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NITRIFICATION PROCESS IN A PACKED BED REACTOR WITH A CHEMICALLY ACTIVE BED

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Abstract—A laboratory scale submerged filter filled with crushed marble was used for the nitrification process investigation. The results obtained showed that the alkaline reactor filling material react with the hydrogen ions released during the process course which enables reactor exploitation without any pH value or alkalinity control.

INTRODUCTION

Nitrification is mainly performed by autotrophic bacteria of the Nitrosomonas and Nitrobacter genera. Nitrosomonas oxidizes ammonium to nitrite and Nitrobacter oxidizes the nitrite generated by Nitrosomonas to nitrate. The overall stoichiometric reactions in nitrification can be presented as follows:

$$NH_4^+ + 1.5\,O_2 = 2H^+ + H_2O + NO_2^- + 58 \div 84\ \text{kcal} \quad (1)$$

$$NO_2^- + 0.5\,O_2 = NO_3^- + 15.4 \div 20.9\ \text{kcal}. \quad (2)$$

The energy released in these reactions is utilized for cell maintenance and assimilation of cell carbon from carbon dioxide. Adams & Eckenfelder (1977) pointed out that the rate limiting step in the nitrification reaction is the conversion of ammonia to nitrite by the Nitrosomonas organisms. The nature of nitrification has been reported by numerous authors as zero-order reaction (Wild *et al.*, 1971; Wong-Chong & Loehr, 1978). The growth rate of nitrifiers is quite small because the reactions yield little energy. In pounds of VSS grown per pounds of substrate–N oxidized the yields of nitrifiers are in the range 0.04–0.13 in the case of Nitrosomonas and 0.02–0.07 in the case of Nitrobacter (EPA, 1975). According to McHarness *et al.* (1975) the nitrification of 20 mg l^{-1} NH_4–N produces only about 3 mg l^{-1} of Nitrosomonas and about 0.5 mg l^{-1} of Nitrobacter. If $C_5H_7O_2N$ is assumed to be the empirical cell formulation for nitrifying bacteria the following equation for nitrifiers synthesis and nitrification has been suggested by EPA (1975):

$$NH_4^+ + 1.83\,O_2 + 1.98\,HCO_3^- = 0.021\,C_5H_7O_2N + 0.98\,NO_3^- + 1.04\,H_2O + 1.88\,H_2CO_3. \quad (3)$$

The nitrification rate is strongly influenced by pH. The question in this work is to avoid the effect of pH change during the course of nitrification process. According to equation (1) nitrification produce 2 mol of hydrogen ions for each mole of ammonia oxidized what leads to pH lowering during the process course. The decreasing of pH value causes the lowering of nitrification rate and the nitrifiers growth rate. Apart from that the change of pH could influence the reaction rate indirectly. High concentration of ammonia and/or nitrate in wastewater could inhibit the nitrification. Anthonisen (1974) pointed to the mechanism by which pH affects the inhibitory effect. The experiments conducted to examine the inhibitory effects of ammonium and nitrite concentration proved that the inhibitory materials are not ammonium or nitrite but the unionzed components, free ammonia and free nitrous acid. Both the ammonia–ammonium and nitrite–nitrous acid equilibrium in water depend on pH according to the following equations:

$$NH_3 + H_2O = NH_4OH = NH_4^+ + OH^- \quad (4)$$

$$HNO_2 = H^+ + NO_2^-. \quad (5)$$

The pH optima for the nitrifiers appear to be in the range of about 7.8–8.2. During the start-up procedure of the nitrification reactor when pH is about 8 and water contains mainly ammonium ions NH_4^+ the equivalent concentration of free ammonia happens to be the main inhibitor. When the reactor is succesfully seeded it starts to work and the nitrification reaction is on course, the ammonium ions concentration inside the reactor is lowered and the free ammonia concentration is lowered equivalently. According to the nitrification rate the hydrogen and nitrite ions are released. The conditions in the reactor are changed. The increasing of hydrogen ions concentration in the system causes the reduction in free ammonia concentration, according to equation (4). From the other side the hydrogen ions change the pH value and affect the nitrite–nitrous acid equilibrium that causes the increasing of free nitrous acid concentration, according to equation (5). Now, in turn the free nitrous acid happens to be the main inhibitor.

Generally, if the start-up procedure of the nitrification reactor is carried over succesfully, the main problem during the process course is that of removing the

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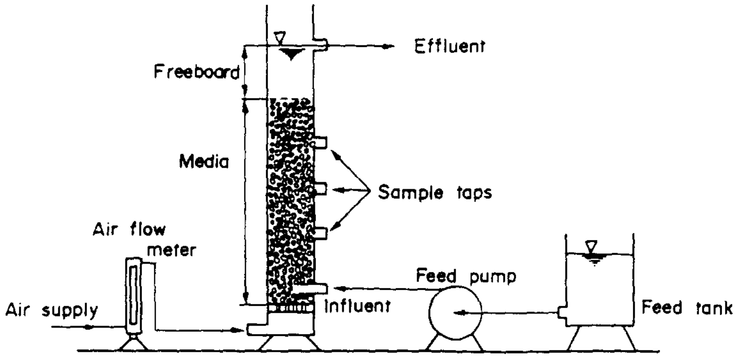

Fig. 1. Laboratory apparatus.

released hydrogen ions to maintain the free nitrous acid at a low concentration and the pH value in the optimum range. Under the conditions existing in domestic sewage complete nitrification could be obtained without pH control but when nitrogen concentrations are high inhibition due to ammonia and nitrous acid may occur. The production of hydrogen ions results in a decrease of alkalinity of 7.14 mg $CaCO_3$ per mg NH_4-N oxidized. In order to maintain the pH value at a proper level some alkalinity must be dosed during the process course. Normally, the packing material in packed bed reactors serves entirely as a solid support for bacteria growth. The principle of the experiment described is applying a chemically active material like crushed marble which reacts with the products of bacteria metabolism. The neutralization reaction between hydrogen ions generated during the nitrification process course and packing material was expected.

EXPERIMENTAL PROCEDURE

Two laboratory scale submerged filters, presented in Fig. 1, were constructed. Each filter consisted of a plexiglas column 50 mm i.d. and 1.1 m tall. The waste to be treated entered at the bottom part as well as the air for aeration, and flowed upward. The effluent ports were placed at the top of the filters. Columns were packed with gravel and crushed marble respectively, 3–8 mm in dia. and filled to a depth of 1 m. The porosity of the rocks within the filters were 0.250 in the case of marble and 0.204 in the case of gravel, liquid volumes were 0.49 and 0.40 l. respectively. The detention time, based on the liquid volumes, was 2 h in both cases. Each of the filters operated with an air flow rate 0.5 l min^{-1}. The flow rate was measured continously by means of two gas meters. The wastes were supplied to the columns with the use of peristaltic pumps. Air pressure was supplied from a compressor.

The synthetic wastes were prepared on the base of tap water. Before the treatment process the water characteristics was changed by dissolving of 2 mg l^{-1} PO_4-P (as Na_2HPO_4) and ammonium salt-ammonium chloride (NH_4Cl). The ammonium ions concentration was changed according to the experimental programme from 30 up to 200 mg l^{-1} NH_4-N. As the seeding material activated, sludge containing the active nitrifiers was used. The inoculum composition was as follows:

100 mg l^{-1} NH_4-N; 5 mg l^{-1} PO_4-P; 100 ml of thickened activated sludge; 1 l. of tap water. The inoculum was poured into the filter, retained and aerated for 5 days. After this the start-up time was considered complete and the experiment programme was started.

Measurements for pH were made by means of pH meter, for ammonium ions concentration by means of an ion-selective electrode. The other analyses were made by following the procedures outlined in *Standard Methods* (APHA, 1965).

RESULTS AND DISCUSSION

The results of nitrification obtained in the reactor filled with the gravel (Fig. 2) showed the possibility of oxidation of about 35 mg l^{-1} NH_4-N in influent with efficiency over 95%. Further increase in influent ammonium concentration brought about a reduction in ammonium removal. Water alkalinity and pH were the process limitations. When the residual alkalinity was close to zero and pH dropped down to about 6 the total amount of ammonium oxidized remained constant, at about 35 mg l^{-1} and did not depend on ammonium ions concentration in influent (within the experimental limits). The hardness of water did not show any changes during the whole experimental period.

The results of nitrification obtained in the reactor filled with crushed marble (Fig. 3) showed the possibility of nitrification of 170 mg l^{-1} NH_4-N in one step oxidation. During the whole experimental period, 180 days, the removal efficiency did not drop down below 95% and all of the ammonia oxidized was converted to nitrate. The experiment data confirmed the presumptions, neutralization reaction between the hydrogen ions released during the process course and the reactor packing material occurred and resulted an increase in effluent hardness. Hardness of the effluent at the beginning was 325 mg l^{-1} $CaCO_3$ and increased to 1250 mg l^{-1} $CaCO_3$ when 170 mg l^{-1} NH_4-N was oxidized. The pH value dropped down to 4.5 and residual alkalinity to almost zero.

Further increase in ammonium ion concentration in the influent to over 170 mg l^{-1} NH_4-N affected the process efficiency and resulted in an increase of ammonium ion concentration in effluent.

The nitrifiers growth out on the solid support, in our case on the marble's surface. The biological film they make is strongly attached to the rock's surface.

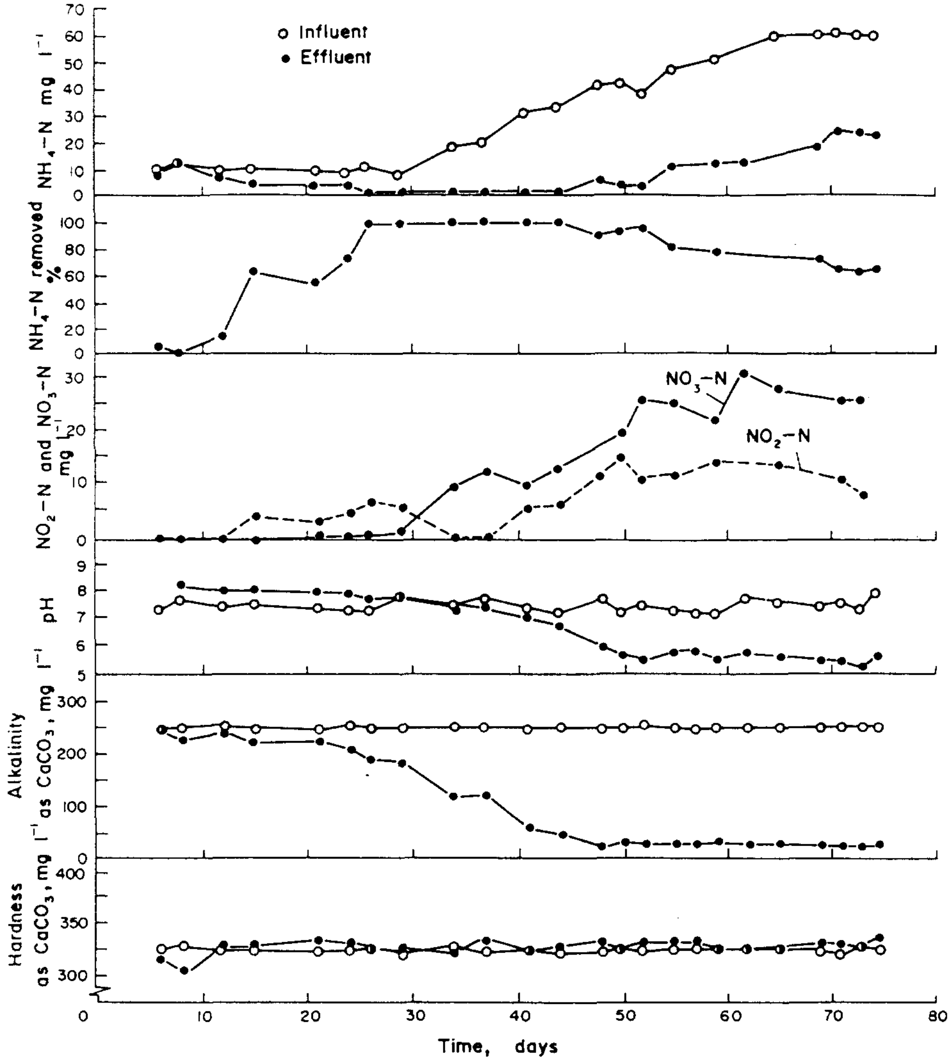

Fig. 2. Results of nitrification in packed bed reactor filled with gravel.

Through this film all the transport phenomena must occur, especially diffusion of ammonia as substrate and hydrogen ions as product. The biological film shows some resistance to mass transfer that effects the concentration of the ions that is greatest in the place in which they are produced, and their concentration decreases with distance from the origin. In the case of the experiment described, the biological film is limited from one side with the rock's surface and from the other with the bulk medium. Inside the biological film the hydrogen ions concentration is greatest and becomes smaller towards the outside borders. In the direction of bulk medium the hydrogen ions concentration decreased according to the general diffusion model. In the direction of the rock's surface, apart from the diffusion phenomena, the hydrogen ions react with the support material. It results in greater decreasing of hydrogen ions concentration in this direction than could be expected entirely on the diffusion model basis.

The pH value at the support's surface must be greater than that at the outside surface of the film. The stratification of the pH value within the biological film surely results in the stratification of the nitrifiers activity. They will show the greatest activity close to the marble's surface, smaller inside the film and at the outside border where the hydrogen ions concentration is the greatest.

Of course the presented explanation is only hypothetical because the experiment described did not allow to make the appropriate measurements but it can explain the process behavior on the basis of the obtained results. Moreover the explanation fits the rules accepted in the similar cases presented by Williamson & McCarty (1976).

CONCLUSIONS

1. Successful nitrification of 170 mg l^{-1} NH_4-N with the efficiency over 95% in one step oxidation system without any addition has been demonstrated.
2. The submerged filter filled with crushed marble is able to nitrify without chemical addition for pH value and alkalinity control.

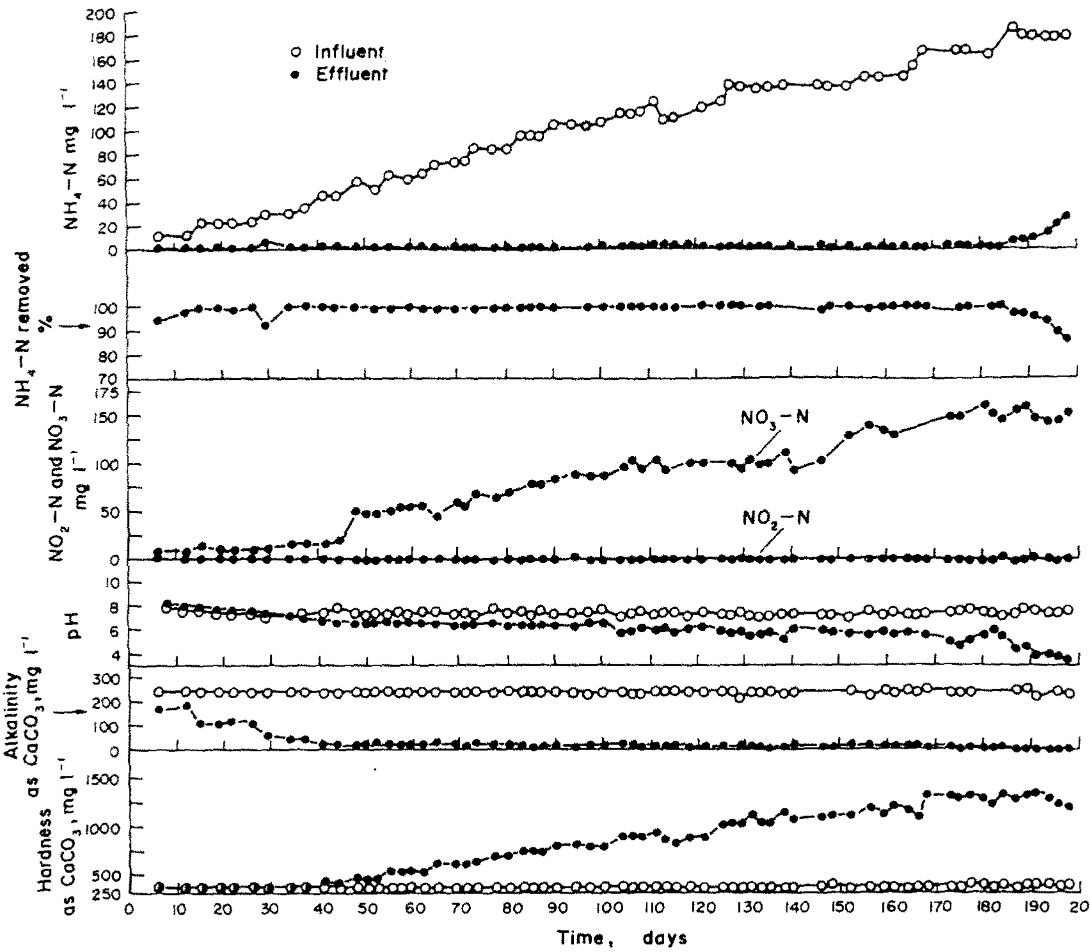

Fig. 3. Results of nitrification in packed bed reactor filled with crushed marble.

3. The nitrification process in submerged filter filled with inert material is naturally limited with pH and alkalinity of treated water.

4. The nitrification process in submerged filters filled with alkaline materials does not show the limitations caused by pH value and alkalinity of treated water. Nitrification course proceeds with full efficiency down to a pH value of 4.5 and alkalinity close to zero. This is probably due to the process occurring in the micro-environment around the filling grains where the conditions are quite different than the ones in the surrounding environment. In this micro-environment, especially profitable conditions prevail in terms of pH value, alkalinity and CO_2 concentration for nitrifiers growth.

5. The natural limitation of the process efficiency in the packed bed reactor with the chemically active bed seems to be the wash-out velocity of the alkaline packing media.

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REFERENCES

Adams C. E. Jr & Eckenfelder W. W. (1977) Nitrification design approach for high ammonia wastewaters. *J. Wat. Pollut. Control Fed.* **49**, 413.

Anthonisen A. C. *et al.* (1976) Inhibition of nitrification by ammonia and nitrous acid. *J. Wat. Pollut. Control Fed.* **48**, 835.

APHA (1965) *Standard Methods for the Examination of Water and Wastewater*. Twelfth Edition. American Public Health Association, New York.

Environmental Protection Agency (1975) Process design manual for nitrogen control. Office of Technology Transfer, Cincinnati, Ohio. Cited in Shrama B. & Ahlert R. C. (1977) Nitrification and nitrogen removal. *Water Res.* **11**, 897.

McHarness *et al.* (1975) Field studies of nitrification with submerged filters. *J. Wat. Pollut. Control Fed.* **47**, 291.

Wild H. E. *et al.* (1971) Factors affecting nitrification kinetics. *J. Wat. Pollut. Control Fed.* **43**, 1845.

Williamson K. & McCarty P. L. (1976) Verification studies of the biofilm model for bacterial substrate utilization. *J. Wat. Pollut. Control Fed.* **48**, 281.

Wong-Chong G. M. & Loehr R. C. (1978) Kinetics of microbial nitrification: nitrite-nitrogen oxidation. *Water Res.* **12**, 605.