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EXAMINATION OF THE USE OF SUPPORT MATERIALS OF NATURAL ORIGIN IN WASTEWATER TREATMENT

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Wastewater has become continuously concentrated since 1990 in Hungary as the price of drinking water started to increase intensively from that year. Adding to that, reject water, leakages from landfills, and technological effluents of meat waste processing resulted in high specific nitrogen removal requirements at waste liquids of low COD/TKN ratio. Separated treatment of such waste streams is strongly recommended. We applied zeolite and alginite (supporting materials of natural origin and low price) in three parallel experiments to examine their effects on nitrogen removal using synthetic wastewater in these trials. First we measured the efficiency of a cyclically aerated biofilter (zeolite bed). Then we studied the efficiency of an AS SBR (zeolite powder containing activated sludge unit, operated as sequencing batch reactor), finally we substituted zeolite with alginite. The last one has not been examined for improving nitrogen removal in wastewater treatment in our country till now. We tested the three versions parallel with their proper controls. That is why one of the reactors always contained the seeding activated sludge exclusively to compare the effect of the subsidiary component (zeolite/alginite). The best results were received with using zeolite to the activated sludge. It improved both nitrogen removal and sludge settling. Addition of alginite to the AS also considerably improved sludge settling even at low dosages; therefore further pilot plant controls are recommended before any industrial application of the two support material.

Keywords: zeolite, alginite, SBR, wastewater

Introduction

Water consumption started to decrease at the beginning of 1990 in Hungary. The main reason for this was the significant change in the price of water. The average personal water consumption is 80–120 liters/day in the cities and 50–60 liters/day in the country (it is 150 liters/day in average in Europe). In spite of that the amount of collected and purified sewage in the country has not decreased, moreover it slightly has increased because considerable areas have been canalized in the meantime.

Increase of concentration of the sewage is not serious problem in COD or BOD removal, but it is for fulfilling the strict nutrient limits of the recipients or the discharge regulation especially in the TN figures.

Biological systems for nitrogen removal can be improved by separate treatment of highly concentrated waters, such as supernatant produced during dewatering of digested sludge, effluents from the fertilizer and fish canning industry, manure systems and landfill leachates.

In wastewater treatment plants (WWTP) with anaerobic sludge digestion, a recirculated supernatant contributes to 10–15% of the influent nitrogen load. Therefore, it is proposed to treat the supernatant separately rather than return it to the WWTP inlet for treatment as a part of the main flow [1–3].

As the specific nitrogen uptake and oxidation capacity of the activated sludge in the main stream can hardly be increased, this increase of ammonium load requires similar increase in treating volumes and biomass, or mixed liquid volumes. On the other hand the extra ammonium load of the highly concentrated reject water (0.5–1.5 g NH_4-N/l in about 1 % of the main sewage flow) can separately be treated with sophisticated technologies nowadays [4–6].

Aim of the experiments

The aim of our experiments was to establish whether support materials of natural origin and low price (like zeolite and alginite) are suitable to be used as biofilm carriers. Besides we were about to determine the capacity of ammonium fixation on zeolite in various surroundings and granulation size.

We wanted to examine the influence of possibility of the zeolite used in sewage purification in various reactor constructions. For this reason we examined both biofilter and moving bed reactors [7-9].

We carried out measurements in terms of the efficiency of TOC and nitrogen removal and sludge settling. Furthermore we studied the suitability of using alginite for the same purpose.

Support materials used

Synthetic wastewater was prepared using demineralized water, a nutrient mix necessary to maintain the bacterial growth. Composition of the synthetic wastewater composition is shown in *Table 1.*

Table 1: Composition of synthetic wastewaters

Raw materials	Concentration (mg/l)
Milk-powder	0.52
Urea	0.08
$(NH_4)_2SO_4$	0.10
$CaCO_3$	0.05
$Na_3PO_4 \cdot 12\ H_2O$	0.18
$CH_3COONa. \cdot 3\ H_2O$	0.03
$C_6H_{12}O_6$	0.06
NH_4Cl	2.88

Zeolites are aluminosilicates containing certain amount of water. Their use in wastewater treatment is cited in several foreign and some Hungarian publications.

The main reason for their application is their considerable ion exchange capacity and selectivity to ammonium. The Hungarian zeolite applied in the experiments had 82–84 % clinoptilolite content.

When investigating the ammonium fixation capacity we intensively mixed certain grain sizes of zeolite in solutions with known ammonium content and finally measured the remaining ammonium concentration in the solutions. From that the amount of adsorbed ammonium was determined. The results can be seen in *Table 2.* Fraction of zeolite with bigger grain size was able to adsorb less than half of the amount of ammonium.

Table 2: Capacity of ammonium fixation of zeolite fractions with various grain size

Grain size (mm)	Capacity of ammonium fixation (mg/g)
>2	3.0625
0,5–1	7.3125
<0.5	6.8750

Alginite is a rock with considerable organic material content formed of fossil biomass, basaltic tuff and limestone. It is rich in micro-, and macro-components, therefore we supposed that it can result in improving the nutrient supply of the activated sludge as well.

We made a dissolution experiment with alginite. The results showed that organic material, equivalent of 40 mg COD/g alginite dissolved into a solution at 0.5 g alginite/liter dosage with intensive mixing.

Experimental device

The experiments were carried out in sequencing batch reactors (SBR – *Fig. 1*) with a parallel control unit containing only seeding activated sludge. The feed solution was synthetic sewage with high nitrogen (700–800 mg NH_4/l) and organic material (800–900 mg COD/l) content.

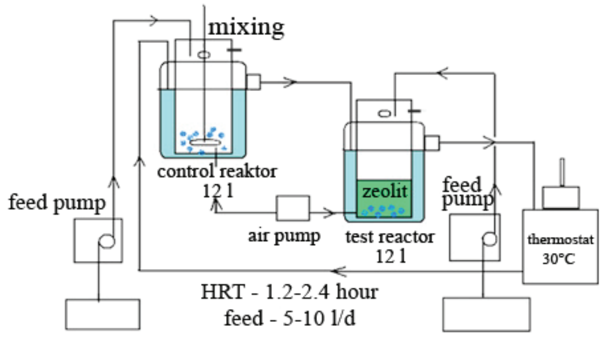

Figure 1: Experimental reactor

Analytical methods

All analyses were performed on grab samples taken from the reactors (once a day at the same time from the control and the test reactor) and completed in accordance with standard methods from filtrated samples.

Ammonium concentration was determined by Lovibond 535650 Vario AM Tube Test Reagent Set HR 0–50 mg/l NH_3-N and with Lovibond PC MULTIDirect spectrophotometer.

Chemical oxigen demand was measured after a destruction with potassium-dichromate by LOVIBOND PCSPECTRO spectrophotometer. The concentration of nitrate-nitrogen was measured according directions of MSZ 12750/18-74 standard.

Biomass concentrations were determined by measuring MLSS and MLVSS after desiccation of sludge on 105 °C and ignition on 600 °C. TN concentrations were measured by TELEDYNE TEKMAR TN analyzer, while TOC concentration by TEKMAR DOHRMANN Apollo 9000 analyzer. pH and DO was measured by specific electrodes.

Discussion and conclusions

Figure 2 shows the nitrogen removal of the test and control reactor and the theoretical ammonium concentration in the reactors formed by the influent. As it can be seen on the figure, the ammonium removal capacity of the biofilter made of zeolite grains was about twice as the control reactors. It might be due to the ammonium fixation of the zeolite or an advantageous surrounding for activity of the nitrifiers on the surface of zeolite grains. The reactor containing zeolite was able to remove almost the whole amount of influent ammonium. Although the biofilter we made with the zeolite grains improved nitrogen removal it can not be used in practical application because the zeolite bed churned very fast and the sludge without mixing and aeration turned to anaerobic and began to rot.

In the experimental period of the moving bed reactor (practically AS) with zeolite we applied 1 g/l zeolite concentration. It improved the nitrogen removal as can be seen in *Fig. 3.* Besides the previously mentioned facts it is important to note that the zeolite added to the activated sludge had a favourable effect even on sludge settling parameters.

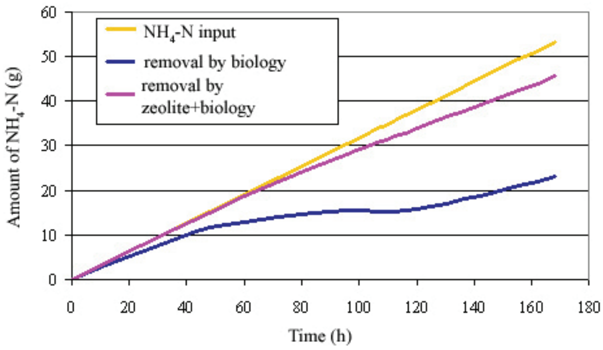

Figure 2: Nitrogen removal with the zeolite grains

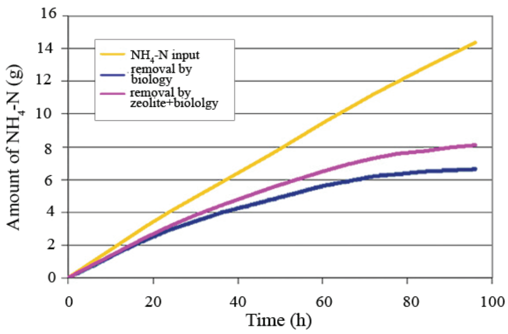

Figure 3: Nitrogen removal in moving bed reactor with zeolite

The sludge of the reactor containing zeolite concentrated better then that of the control unit (with averagely 0.5–1 liters in the volume of 12 liters) during the settle phase of the SBR cycle. The incremental mass of sludge was not considerable, but the difference between the sludge concentration in the test and the control reactor remained the same during the whole experimental period.

The sludge in the reactors is regarded to be underloaded with TOC (that is the reason why the sludge degradation happened) but it is strongly overloaded with ammonium. The seeding sludge was not especially adapted for this application. Nitrifying sludge with far better specific ammonium oxidation capacity is used at our simultaneous pilot-plant tests where the biofilm carrier is Kaldnes ring support.

Using zeolite in this concentration and grain size can easily be realized in industrial application because on one hand the price of the amount of zeolite needed to form the 1 g/l concentration in the reactor is much less than that in the biofilter and on the other hand the possibility of rotting is not considerable in this configuration.

Longer experimental periods are recommended to make sure that biology is capable of the regeneration of zeolite saturated with ammonium and being a perfect carrier of well-nirtifying biofilm (as it is stated in several publications). The industrial application however is preferred for municipal wastewater treatment plants where a slight improving in the nitrogen removal with zeolite can be enough to fit the limit values or where the slow settling of sludge should be improved. Zeolite as a support material might be suitable to reduce the amount of suspended solids in the effluent that is caused by biofilm detachment from the carrier, because the concentration of suspended solids in the effluent of the reactor containing zeolite was far lower than in the treated effluent of the control reactor. Further experiments are needed to final proposal of the correct dosing of the zeolite.

We measured in our next trials whether the dissoluble components of the alginate will disturb the TOC or the ammonium removal. Dosing of 0.5 g alginite/l obviously improved sludge settling which is shown in *Fig. 4*

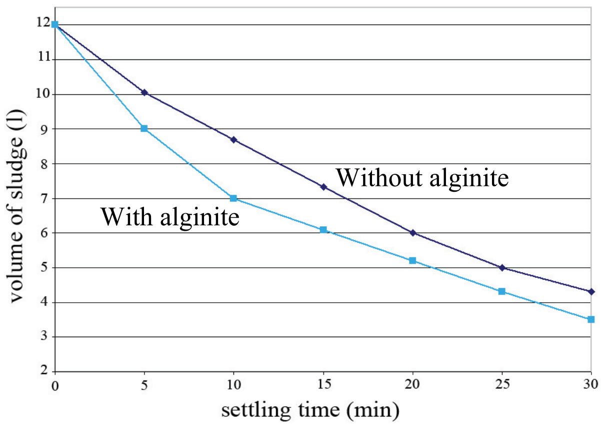

Figure 4: Sludge settling with and without alginite

The results of our experiments show that the alginite is similarly useful material in wastewater treatment as zeolite is. However the price of the alginite is much lower. So it can be preferred as flocculating aid and biofilm support in hybrid AS-biofilm sewage treatment systems. Alginite costs 18 €/tons while zeolite costs 100–120 €/tons.

Its addition in such systems will also decrease the amount of suspended solids remaining in the effluent. Further pilot plant experiments are designed to determine the right dosage requirements.

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