Anaerobic granular sludge properties at high salinity

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Abstract
Laboratory experiments were carried out to investigate the granule properties evolution in upflow anaerobic sludge blanket (UASB) reactors treating high salinity wastewater (20 g Na^+/L), operated under variable conditions. The UASB reactors were fed with either fully acidified substrate (FAS) consisting of an acetate medium (reactors R1 and R2) or partially acidified substrate (PAS) consisting of acetate, gelatine and starch medium (reactors R3 and R4). Granule properties assessment was based on various physicochemical characteristics. The experiment results demonstrate that PAS–grown granular sludge showed an important increase in particle size during the operation of the UASB reactors. Addition of 0.3 gCa^{2+}/L to the high salinity wastewater increased the granules strength, probably due to the formation of $CaCO_3$ precipitation, but lead to unstable reactor performance. It is apparent that the used methanogenic granular sludge tolerates a high salinity wastewater. Substrate composition plays an important role in the formation and growth of anaerobic granules, also under saline conditions.

Keywords
Anaerobic granules; fine particles; granule properties; high salinity; particle size distribution

INTRODUCTION

High salinity wastewater results from industrial water loop closure as well marine-based food processing industries. In addition, high influent COD concentrations are often accompanied by high salinity. The treatment of these wastewaters is becoming a major concern for researchers, regulators and engineers (Xiao and Roberts, 2010). Considering its advantages, there is a growing interest to treat the (highly concentrated) saline wastewaters by anaerobic wastewater treatment using sludge bed technology (van Lier, 2008). This study focuses on anaerobic treatment of wastewaters containing high level of sodium, with particular attention on the anaerobic granular sludge properties under such conditions. Four upflow anaerobic sludge blanket (UASB) reactors were operated at 20 g Na^+/L. Two of them were fed with partially acidified substrate (PAS) and the other two with fully acidified substrate (FAS) to compare the effect of different substrates on granules' activity, stability and growth. The effect of Ca^{2+} augmentation on anaerobic granules properties was studied both in continuous flow and batch reactors. The K^+/Na^+ ratio in the feed water was based on seawater concentrations. The performance of all reactors was compared during 120 days of operation. The physical-chemical properties of the granules were analysed and are discussed.

MATERIALS AND METHODS

UASB reactor operation The reactors were inoculated with granular sludge from a full-scale UASB treating saline (10 g Na^+/L) chemical wastewater, Moerdijk, the Netherlands (Ismail *et al*., 2010). The experiments were performed in a temperature-controlled room at 30±2 ^{0}C using four glass UASB reactors with a volume of 3 L each. Operational and influent parameters for the reactors are given in Table 1. The nutrient solution consisted of macro and micronutrients and was prepared according to Vallero *et al*. (2003).

Batch experiments Batch experiments were performed in parallel in two sets of 0.1 L bottles (sets A and B). Each set consisted of 10 bottles and one bottle was sacrificed for every sampling. The inoculums were exposed to 20 g Na^+/L in the absence of feeding. Set B was augmented with

$CaCl_2.2H_2O$ at 0.3 mgCa^{2+}/L. Set A received no Ca^{2+} and served as a control. The bottles were placed on a reciprocal shaker (120 rpm) at 30^0C. The experiments were performed in duplicate.

Table 1: Operational and influent parameters for the reactors fed with fully acidified substrates (FAS) (reactors R1 and R3) and partly acidified substrates (PAS)(reactors R2 and R4)

	Reactor			
	R1	R2	R3	R4
OLR[1] (kgCOD/m^{3}d)	23	23	23	23
HRT[2] (/day)	1.34	1.34	0.34	1.34
COD (g/L)	16	16	16	16
Ac:Gel:Sta[3] ratio	01:00:00	0.7:0.2:0.1	01:00:00	0.7:0.2:0.1
	FAS	PAS	FAS	PAS
Sodium influent (g/L)	20	20	20	20
Calcium influent (g/L)	0	0	0.3	0.3
Potassium influent (g/L)	0.7	0.7	0.7	0.7
M/D[4] ratio (g/L)	1540	1540	770	770

[1]OLR = organic loading rate; [2]HRT = hydraulic retention time; [3]Ac: Gel: Sta = acetate : gelatine : starch (w:w, based on COD equaivalent); [4]M/D = monovalent (Na^+) / divalent (Ca^{2+})

Granule properties determination Physical properties were determined by accessing the surface morphology, strength, and particle size distribution of the anaerobic granules. Scanning microscope (SEM) tools was used to show Ca^{2+} distribution in granules. For extracellular polymeric substances (EPS) extraction, the cation exchange resin (CER) method was used. Strength and particle size distribution were determined by assessing the formation of fines sludge under conditions of high shear rate and by laser diffraction, respectively. Details of all methods have been described elsewhere (Ismail *et al.*, 2010).

RESULTS AND DISCUSSION

Reactor performance

Figure 1 presents the applied organic loading rate and influent and effluent COD concentrations during the 120–days operation of the UASB reactors. Until day-60, at an organic loading rate of 18 kg COD/m^{3}d, the COD removal efficiency, irrespective of the type of substrate and presence of Ca^{2+}, was remained relatively stable for all reactors, i.e. between 92 – 98 %. The FAS grown granules of reactors R1 and R3 gave somewhat higher removal efficiencies of 98 and 97 % compared to the PAS grown granules of reactors R2 and R4 of 95 and 92 %, respectively. Strikingly, COD removal efficiencies of the Ca^{2+} augmented reactors (reactors R3 and R4) exhibited a 1 to 2 % lower removal efficiency compared to the non-augmented reactors.

Granules development

After 120 days of operation, granular sludge from all reactors clearly increased in particle size compared to the inoculum (305 µm) with the largest granules' size for the reactors fed with PAS: 763 µm for reactor R2 and 581 µm for reactor R4, which received additional Ca^{2+}. The granules of the FAS fed reactor were slightly smaller: 537 µm for reactor R1 and 408 µm for reactor R3 with additional Ca^{2+}. Apparently, both with PAS and FAS addition of Ca^{2+} resulted in considerable smaller granule size.

The particle size distribution of fine particles was analysed at the end of reactor operation (results not shown). The fines from Ca^{2+} augmented granules in reactors R3 and R4 showed a similar distribution with an average size of approximately 70 – 80 µm. Although the distribution of the fines in reactor R2 was different, the average particle size was similar to this. The average size of the fines in reactor R1 was considerably bigger, i.e. 133–140 µm.

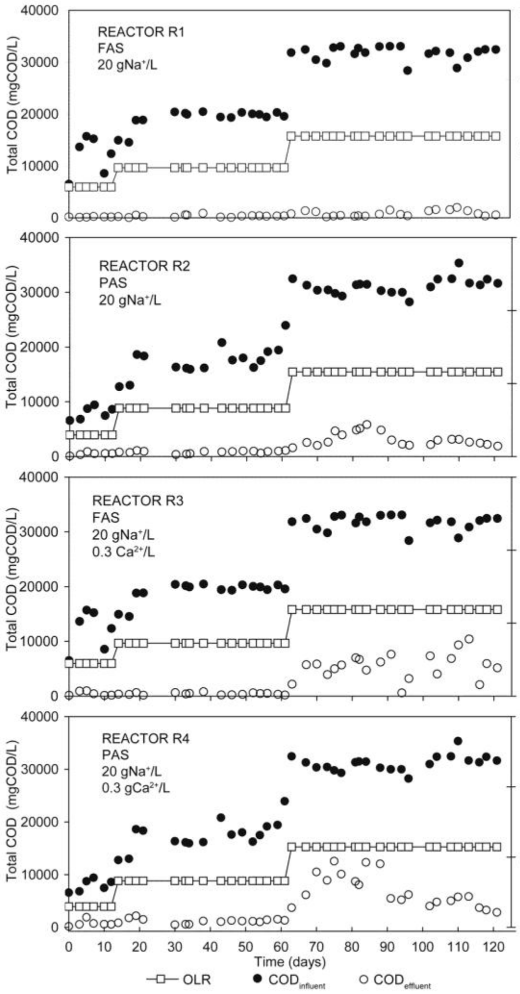

Figure 1: COD removal in percentage and applied OLR, during the operation of the UASB reactors.

After 120 days of operation, granular sludge from all reactors showed an increase in strength compared to the inoculum. Ca^{2+} augmented granules from reactors R3 and R4 had the highest strength in comparison to the other granules. In contrast, the granules without Ca^{2+} augmentation (reactors R1 and R2) were weaker. Moreover, Ca^{2+} augmented PAS grown granules (reactor R4) were more fragile than Ca^{2+} augmented FAS grown granules (reactor R3).

Ca^{2+} augmentation

To observe elements distribution within cross-sectioned anaerobic granules, random granules were selected and viewed by SEM-BSE imaging. SEM–BSE imaging allows to differentiate organic–rich (displayed with dark) and (earth-alkali) metal–rich (displayed with bright) zones. Figure 2 shows SEM–BSE images of the inoculum, a granule incubated with both 20 g Na^{+}/L and 0.3 gCa^{2+}/L, and a granule solely exposed to 20 g Na^{+}/L– Metal rich zone (bright) was predominantly present at the inner part of both the inoculum granules and the granules incubated with solely 20 g Na^{+}/L (Figure 2, top row). The Ca^{2+} augmented granules showed metal-rich zones in larger parts of the cross-sectioned granule.

CONCLUSIONS

The following conclusions can be drawn from the present research:

1. PAS grown granules are characterized by a larger size and higher strength than FAS grown granules.
2. Problems related to granule structure and strength due to high salinity partly can be overcome by application of an appropriate amount of a divalent ion (in our research 0.3 gCa^{2+}/L) in the influent.

3. Size distribution of granules fed with 20 g Na^{+}/L was increased compared to the inoculum fed with 10 gNa^{+}/L, but shear strength results show that the granules fed with 10 gNa^{+}/L are distinctly stronger.
4. Fine particle production was increased in the reactors with 0.3 g Ca^{2+}/L addition, likely due to disintegration.
5. Batch studies demonstrated that Ca^{2+} will leach to the bulk liquid when high level of Na^{+} is applied ***(results not shown in this abstract)***. By adjusting the divalent/monovalent cation ratio, applying increased bulk liquid Ca^{2+} levels, Ca^{2+} content increased in the granule, possibly preserving granule stability.

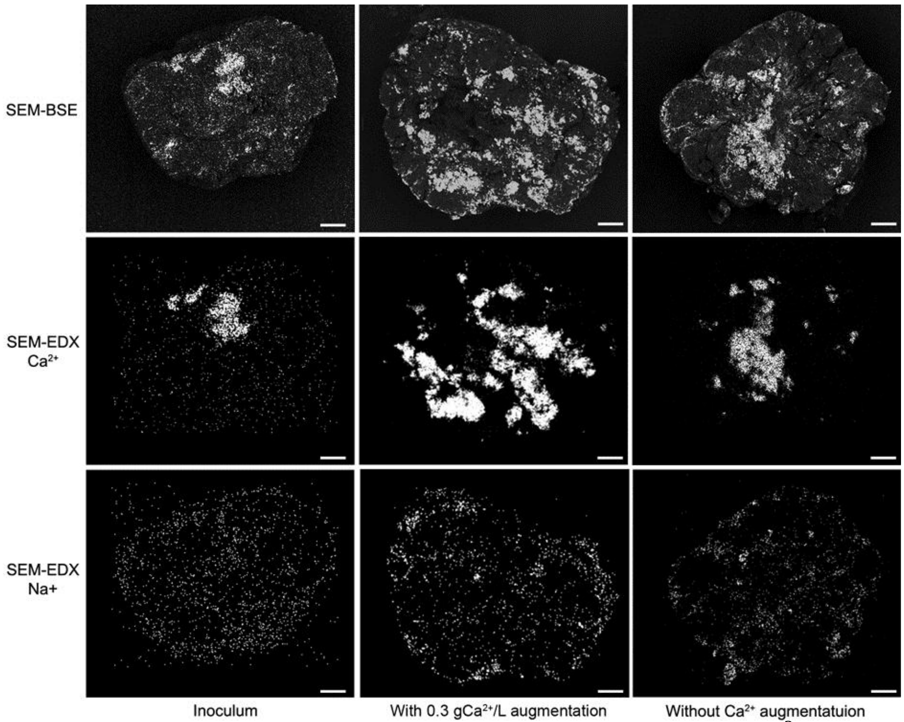

Figure 2: SEM images of cross-sectioned of inoculum, granule with 0.3 gCa^{2+}/L augmentation and granules without Ca^{2+} augmentation. Dark areas show organic rich zones; light areas show metal rich zones (for SEM-BSE images). Dot map images of a cross- sectioned granules by SEM-EDX analysis showing the distribution of calcium (Ca^{2+}) and sodium (Na^{+}). Bright spots indicate Ca^{2+} and Na^{+} abundance, respectively.

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