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Biological denitrification of brines from membrane treatment processes using an upflow sludge blanket (USB) reactor

M. Beliavski, I. Meerovich, S. Tarre and M. Green

ABSTRACT

This paper investigates denitrification of brines originating from membrane treatment of groundwater in an upflow sludge blanket (USB) reactor, a biofilm reactor without carrier. A simulated brine wastewater was prepared from tap water and contained a nitrate concentration of 125 mg/l as N and a total salt concentration of about 1%. In order to select for a suitable energy source for denitrification, two electron donors were compared: one promoting precipitation of calcium compounds (ethanol), while the other (acetic acid), no precipitation was expected. After extended operation to reach steady state, the sludge from the two reactors showed very different mineral contents. The VSS/TSS ratio in the ethanol fed reactor was 0.2, i.e., 80% mineral content, while the VSS/TSS ratio in the acetic acid fed reactor was 0.9, i.e., 10% mineral content. In spite of the low mineral content, the sludge from the acetic acid fed reactor showed remarkably excellent granulation and settling characteristics. Although the denitrification performance of the acetic acid fed reactor was similar to that of the ethanol fed reactor, there was a huge difference in the sludge production due to mineral precipitation, with the corresponding negative aspects including increased costs of sludge treatment and disposal and moreover, instability and difficulties in reactor operation (channeling). These arguments make acetic acid a much more suitable candidate for brine denitrification, despite previous findings observed in groundwater denitrification regarding the essential role of a relatively high sludge mineral fraction for stable and effective USB reactor operation. Based on a comparison between two denitrification reactors with and without salt addition and using acetic acid as the electron donor, it was concluded that the reason for the excellent sludge settling characteristics found in the acetic acid fed reactor is the positive effects of higher salinity on granular sludge formation.

Key words | brine, denitrification, granular sludge, settling characteristics, USB reactor

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INTRODUCTION

Recently developed membrane processes for water treatment inherently produce brine with problematic disposal to the environment. The volume of brine produced is approximately 10 to 20% of the water volume treated and the concentration of salts in the brine likewise varies between 5 to 10 times higher than the original source water. Today, in coastline areas, the most obvious disposal method is to sea. Strict regulations generally require treatment of brines before sea disposal to meet established criteria mainly for nitrogen compound removal. The relevant brine sources include brines from membrane desalination of brackish water that contain nitrogen compounds, brines from well reclamation plants treating well water rich in nitrogen compounds, and brines from membrane desalination of treated municipal wastewater. These brines generally contain high concentrations of

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salts and nitrogen compounds. The release of nitrogen compounds from the brine to the receiving body of water can cause algae bloom resulting in the negative effects on water quality of oxygen demand, color, turbidity, damage to existing the flora and fauna, etc.

Presently methods for brine disposal include disposal to sea or other bodies of water, disposal to existing wastewater treatment plants, dilution, injection wells, disposal to barren areas or landfills and more (Mickley 2001). The high concentration of salts and in particular nitrogen compounds and the potential for environmental damage severely limits the use of the aforementioned solutions. Indeed, the present recommendations by the Israel Ministry of the Environment for environmental regulations of sea water quality are 1 mg/l of nitrogen compounds as N. Because membrane processes and the resulting brines are relatively new processes, regulations worldwide are not in place for dealing with brine disposal. However, the US EPA has classified brines from reverse osmosis processes as industrial effluents and in the state of Florida a special permit is required for brine disposal (AMTA 2007).

The best solution for nitrogen compounds from brines is biological denitrification that selectively eliminates nitrate from the brine and converts it into nitrogen gas (Clifford & Liu 1993). Other processes such as electrodialysis, ion exchange or combinations of physicochemical processes with evaporation and more only concentrate nitrate, but do not eliminate it (Grasmick *et al.* 2002). The differences between denitrification of brine and denitrification of groundwater are mainly the higher salinity and higher nitrate concentrations in brines with its effect on water chemistry and sludge production.

This research work investigates the biological removal of nitrate from brines created in RO processes. Heterotrophic denitrification of brines was carried out in upflow sludge blanket (USB) reactors comparing the use of ethanol and acetic acid as the carbon source. An USB reactor is a biofilm reactor characterized by a self-agglomerating granular biomass that has no carrier. The efficiency of the USB reactor depends on the creation of biomass with good self-agglomerating and settling characteristics. Biomass that does not settle well washes out from a USB reactor with the effluent, and as a result the efficiency of the process can be reduced.

Previous results (Tarre & Green 1994; Tarre *et al.* 2000) of denitrification of groundwater and greenhouse leachates in USB reactors showed that the efficiency and stability of the process mainly depends on the mineral content of the biomass granules resulting from the increased precipitation potential in the reactor. Denitrification USB reactor precipitation potential depends on the chemical components of the water, the concentration of nitrate removed and on the selected electron donor. In this paper two different carbon sources were compared as the electron donors for denitrification of waste brine from membrane processes (about 1% salts): acetic acid and ethanol. When ethanol is used as the carbon source and electron donor for denitrification, more alkalinity is released than acidity in the reactor resulting in increased reactor pH, $CaCO_3$ precipitation potential and mineral sludge production. In contrast, when acetic acid is used as the carbon source and electron donor, more acidity than alkalinity is present in the reactor after denitrification reducing the potential for mineral precipitation.

MATERIALS AND METHODS

Reactors

Two USB reactors with a working volume of 2.8 litres (9 cm diameter) were used for denitrification experiments. The reactor top was equipped with a gas/solid separator to ensure efficient gas bubble removal from the granules. Intermittent mixing was also provided. All the experiments were carried out at 25°C. Feeding solutions for the reactors were made up of tap water and the following components outlined in Table 1.

USB reactor startup and operation using ethanol and acetic acid as electron donors

Sludge with a high mineral fraction (approximated 80% inorganic) from an USB reactor denitrifying low salinity ground water with ethanol as the electron donor was used as seeding material in the two USB reactors designated for brine treatment. Each reactor received between 600 to 700 ml of sludge (160 grams TSS) containing about

Table 1 | Influent solution composition (all the units are given in mg/l except pH)

Parameter	Brine with ethanol	Brine with acetic acid
pH	7	4.3
NO_3^- as N	125	125
$CaCl_2{\cdot}2H_2O$	750	750
$MgCl_2{\cdot}6H_2O$	750	750
NaCl	7,500	7,500
KH_2PO_4	2	2
C_2H_5OH	330	–
CH_3COOH	–	455

35 g VSS. As described above, one reactor received ethanol as the electron donor, while the other was fed acetic acid.

Analyses

All analyses were carried out according to Standards Methods (APHA 1995). Nitrate (ion chromatography suppressed anion method) and nitrite (colorimetric method) were measured to monitor reactor denitrification efficiency. The total and volatile suspended solids (TSS and VSS) concentrations were measured and VSS was used as the measure of biomass concentration. Calcium was measured using the EDTA titration method. Particle size distribution was measured using standard ASTM filter with pore sizes of 0.125, 0.25, 0.5, 1, 2 mm.

RESULTS AND DISCUSSION

Denitrifying USB reactor receiving ethanol

The startup and adaptation period to brine lasted for about 20 days with the reactors operating at a loading rate of 3 grams N/day (Figure 1). A brine concentration of about 1% did not significantly affect bacterial denitrification activity. Denitrification removal exceeded 95% with nitrate and nitrite effluent concentration close to zero (Figure 2). However, the ethanol fed reactor showed problems of instability as evidenced in the large range of the results between excellent and poor effluent quality (Figure 2).

Reactor instability was mostly due to the large amount of calcium precipitation (Figure 3) as a result of the higher reactor pH (usually above pH 8, Figure 4) from

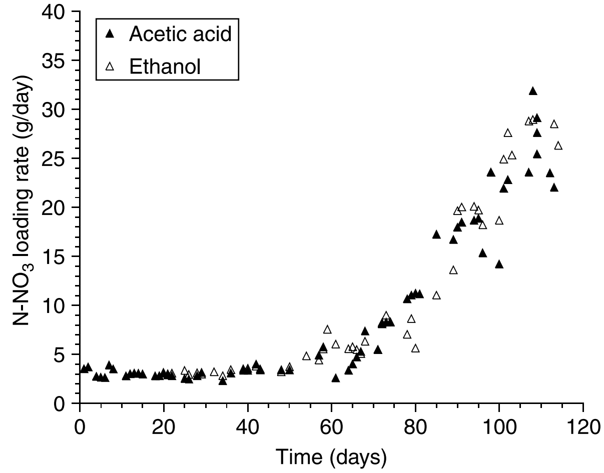

Figure 1 | Nitrate loading rate (grams N/day) of denitrifying USB reactors.

denitrification. The sludge had a correspondingly low organic fraction as shown in Figure 5 (20%) and channeling of the influent stream in the sludge blanket was observed. After day 20, the intermittent mixing system of the reactor was adjusted to higher rotational speed, and more frequent mixing intervals and a more stable performance was achieved at lower loading rates. With stable performance achieved, the sludge content of the reactor continued to increase and doubled in 30 days (Figure 6). The high sludge production reflected the high mineral precipitation rate caused by the use of ethanol as electron donor and presents a significant process disadvantage.

After day 60, excess sludge was removed from the USB reactor (Figure 6) and the nitrogen loading rates were

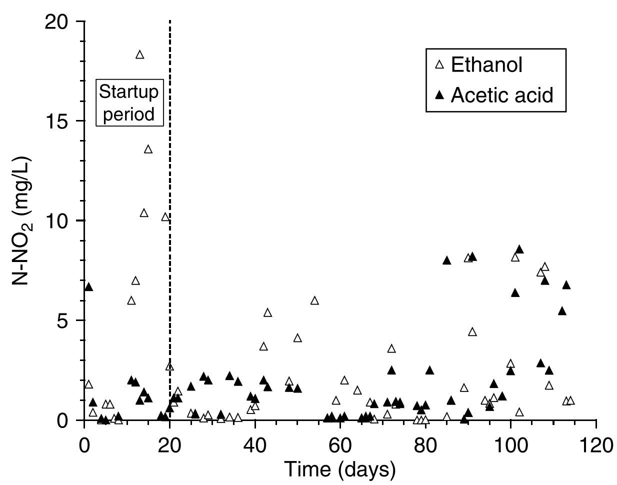

Figure 2 | Effluent nitrite concentration in the denitrifying USB reactors.

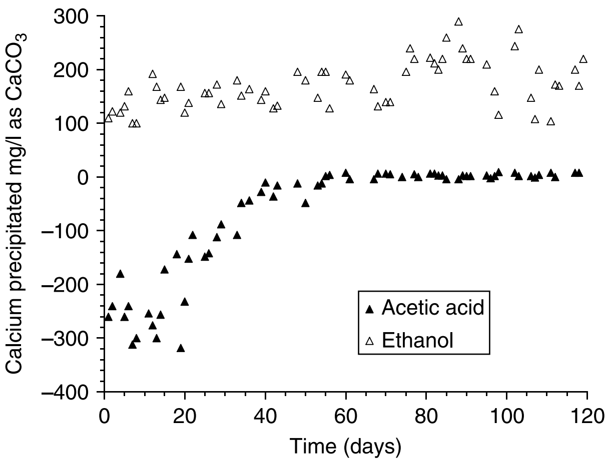

Figure 3 | Calcium precipitation and dissolution in the denitrifying USB reactors.

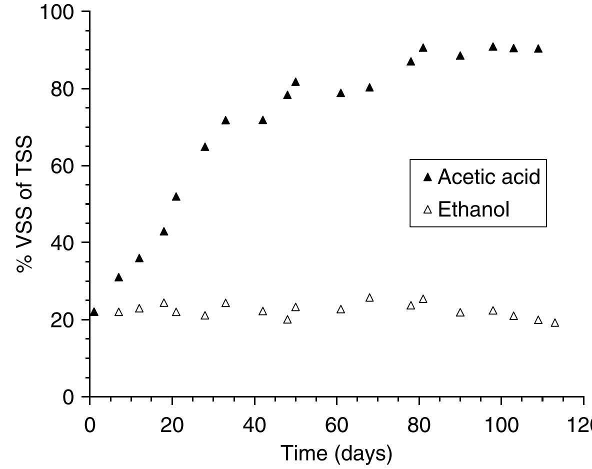

Figure 5 | Biomass content (VSS) as % TSS in the denitrifying USB reactors.

increased gradually from about 5 g N/day to 30 g N/day by increasing the flow rate (Figure 1). This increase in loading was followed by a corresponding increase in reactor TSS (from 200 to 300 g VSS) in 20 days. This demonstrates again the high sludge formation rate under conditions of calcium compound precipitation as evidenced by the low ratio of VSS to TSS throughout the experimental run (Figure 5). In continued USB reactor operation at higher loading rates, with routine excess sludge removal, the effluent quality was not stable and there were many days with N-NO_x concentrations exceeding 5 mg/l and even 10 mg/l (Figure 2), with most of the nitrogen being in the form of nitrite. The instability was due to influent channeling in the mineral dominated sludge blanket.

Denitrifying USB reactor receiving acetic acid

In comparison to the startup and acclimation period using ethanol as the electron donor, the USB reactor fed with acetic acid showed higher stability and better effluent quality (Figure 2). As was already mentioned, a highly mineralized sludge taken from an ethanol denitrifying USB reactor was used as inoculum for both reactors. For the first 50 days the acetic acid fed USB reactor sludge content decreased from 150 to 65 g TSS (Figure 6). This was due to the fact that the large inorganic fraction in the seeding sludge (80%) slowly dissolved (Figure 3) because more acidity than alkalinity remained after denitrification (reactor pH about 7, Figure 4) and the reactor was under

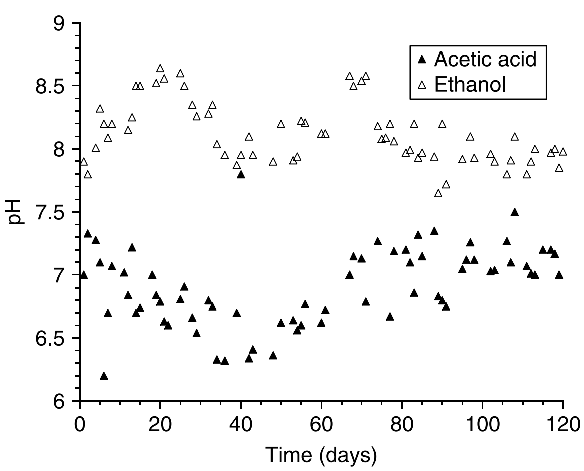

Figure 4 | pH in the denitrifying USB reactors.

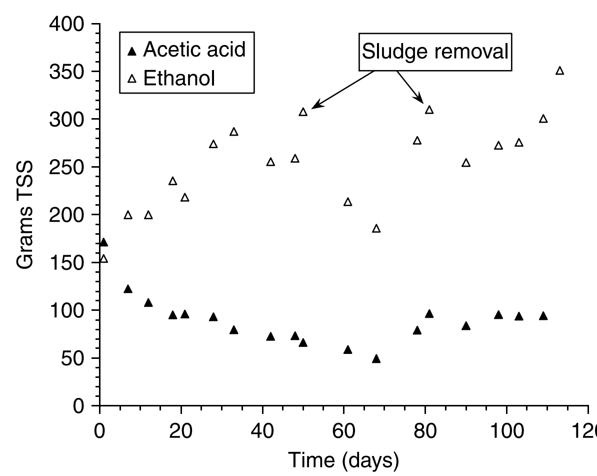

Figure 6 | Sludge content (grams TSS) of denitrifying USB reactors.

saturated with regard to $CaCO_3$. The phenomenon is clearly shown in the change in the sludge's VSS/TSS ratio from 20% to more than 80% after 50 days (Figure 5) and in the extra calcium concentration observed in the effluent. On the other hand, during the same time period the reactor VSS content (biomass) increased from about 35 to 55 g VSS. After day 60, when the nitrogen loading rate was increased, the overall amount of sludge in the reactor did finally increase to about 100 grams TSS (Figure 6), but sludge was never wasted from the reactor in the duration of the experiment. Despite the decrease in mineral fraction, SVI values remained under 20 ml/g and the sludge settling characteristics were excellent (Figure 7). This is in contrast with previous results in our lab using groundwater, which showed that denitrifying USB reactors can only operate efficiently with granules containing a relatively high mineral fraction (Tarre & Green 1994; Tarre *et al.* 2000).

While the reactor fed with ethanol was stable only with loads of up to 4 grams N/day, the reactor fed with acetic acid as electron donor was stable even at loads as high as 10 gram N/day. During the same period when the nitrogen loading rate was increased, there was a similar but less pronounced decrease in effluent quality as opposed to the ethanol fed reactor. The deterioration of effluent quality was also ascribed to some influent channeling in the sludge blanket at higher flow rates, as opposed to the pronounced phenomenon that was visibly apparent in the ethanol mineral sludge.

Saline vs. non saline operating conditions

In order to further investigate sludge formation under saline conditions, and to separate the effect of the electron donor used from the effect of salt concentration, a long term experiment was made where sludge from the acetic acid fed reactor was split equally between two USB reactors. The two reactors were operated under identical conditions and with same influent solution, except for one change: one reactor was fed with the brine influent solution (see Table 1) and the second reactor was fed with influent solution without additional salts (only tap water). A transition period of two weeks of changing salinity was given in order to adapt the saline grown sludge to tap water conditions.

Figure 8 shows the change in the biomass concentration in the sludge blanket for the two reactors over time. While the biomass concentration remained high for the brine fed reactor, the biomass concentration in the other reactor (no additional salts) dramatically dropped to less than 25% the original amount. The total volume of sludge in the reactor without additional salts did not drop as dramatically, indicating that the sludge was "less compact" and taking up more volume. This is clearly shown in Figure 9 by the large increase in sludge volume index (SVI) for the reactor fed without salts, while the SVI for the 1% brine reactor remained low. The low SVI values in the 1% brine reactor reflected the excellent sludge settling characteristics and the dense, well defined granule structure. In contrast, the sludge from the reactor fed without salts had poorer settling characteristics and the granules were

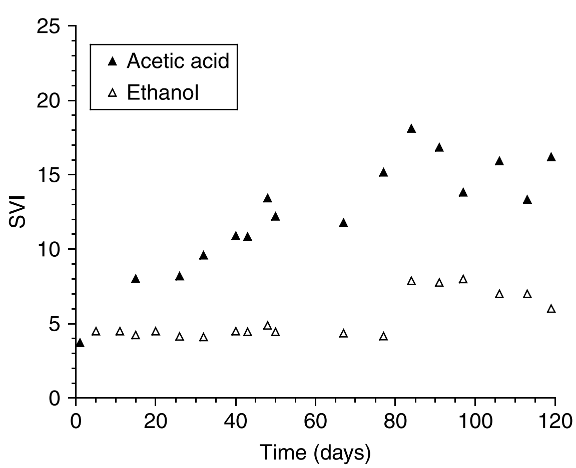

Figure 7 | Sludge volume index (SVI) of the denitrifying USB reactors.

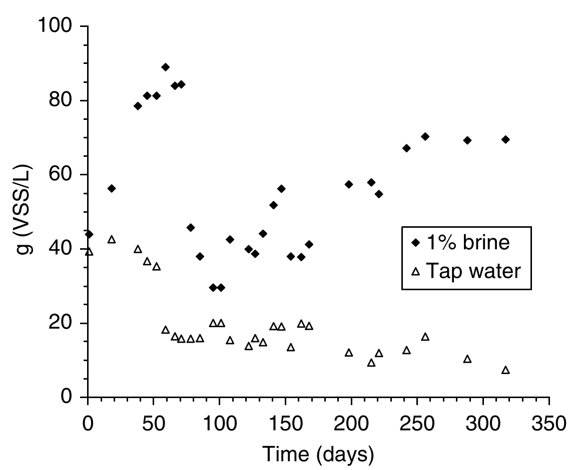

Figure 8 | Biomass concentration in the sludge blanket of the USB reactors.

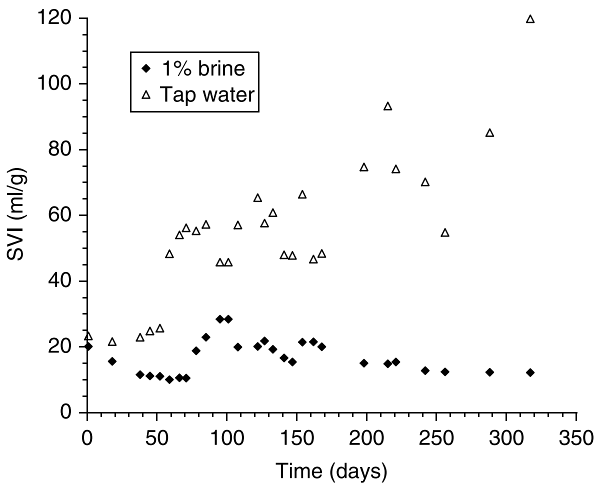

Figure 9 | Change in SVI for sludge of the USB reactors.

looser in structure with a tendency to disintegrate. Possible reasons for the excellent granule formation under brine conditions can be the effect of higher ionic concentrations compressing the biofilm electric double layer or conditions promoting the selection of bacteria populations with better granule settling characteristics (Zita & Hermansson 1994).

The particle size distribution and porosity of both reactors also showed significant differences. The sludge from the reactor that was fed with brine was mainly composed of particles between 0.5–2.0 mm (91%). The sludge from the reactor that was fed without salts addition was mainly composed of particles between 1–2 mm (68%) and from particles larger than 2 mm (20%). This means that particles from the reactor fed without the addition of salts were larger, and together with the corresponding higher SVI, lighter and easier to wash out than the particles from the reactor fed 1% brine. The smaller size particles produced in the brine fed reactor means a larger surface area to bioparticle volume and translates into a higher overall biofilm surface area in the reactor. This quality gives the sludge from the brine reactor the ability to work at higher nitrate loads and upflow velocities.

CONCLUSIONS

Heterotrophic denitrification of brines was carried out in an upflow sludge blanket (USB) reactor using simulated 1% brine. Two different energy sources were investigated, one promoting precipitation of calcium compounds (ethanol, where more alkalinity than acidity is released during denitrification), while with the other (acetic acid) no precipitation occurred (higher overall acidity than alkalinity). It was found that the efficiency of nitrate reduction in the reactor that was fed with ethanol was high, but only stable at lower loads. At higher loads, channeling was evident and effluent quality degraded. As expected, the sludge in the ethanol fed reactor contained a very high mineral fraction and very low SVI. The efficiency of denitrification in the acetic acid fed reactor was also high and showed stable operation at higher loading rates. The biomass VSS to TSS ratio in the acetic acid reactor changed dramatically from being a highly mineralized sludge (0.2) to one with a high concentration of bacteria (0.9) as a result of calcium carbonate dissolution that occurred under the unsaturated conditions prevailing in the reactor. Despite the decrease in mineral fraction, the SVI values remained low and the sludge settling characteristics were excellent. Under saline conditions, the high calcium carbonate precipitation in the ethanol fed reactor is disadvantageous due to the production of large quantities of sludge and unstable effluent quality.

Further experiments conducted to investigate granule sludge formation under little or no mineral precipitation in a denitrifying USB reactor showed that higher salt concentrations positively affected the settling characteristics of granules. In a USB reactor operating without additional salts, the SVI increased and the sludge settling characteristics deteriorated. In a similar reactor fed with a 1% brine solution, no change in the sludge properties was observed and the sludge was very dense and settled well. Based on the results presented in this paper, it can be concluded that the USB reactor is suitable for denitrification of brine under conditions minimizing mineral precipitation.

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