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TECHNICAL NOTE

NITRIFICATION PROCESS IN ACTIVATED SLUDGE WITH SUSPENDED MARBLE PARTICLES

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Abstract—The process of nitrification in activated sludge was investigated. As the solid support for nitrifiers' growth a suspension of marble particles has been used. The results proved the possibility of successful nitrification of $100\,mg\,l^{-1}$ NH_4–N simultaneously with the removal of $600\,mg\,l^{-1}$ COD.

Key words—nitrification, high nitrogeneous waste water

One of the serious problems during the nitrification of high nitrogeneous wastewater is pH control. Nitrification is mainly performed by autotrophic bacteria of the Nitrosomonas and Nitrobacter genera. The stoichiometric reaction in nitrification can be presented as follows:

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

$$NO_2^- + 0.5\,O_2 = NO_3^- \ \text{(Nitrobacter)}. \quad (2)$$

The nature of nitrification has been reported by Wild *et al.* (1971) and Wong Chong and Loehr (1978) as a zero order reaction. As ammonia oxidation occurs, there is a release of hydrogen ions that decreases the pH to an extent related to the buffering capacity of the system. Usually the wastewater alkalinity is sufficient to buffer the pH during nitrification of domestic wastewater.

According to equation (1) nitrification produces 2 mol of hydrogen per mol of ammonia oxidized. When the alkalinity of water is not sufficient the pH change during the process causes the lowering of the nitrification rate and the nitrifiers' growth rate. The pH influence on the nitrification rate is presented in Fig. 1 according to some literature data after Srna and Baggaley, 1975.

To eliminate the negative influence of the decrease pH value during the nitrification of the high nitrogeneous wastewater, Packed Bed Reactors (PBR) with a chemically active bed has been proposed by Kowalski and Lewandowski (1983). The PBR was filled with crushed marble. The nitrifiers grow on the marble surfaces and the protons released during the first stage of nitrification react with the support material being neutralized.

A similar effect to pH control was obtained. The laboratory scale unit showed the possibility of complete nitrification of $170\,mg\,l^{-1}$ NH_4–N within 2 h. During the process the pH value of the effluent dropped to the value of 4.5 with no influence on the process. It proved that the nitrification occurred

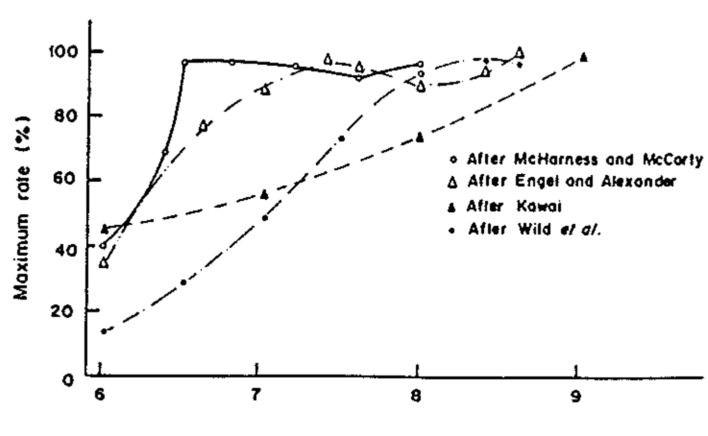

Fig. 1. The effect of the pH on the rate of oxidation of ammonium ion (Srna and Baggaley, 1975).

within the biological film on the marble surfaces where conditions in terms of pH and alkalinity were quite different from those in the bulk liquid. Unfortunately when the simultaneous nitrification and the oxidation of organic carbon compounds was tried the PBR was clogged with heterotrophs in a relatively short time. This was the origin of the idea of trying the same process within the activated sludge. In the work described the activated sludge unit was prepared with small particles of marble suspended within the slude liquor. The growth of nitrifiers on the marble surfaces with the effect of pH buffering was expected.

MATERIALS AND METHOD

The activated sludge unit shown in Fig. 2 was prepared. It consisted of the glass reactor of 5 l. volume connected with the settling tank of 3 l. volume. The activated sludge was taken from the bottom part of the tank and continuously aerated by means of a mammoth pump, being recirculated to the upper part of the tank. The settled sludge in the settling tank was recirculated to the sludge tank every 10 min by means of mammoth pump. This pump was

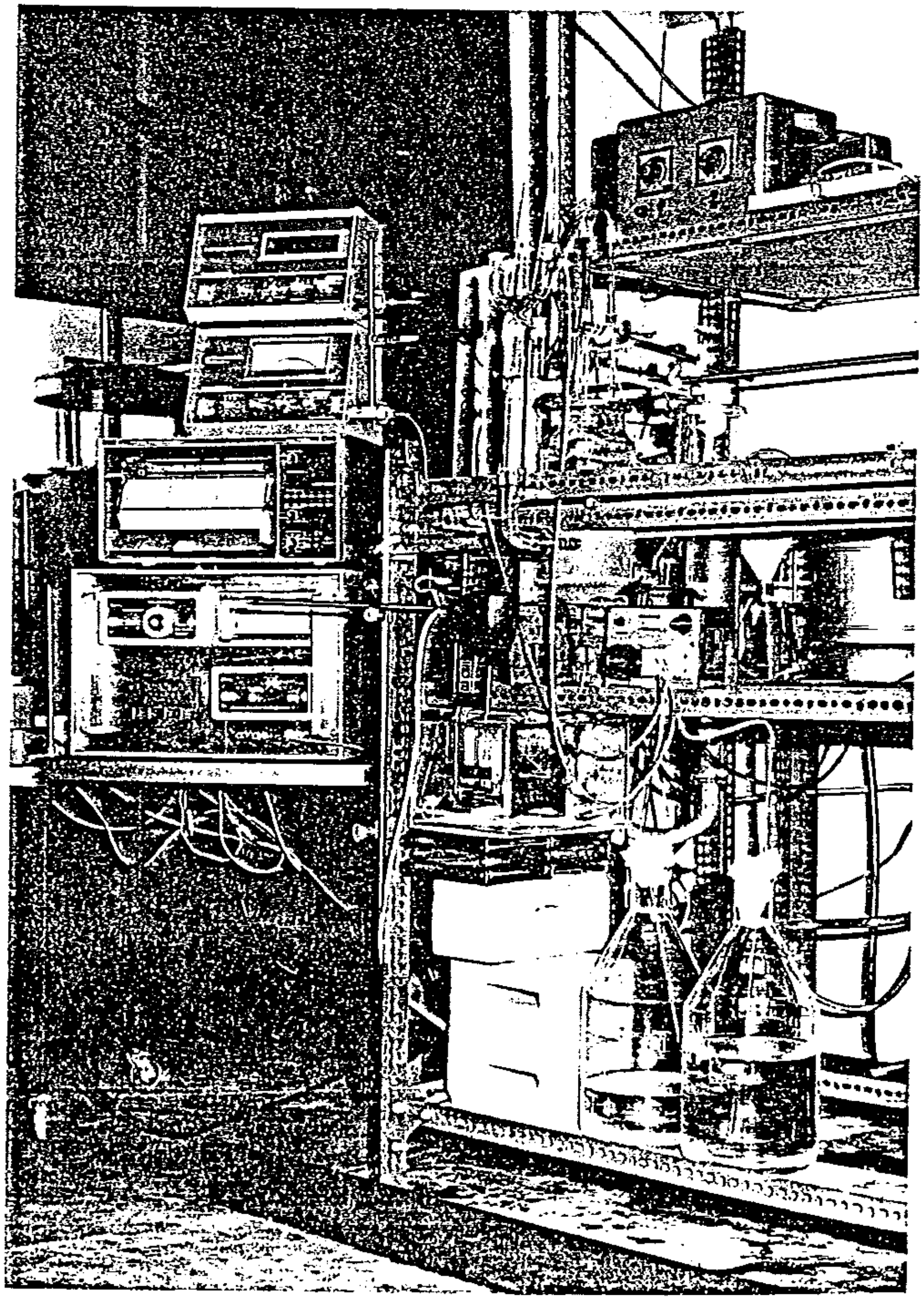

Fig. 2. The laboratory scale continuous flow activated sludge unit.

switched on every 10 min for 5 s by means of a timer. The activated sludge tank was thermostated at 25°C. The activated sludge with the active nitrifiers for seeding was taken from the Municipal Wastewater Treatment Plant. During the seeding procedure 100 g of crused marble (<0.5 mm in dia) a product of Zimmerli Mineralwork was added to the sludge tank. For the seeding procedure 2 l. of activated sludge and 3 l. of tap water was placed in the activated sludge unit and continuously aerated for 48 h. The ammonium concentration was adjusted to 100 mg l^{-1} NH_4-N by addition of NH_4Cl. The COD was adjusted to 600 mg l^{-1} O_2 by means of glucose ($C_6H_{12}O_6$) addition; phosphate to 2 mg l^{-1} PO_4-P by addition of Na_2HPO_4. After 48 h the start-up procedure was considered to be completed and the reactor started to work. The feed solution was based on tap water with addition of ammonium chloride (NH_4Cl), glucose ($C_6H_{12}O_6$) and sodium phosphate (Na_2HPO_4) to obtain 100 mg l^{-1} NH_4-N, 600 mg l^{-1} O_2 COD and 2 mg l^{-1} PO_4-P. Detention time was fixed on 6 h. The excess sludge was wasted daily to obtain the concentration of about 3 g l^{-1} VSS within the activated sludge tank. After wasting of sludge the appropriate amount of the crushed marble was added to maintain a constant concentration in the sludge liquor. Samples were taken daily from the feed tank and

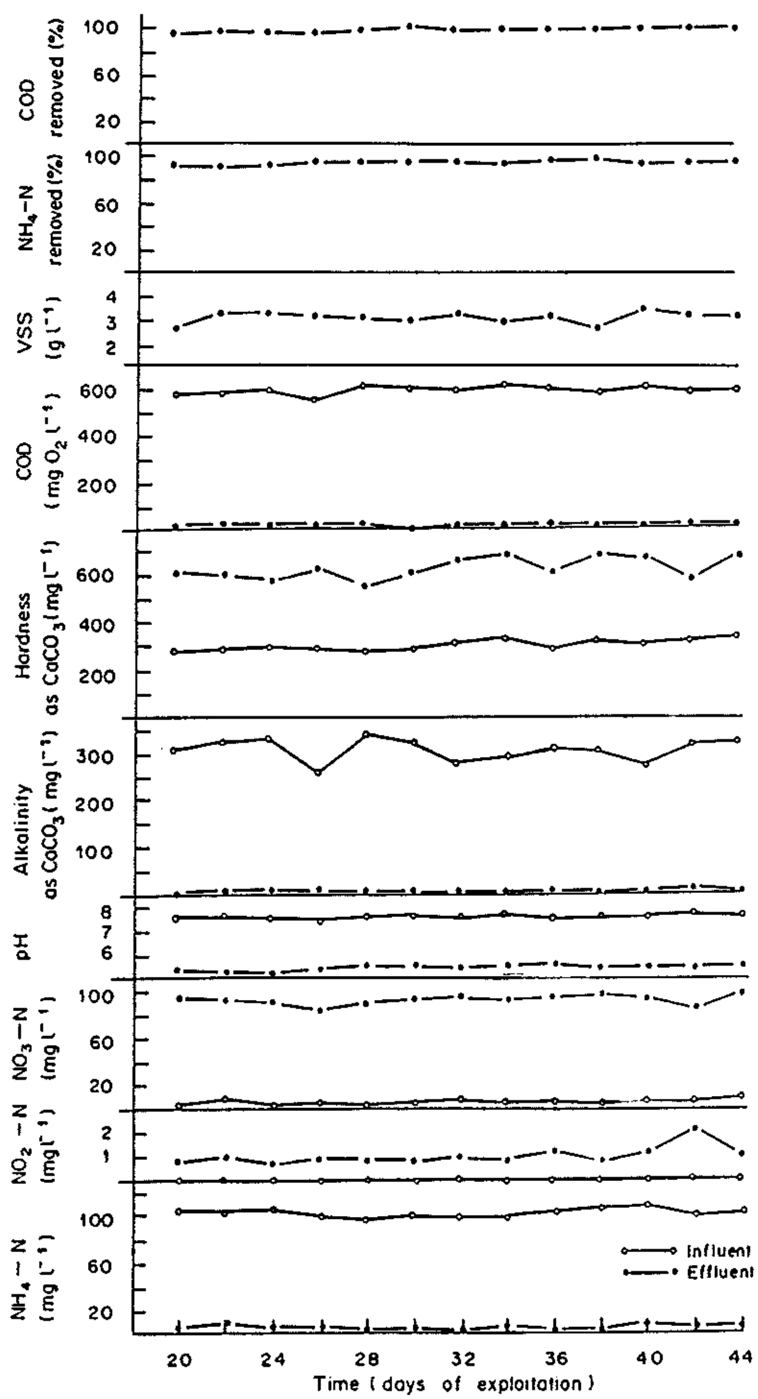

Fig. 3. Results of the process course in continuous flow reactor.

from the activated sludge tank. The samples were analysed after filtration through the membrane filter Sartorius SM 11306 0.45 μm. The ammonium concentration was analysed according to Wagner (1969), nitrate, nitrite, alkalinity and hardness was measured by following the method outlined in *Standard Methods* (APHA, 1975). The TSS and VSS was measured after filtration of the sample of sludge through glass microfibre filters Whatman GF/C. The reaction rates measurements was performed in 1 l. glass jar. The sludge taken from the aeration chamber was washed and suspended in tap water and introduced into the jar and continuously aerated for 2 h in 25°C to oxide the ammonium and nitrite. After this the aliquot of NH_4Cl dilution was added to obtain a concentration of about 30 mg l^{-1} NH_4–N. The value of pH was adjusted on 8.0 by means of NaOH addition. Samples of sludge were taken from the reaction chamber every 10 min for 2 h. After filtration the concentration of ammonium was measured in the filtrate. The measurement for NO_2–N oxidation rate was made in the same way after addition of $NaNO_2$. The concentration of nitrite was measured in the filtrate.

RESULTS AND DISCUSSION

The investigation lasted for 8 weeks. During this period, after the start up procedure, the relatively constant results of the process were obtained. The changes of the effluent quality in relation to the influent quality is presented in Fig. 3. During the process the ammonium concentration dropped from 100 mg l^{-1} in the influent to below 5 mg l^{-1} in the effluent. Practically all the ammonia was oxidized to nitrate, the concentration of which increased from 5 mg l^{-1} in the influent to 95 mg l^{-1} in the effluent. The pH value in the aeration tank dropped to 5.5 and the alkalinity to zero, with no influence on the process. During the same time the hardness of the water increased from 300 mg l^{-1} $CaCO_3$ to 600 mg l^{-1} $CaCO_3$, which supports the expectation that the suspended marble particles react with the protons and buffer the system. At the same time the COD concentration dropped from 600 to 20 mg l^{-1} O_2.

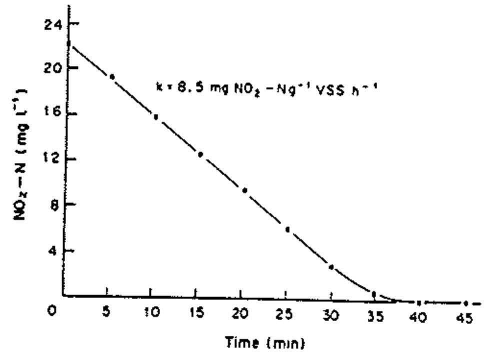

Fig. 5. The kinetic of nitrite oxidation in a bath reactor.

The results of the ammonium and nitrite oxidation rates measurements are presented in Figs 4 and 5. The data show that the value of the ammonium oxidation rate $k_{NH_4\text{-}N} = 8.1$ mg NH_4–N g^{-1} VSS h^{-1}, and the nitrite oxidation rate $k_{NO_2\text{-}N} = 8.5$ mg NO_2–N g^{-1} VSS h^{-1}. The experiment data confirmed the presumptions that neutralization reactions between the hydrogen ions released during the process and the suspended marble particles occurred, and resulted an increase in effluent hardness. It is somewhat confusing that the nitrification process runs with full efficiency at a pH value of the sludge liquor equal to 5.5. The nitrifiers and heterotrophs grow on the solid support on the marble surfaces. The biological film they make is shown in Fig. 6. The biological film is strongly attached to the mineral surface. Through this film all the transport phenomena must occur, especially diffusion of ammonia as substrate and hydrogen ions as products. The biological film shows some resistance to mass transfer, which affects the concentration of the ions 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 on one side with the mineral

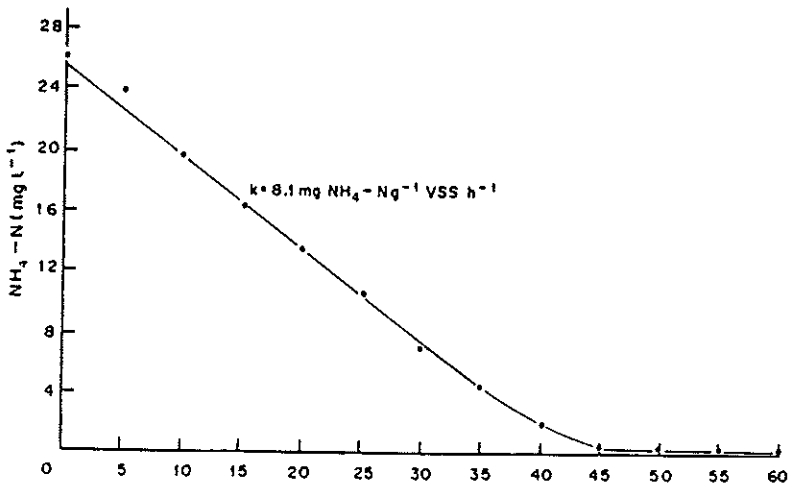

Fig. 4. The kinetic of ammonium oxidation in a bath reactor.

Fig. 6. The grain of marble taken from the aeration tank with the biofilm on the surface.

surface and on the other with the bulk medium. Inside the biological film the hydrogen ions' concentration is the greatest and decreases towards the outside edge. In the direction of the bulk medium the hydrogen ions' concentration decreases according to the general diffusion model. In the direction of the mineral surface apart from the diffusion phenomena, the hydrogen ions react with the support material. This results in a greater decrease of hydrogen ions' concentration in this direction than could be expected entirely on the diffusion model basis. The pH value at the support surface must be higher than that at the outside surface of the film. This is the reason why the nitrification process runs with full efficiency despite the pH value of the bulk medium equalling 5.5.

CONCLUSIONS

(1) Successful nitrification of 100 mg l^{-1} NH_4–N with an efficiency of over 95%, simultaneously with the removal of 600 mg l^{-1} COD with an efficiency of over 98% in activated sludge containing suspended marble particles was proved.

(2) The activated sludge with suspended marble particles is able to nitrify without chemical addition for pH and alkalinity control.

(3) The nitrification process in activated sludge with suspended marble particles does not show the limitations caused by pH value and alkalinity. Nitrification proceeds with full efficiency down to a pH value of 5.5 and alkalinity close to zero.

(4) The natural limitations of the nitrification process efficiency is determined by the wash-out velocity of the marble particles.

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