASB reactor treating confectionary waste of a large industry (EID Perry, henceforth referred as EIDS). The characteristics of the sludge were as in Table 1. Each set of reactors were spiked with 0, 100, 200 or 300 mg/L of Al$^{3+}$. Each reactor was also fed with wastewater of characteristics as in Table 1 but appropriately diluted with distilled water to a COD of 3000 mg/L.

All the reactors were started up simultaneously at a hydraulic retention time (HRT) of 48 h. After a reactor attained steady state, as reflected from the extent of COD reduction reaching a plateau and fluctuating within a narrow range for a week, the spiking of the feed with Al$^{3+}$ was discontinued and its HRT was lowered to 24 h. On reaching steady state at this HRT, the HRT was again lowered to 12 h, then to 6 h, and finally to 4 h. In this manner, the HRT of each reactor was lowered in stages of 48, 24, 12, 6, and 4 h. Throughout reactor operation, pH, COD, TS (total solid), VS (volatile solids) and VSS were monitored as per standard methods.$^{14}$ The biogas yield was quantified daily by the volume of distilled water and acidified to pH 4 to prevent dissolution of CO$_2$ it replaced.$^{15,16}$ The gas production was normalized by calculating the volume the gas would occupy at NTP (normal temperature and pressure). Every week a sample of the biogas was analysed for its methane content by gas chromatography.

The statistical significance of the difference in performance between successive sets of reactors or of individual sets of reactors, but at successive HRTs, was assessed by employing the Student’s test.$^{17,18}$

**Particles Size Distribution, Settling velocity (SV) and Sludge Volume Index (SVI)**

Particle size distribution was estimated by following the method described earlier by Francese et al.$^{19}$, and used successfully by others.$^{20-22}$ Sludge samples were taken from the bottom sampling points.

| Table 1—Characteristics of the seed sludge |
|----------------|-------------------|
| Characteristic                  | EIDS              |
| chemical oxygen demand (COD), mg/L | 51,500            |
| Total solids (TS), g/L          | 61.0              |
| Volatile solids (VS), g/L       | 30.8              |
| Volatile suspended solids (VSS), g/L | 25.7          |
| VSS/TS                         | 0.42              |
| Particle size, mm               | 0.21              |
| Sludge settling velocity (SV), m/h | 10.0            |
| Sludge volume index (SVI), mL/g | 40.0              |

![Fig. 1—Schematic of the UASB reactor employed in the present study.](image)
and separated into six fractions using laboratory sieves with different porosities (0.15, 2.0, 3.0 & 4.0 mm). The sludge particles were first placed in the sieve with the highest porosity (4.0 mm), the sieve was gently submerged in water and shaken to let the smaller particles pass through. The smaller particles were then sieved through the next most porous sieve (3.0 mm) and the procedure was repeated until all the four sieves had been used.

SV was measured by a method similar to the one reported by Laguna et al23 and adopted by others24-26. A glass column of 7.5 cm diameter and 75 cm height was filled with 250 mL of water. To it, 25 mL of sludge was added; the contents were mixed by stirring and allowed to settle. At fixed time intervals (0.5, 1.0, 2.0, 3.0, 5.0, 7.0, 15.0, 30.0 and 60.0 min), the settled and allowed to settle. At fixed time intervals (0.5, 1.0, 2.0, 3.0, 5.0, 7.0, 15.0, 30.0 and 60.0 min), the settled sludge was collected and weighed. The average SV was calculated as:

$$\text{SV} = \frac{\Sigma (\text{Mass of sludge fraction settled} \times \text{settling velocity of that fraction})}{\text{Total wt of sludge sample}}$$

SVI, which is a broad, semi-quantitative indicator of the volume of sludge that will make the sludge column in a UASB reactor (as distinct from the fraction that would be buoyant) was measured as volume in mL of the sludge occupied by 1000 mg of a sludge suspension after 30 min of settling.

**Results and Discussion**

The extent of COD removal at steady state in each of the reactors is presented in Table 2. There was significant (≥95% confidence level) increase in the COD removal between reactors operating at 24 h HRT and the reactors operating at 12 h HRT. There was also a similarly significant lowering in COD removal when HRT was reduced from 12 to 6 h. However, the difference in COD removal between 48 and 24 h HRT, and between 6 and 4 h HRT was not statistically significant. Moreover, at each HRT, the performance of individual reactors was not significantly different from each other.

<table>
<thead>
<tr>
<th>UASB reactor sludge spiked with Al&lt;sup&gt;3+&lt;/sup&gt; (mg/L)</th>
<th>Maximum COD removal (%) at HRT (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (R1)</td>
<td>48</td>
</tr>
<tr>
<td>100 (R2)</td>
<td>74</td>
</tr>
<tr>
<td>200 (R3)</td>
<td>79</td>
</tr>
<tr>
<td>300 (R4)</td>
<td>80</td>
</tr>
</tbody>
</table>

The pattern of onset of granulation in different reactors is presented in Table 3. The reactors wherein granulation occurred within the least time from the start were the ones spiked with 300 mg/L Al<sup>3+</sup> (R4). The reactors spiked with 200 mg/L of Al<sup>3+</sup> (R3) were the next to evidence granulation, followed by the reactors spiked with 100 mg/L Al<sup>3+</sup> (R2). The control reactors (R1) were the last to experience granule formation by 45<sup>th</sup> d. The granule size distribution at steady state and at different HRTs in each of the reactors is presented in Table 4. The data is the average of duplicates, which always agreed within ±10%. It was observed that, at 48 h HRT, all reactors had granules of only dia ≤1.0 mm, except R4 that also had 15% of its granules of the next bigger size (>1.0-2.0 mm). In all reactors, the predominant fraction was of smaller granules of the size 0.2-0.5 mm. At 24 HRT, some granules of higher size-range (>1.0-2.0 mm) formed in R2 as well. As HRTs were lowered in stages to 12 and 6 h, the pattern of granule size distribution shifted in a fairly consistent manner; the fraction of the smallest size granules (0.2-0.5 mm) was progressively reduced, while that of larger size granules progressively increased.

The SVs of different fractions of sludge granules taken from the UASB reactors on the 15<sup>th</sup> and 20<sup>th</sup> d, and at different HRTs, at steady state are presented in Fig. 2. As expected, the SVs increased as the proportion of bigger granules increases, as well as with lowering of HRT in the reactors. The SVI values also display a clear trend towards increasingly more beneficial sludge formation with time (Fig. 3).

The maximum biogas yield at steady state at different HRTs is summarized in Fig. 4. As may be seen, the biogas yield was more a function of HRT than Al<sup>3+</sup> fortification. As HRT was lowered with concomitant increase in OLR (organic loading rate), biogas yield sharply increased but there was little difference in yields among different reactors at the same HRTs. The proportion of methane in the biogas was 60-66% throughout, providing a flammable gas which burnt with a clear blue flame.

The results of the present investigation are more supportive of the earlier report of Boonsawang et al13 in comparison to that of Yu et al10 as mentioned earlier. The present work also reveals that Al<sup>3+</sup> at levels lower than the one (300 mg/L) studied by the previous authors is also helpful in granulation of UASB sludge, but the effect is less pronounced at 200 mg/L and still lesser at 100 mg/L. All-in-all, use
of Al\(^{3+}\) appears to be beneficial in methane capture initiatives of the type needed to reduce greenhouse gas emissions\(^{27-29}\).

### Conclusion

Spiking the UASB reactor feed with Al\(^{3+}\) for the first 45 d after the start-up at levels of Al\(^{3+}\) ranging from 100-300 mg/L facilitated early granulation as well as promoted the formation of more granules of larger size than in the reactors operated with unspiked feed. The effect was most pronounced at the highest of the Al\(^{3+}\) concentrations studied, viz., 300 mg/L, and followed the order 300>200>100>0 mg/L.

The extent of COD removed and the extent of biogas generated were both sensitive to HRT but not to the Al\(^{3+}\) concentrations. It has been reported earlier that more granular the UASB sludge, higher the proportion of larger-sized granules in a UASB sludge, lesser the threat of the sludge getting washed and greater the resilience...
towards shock loads. In that respect, if not in terms of
greater treatment efficiency, Al\textsuperscript{3+} aided granule
development appears to be useful.

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