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THE EFFECT OF A SUPPORT MATERIAL ON
THE NITRIFICATION RATE IN BIOFILM REACTORS

The nitrification process in a Packed Bed Biofilm Reactor (PBBR) was investigated. The inert and carbonaceous materials were tested as the support materials. The results proved the feasibility of nitrification at pH value below 5.0. On the inert support material the bicarbonates and ammonia concentrations decreased simultaneously, but when the bicarbonates present in the bulk liquid were exhausted, the nitrification ceased. For the alkaline support media, the alkalinity in bulk liquid decreased to almost zero, but the carbonaceous support materials (marble, dolomite and Dofiltr™) react with the protons and buffer the system inside biofilm. If the marble or other carbonaceous support materials are used, the packed bed material due to dissolution controls the pH inside the fixed biofilm.

In reactors, the mean residence time and the Peclet number were measured. On the basis of two models (dispersion model and reactors in series model) the nitrification constant rates in reactors were estimated.

NOMENCLATURE

A – biofilm surface (m^2),
a – specific biofilm surface (m^2/m^3),
C_{if}^{in} – concentration of i substrate in bulk liquid in reactor inlet (g m^{-3}),
C_{if1} – concentration of i substrate in bulk liquid in the first reactor in cascade (g m^{-3}),
C_{if2} – concentration of i substrate in bulk liquid in the second reactor in cascade (g m^{-3}),
C_{if} – concentration of i substrate in bulk liquid (g m^{-3}),
C_{ti} – tracer concentration in the reactor outlet (g m^{-3}),
D_i – molar diffusion coefficient of i substrate inside biofilm (m^2 h^{-1}),
E_θ – residence time distribution (dimensionless),
H – reactor height (m),
J_i – substrate flux into biofilm (g m^{-2} h^{-1}),
k – constant reactor rate (g$^{0.5}$ m$^{0.5}$ h^{-1}),
K_{ci} – Monod constant for i substrate (g m^{-3})*,
M_1 – first-order moment (h),
M_2 – second-order moment (h^2),

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n_i – stoichiometric coefficient for the i substrate,
n_T – number of fully mixed reactors (CSTR) in cascade,
Pe – Peclet number,
Q – flow rate ($m^3 h^{-1}$),
r_i – reaction rate per unit volume ($g m^{-3} h^{-1}$),
r_A – overall reaction rate ($g m^{-2} h^{-1}$),
t – time (h),
V – reactor volume (m^3),
X – biomass concentration ($g m^{-3}$),
Y – yield coefficient.

GREEK LETTERS

ε – biofilm porosity ($m^3 m^{-2}$),
μ_{max} – biomass maximal growth rate (h^{-1}),
θ – time (dimensionless),
τ – mean residence time (h),
σ – variance (h),
Γ – substrate concentration (dimensionless).

1. INTRODUCTION

Ammonia nitrogen can be oxidised to nitrate nitrogen in the biological nitrification process by such microorganism species as *Nitrosomonas* and *Nitrobacter*. As a consequence of ammonia oxidation, hydrogen ions are entering the solution causing pH decrease. For a complete ammonia nitrification an excess of oxygen and bicarbonate is obligatory.

The wastewater alkalinity most often is sufficient to maintain the pH value in the optimum range, i.e. from 7.0 to 8.0. If the buffering capacity of the environment is insufficient, a decrease of pH values can be observed. Reaction with bicarbonates results in a decrease of the carbonaceous alkalinity and an increase of carbon dioxide:

$$NH_4^+ + 2O_2 + 2HCO_3^- \rightarrow NO_3^- + 3H_2O + 2CO_2. \tag{1}$$
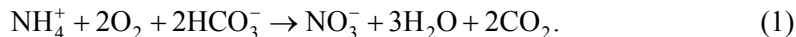
Although there is no unanimous agreement on the optimum pH (approximately 8.2) for nitrification, it is clear that the pH decrease affects negatively the process (SIEGRIST, GUJER [22], VILLAVERDE et al. [28]). The consumption of bicarbonate in the nitrification is proportional to ammonia removal, and was given as 6.2 g $CaCO_3$/g N–NH₄ consumed in suspended-growth systems (GRADY and LIM [8]). The stoichiometric value is somewhat higher and equals to 7.13 g $CaCO_3$/g N–NH₄.

The possibility of an excessive acidifying the environment when wastewater highly polluted with ammonia is treated on fixed film beds is a very specific case. In the biofilm systems, the ratio of its surface area to the volume of the biomass is 10 to

100 times smaller than for suspended biomass, and the rate of substrate uptake in a biofilm is frequently limited by mass transfer (SIEGRIST, GUJER [22]).

The nitrification rate depends on the ammonia nitrogen, oxygen and/or bicarbonate concentration in the biofilm, and each of these can be rate-limiting. The substrate that penetrates the biofilm with the lowest velocity is rate-limiting as well. The penetration depth for the rate-limiting substrate was calculated by Harremoës (WILLIAMSON, McCARTY [33]).

If the nitrifying biofilm has a thickness of about 140 μm and oxygen and ammonia have completely penetrated the biofilm (one-layer biofilm), then pH will be about 0.5 units smaller than that measured in the water layer (SIEGRIST, GUJER [22]). If the biofilm consists of two layers (nitrifying and heterotrophic) and its thickness approaches 400 μm, the difference in pH values will be in the order of one unit (SIEGRIST, GUJER [22], SZWERINSKI et al. [24]). This is the result of acid production within the biofilm and a longer distance for bicarbonate transportation (diffusion resistance).

The decrease of pH value causes the decrease of toxic HNO_2 concentration in the biofilm (ANTHONISEN et al. [1]).

One of the possibilities of assuring an optimum pH within the nitrifying biofilm is to apply a chemically active support material which has a natural ability to dissolve and hence to neutralise the hydrogen ions released (KOWALSKI, LEWANDOWSKI [14]). This work has confirmed that nitrification is possible even at very high ammonia nitrogen concentrations, i.e. in the order of 180 g $N–NH_4 \, m^{-3}$, and a bulk liquid pH of about 4.5, provided that an active alkaline support material composed of calcium and/or magnesium carbonates is used. The chemically active support material assures stable pH within the biofilm. Using carbonates as a support material, it is possible to maintain a much higher value of pH inside the biofilm than that measured in the surrounding bulk liquid (BIESTERFELD et al. [3], GREEN et al. [9]–[11], TARRE, GREEN [25]). Therefore we deal with the situation opposite to that described by SZWERINSKI et al. [24] where the process of nitrification ceased within the biofilm as a result of pH lowering.

The subject of the present work was to describe the mechanism of pH control inside the layer of the biofilm grown on a calcium and/or magnesium carbonate support material.

2. MATERIALS AND METHODS

2.1. THE EXPERIMENTAL SET-UP

For the experiments a laboratory setup was constructed. It consisted of a feed tank, a feed pump, an air compressor and a Packed Bed Reactor (PBR). The construction and

methodology used were described in more detail by KOWALSKI, LEWANDOWSKI [14] (figure 1). Four packed bed reactors were used, one with an inert support material, i.e., a quartz gravel, and the others with such active support materials as marble, dolomite and a market product Doflitr™ used for water deacidification. The size of all support media used ranged from 5 to $8 \cdot 10^{-3}$ m and had a specific surface of 560 $m^2 m^{-3}$. The total surface of the support media in the pilot packed bed filter was approximately 1.1 m^2. The reactor column, $5 \cdot 10^{-2}$ m in diameter, was filled with the support media to a high of 1 m. In all PBRs, a determined mean hydraulic retention time was 2 hours. Each of the PBRs operated with an air flow rate of 50 $dm^3 h^{-1}$ which allowed maintenance of a relatively constant concentration of dissolved oxygen in the effluent, of about 5 mg O_2 dm^{-3}.

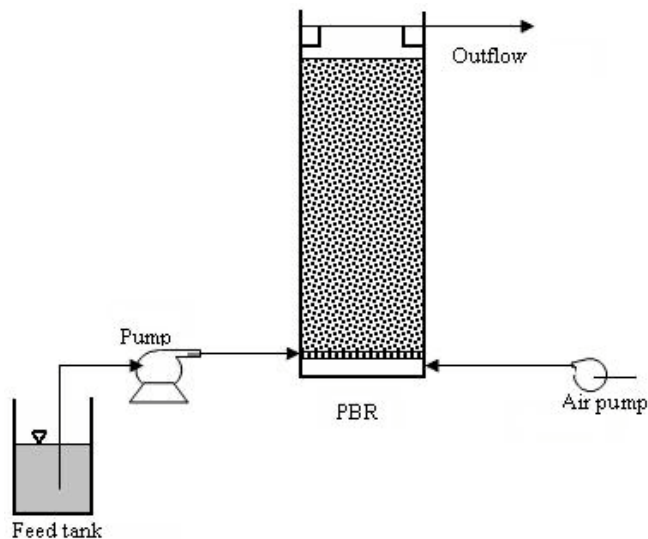Fig. 1. The experimental set-up

The experiments were carried out at a constant temperature of 20 °C controlled by a water jacket.

The longitudinal dispersion number in the packed filters was determined based on the observation of a tracer (NaCl solution) added to the system. The response of the reactor with longitudinal dispersion to this pulse input of tracer in the form the chloride concentration (conductivity) versus time was determined in the effluent.

2.2. INOCULUM AND FEED

Nitrifying cultures from a batch treatment system enriched with ammonium as the only source of energy were used as inoculum.

A synthetic substrate prepared with tap water enriched with phosphates (5 g P m^{-3} as Na$_2$HPO$_4$) and ammonia ions (as NH$_4$Cl) was used. The concentration of ammonia ions varied and increased during the experiments with an increase in the ammonia oxidation rate. The alkalinity of the feed solution was close to 250 g CaCO$_3$ m^{-3}, pH 7.6, and the feed was not buffered.

2.3. EXPERIMENTS

After inoculating the packed bed with nitrifying bacteria under static conditions (with no flow), the addition of the synthetic substrate started. At the beginning the ammonia ion concentration reached 30 g N–NH$_4$ m^{-3} and successively increased up to about 200 g N–NH$_4$ m^{-3} in each run. All of the other parameters were kept constant, including pH, alkalinity and hardness.

For the process control, all analytical measurements were done according to the Standard Methods.

The assays were carried out as long as a constant amount of oxidised ammonia was obtained, irrespective of an increased concentration of ammonia in the inflow to the packed bed. The synthetic substrate enriched with ammonium was fed continuously for a period of 2 up to 3 months.

2.4. REACTOR HYDRODYNAMICS

The mean residence time (τ) and variance (σ^2) allowed the hydrodynamic conditions in the reactor to be calculated. Based on the experimental data both τ and σ^2 were determined according to the method of moments (LEVENSPIEL [16]).

The first-order moment M_1 is equal to the mean residence time (τ):

$$\tau = M_1 = \frac{\sum_{i=1}^{N} t_i C_{ti} \Delta t}{\sum_{i=1}^{N} C_{ti} \Delta t}. \tag{2}$$

The variance σ was calculated using the second-order moment M_2:

$$\sigma^2 = M_2 - M_1^2 = \frac{\sum_{i=1}^{N} t_i^2 C_{ti} \Delta t}{\sum_{i=1}^{N} C_{ti} \Delta t} - \tau^2. \tag{3}$$

The relationship between chloride concentrations and the time at the reactor outlet was transformed into the dimensionless relationship between the residence time distribution (RTS) and the dimensionless time as follows:

$$E_\theta = \tau \frac{C_{ti}}{\sum_{i=1}^{N} C_{ti}\Delta t},$$

$$\sigma_\theta^2 = \frac{\sigma^2}{\tau^2}.$$

(4)

There are three basic models describing axial dispersion in real reactors, i.e. open model, closed model and the model of tanks connected in series.

If the flow is undisturbed at the inlet and the outlet, the "open" model can be used. The residence time distribution has the following form (LEVENSPIEL and SMITH [17]):

$$E_\Theta = \frac{1}{2}\sqrt{\frac{Pe}{\pi\Theta}}\exp\left(-\frac{Pe(1-\Theta)^2}{4\Theta}\right).$$

(5)

The value of dimensionless variation σ_Θ is used to calculate the Peclet number:

$$\sigma_\Theta^2 = \frac{2}{Pe} + \frac{8}{Pe^2}.$$

(6)

THOMAS and MCKEE [26] and YAGI and MIYAUCHI [34] published the analytical solution with the closed boundary conditions in the form:

$$E_\Theta = 2\sum_{n=1}^{\infty} \frac{\alpha_n Pe \exp\left\{\frac{Pe}{2}\left[1 - \frac{\Theta(\alpha_n^2+1)}{2}\right]\right\}}{Pe(\alpha_n^2+1)+4}\left\{\alpha_n\cos\left(\frac{Pe}{2}\alpha_n\right)+\sin\left(\frac{Pe}{2}\alpha_n\right)\right\}, \quad (7)$$

where α_n is given by the positive root of equation (8):

$$\tan\left(\frac{Pe}{2}\alpha_n\right) = \frac{2\alpha_n}{\alpha_n^2-1}.$$

(8)

The third model represents the longitudinal mixing in the continuous stirred-tank reactors (CSTR) connected in series:

$$E_\Theta = \frac{n_T^{n_T}}{(n_T-1)!}\Theta^{(n_T-1)}\exp(-n_T\Theta).$$

(9)

KRAMERS and ALBERTA [15] and ELGETI [6] proposed the following simple relationship between n_T and Pe:

$$Pe = 2(n_T-1).$$

(10)

The comparison of experimentally determined residence time distribution (RTD) with the calculation results based on the above-mentioned models ((7), (9)) for the marble packed reactor are presented in figure 6 as an example.

3. RESULTS

After about 3 months of investigations the amount of oxidized ammonia was constant, reaching the equilibrium despite an increase in the inlet ammonia concentration.

$$N_{NO_3} = 0.197 + 0.764\, N_{NH_4}$$

$$r^2 = 0.8538$$

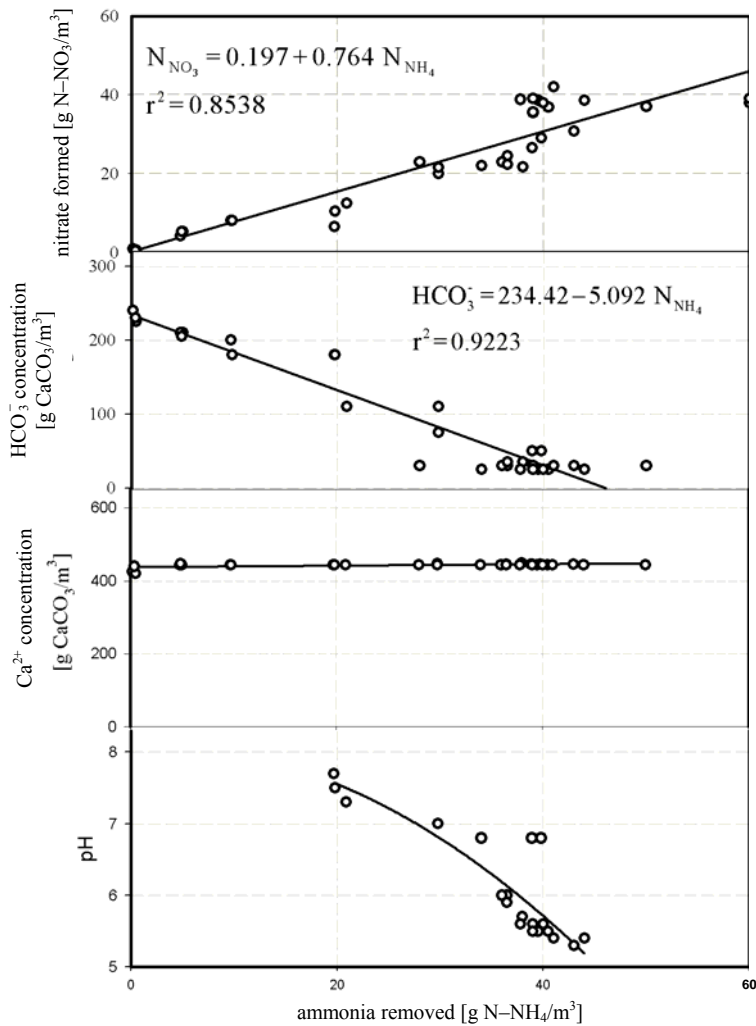$$HCO_3^- = 234.42 - 5.092\, N_{NH_4}$$

$$r^2 = 0.9223$$

Fig. 2. The nitrate formed, alkalinity, calcium concentration and pH values in the effluent of inert reactor

Practically all of the ammonia supplied was oxidized to nitrates (figures 2–5). The effect of ammonia stripping can be neglected.
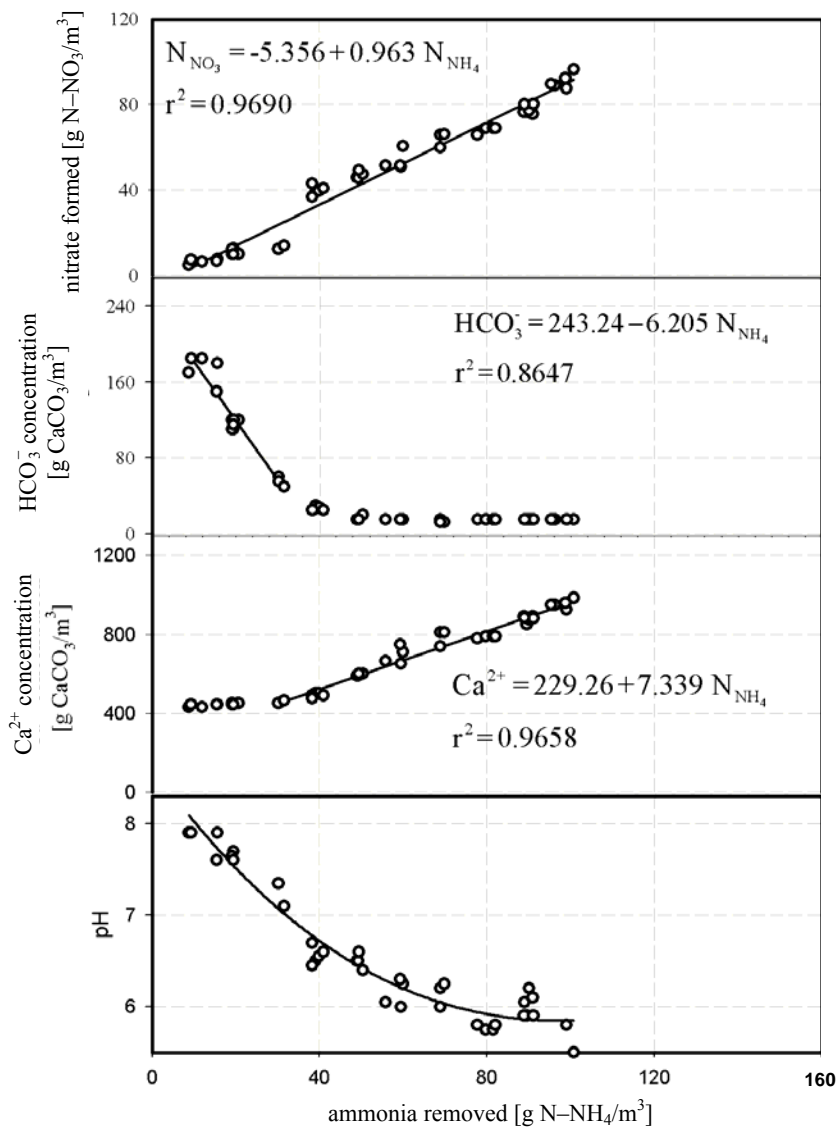

Fig. 3. The nitrate formed, alkalinity, calcium concentration and pH values
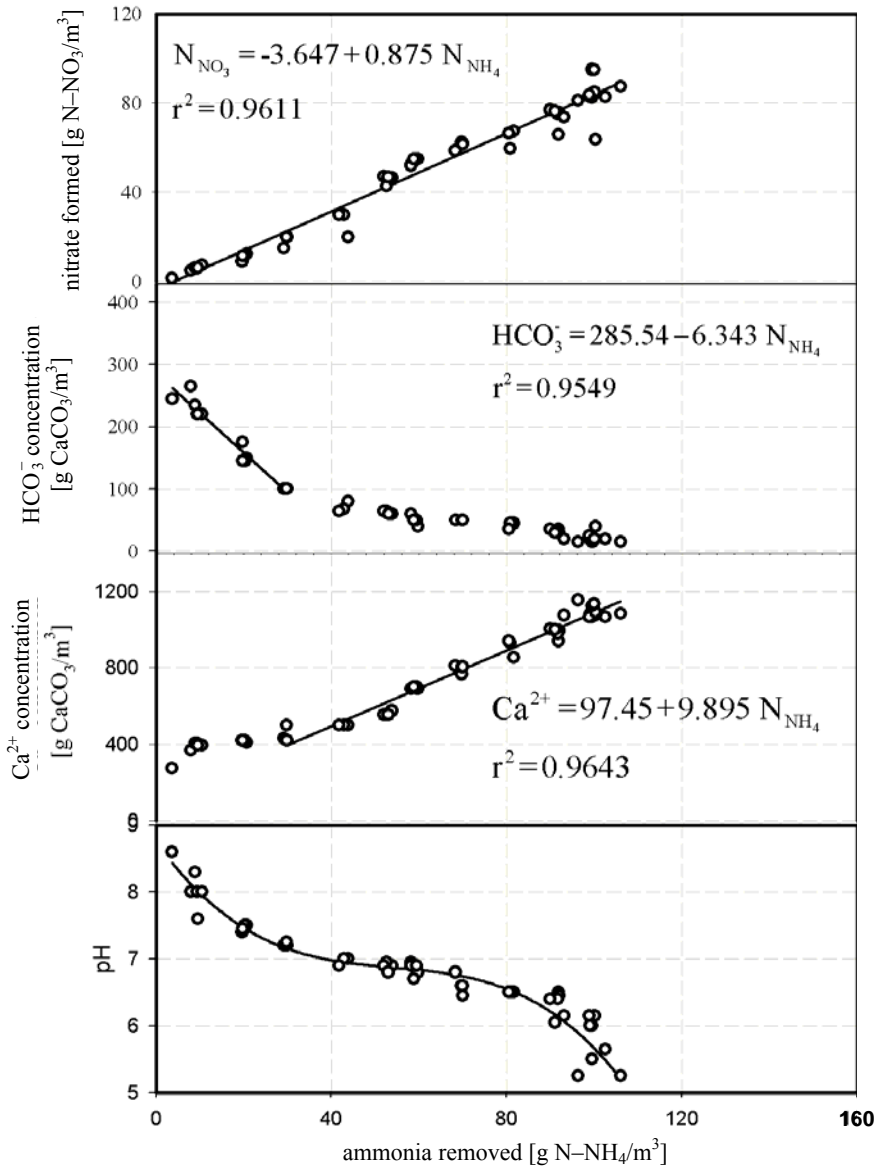in the effluent of dolomite reactor

Fig. 4. The nitrate formed, alkalinity, calcium concentration and pH values
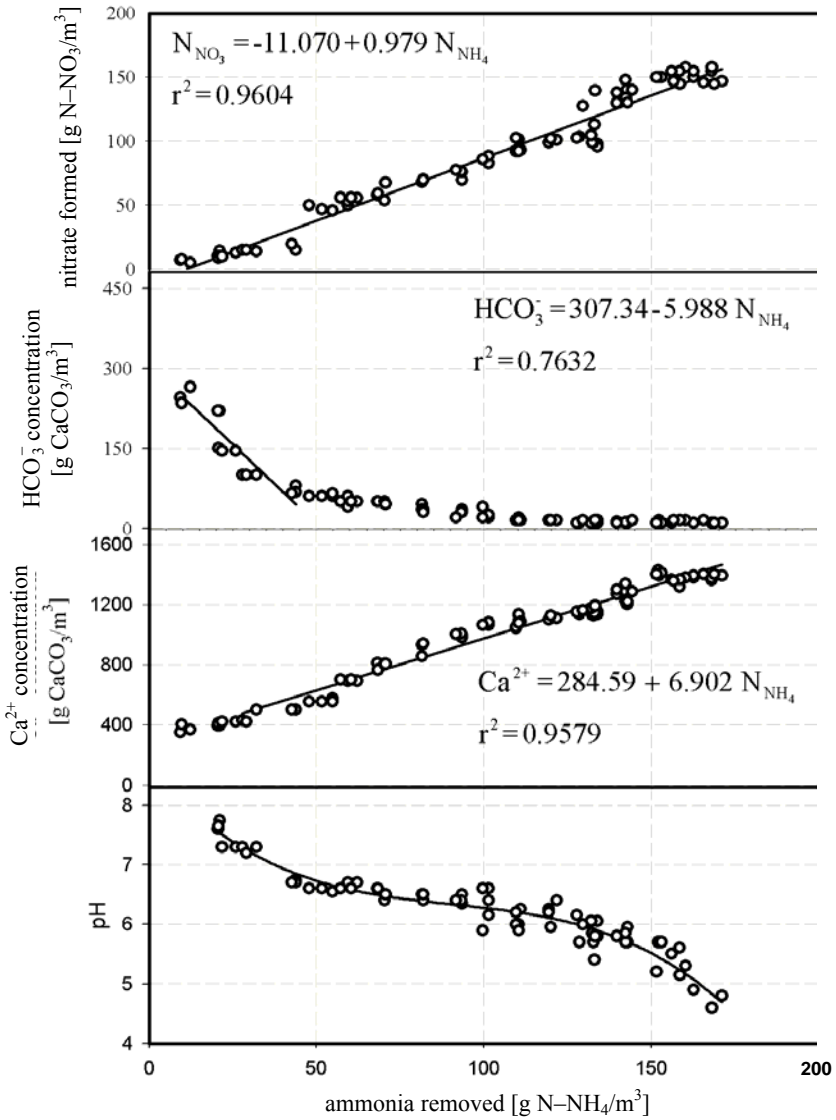in the effluent of Dofiltr™ reactor

Fig. 5. The nitrate formed, alkalinity, calcium concentration and pH values
in the effluent of marble reactor

The oxidation yield coefficient ranged from 0.875 for Dofiltr™ to 0.979 for marble packing material, but for inert support material this value was significantly reduced (to 0.764).

If the inert support material was used, the concentrations of bicarbonates and ammonia decreased simultaneously. The relationship between bicarbonates and ammonia

was nearly stoichiometric (5.09 g $CaCO_3$/g $N–NH_4$). If bicarbonates present in the bulk liquid were exhausted, pH value decreased dramatically (figure 2) and the nitrification ceased.

On the surface of alkaline support media, pH value dropped to 5.0–5.5 and the alkalinity (bicarbonates concentration) decreased to almost zero, with no impact on the nitrification effectiveness. During the same time the carbonaceous material is dissolved and the calcium ion concentration increased from about 400 mg to about 1000–1500 mg $CaCO_3$ dm^{-3} (figures 3–5). The support material (marble, dolomite and Dofiltr™) reacts with protons which buffers the system.
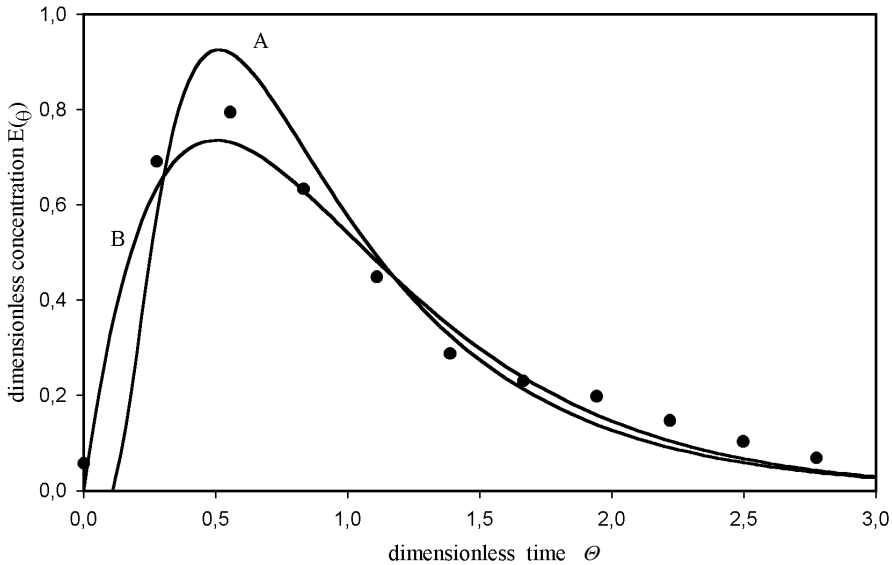

Fig. 6. The experimental residence time distribution (RTS); the comparison of the plot representing a "closed" model ($Pe = 3$) (A) with that of the tanks connected in series ($n_T = 2$) (B)

The mean residence time and the Peclet number for each reactor were calculated and collected in table 1.

Table 1

Mean residence time for reactors and respective Peclet number

Reactor packing material	Mean residence time (h)	Peclet number
Inert	2.36	2.8
Dolomite	2.30	2.6
Dofiltr™	2.30	2.9
Marble	2.35	3.1

4. DISCUSSION

The results of the longitudinal dispersion show that the nitrification reactors can be modelled as a cascade of two equally-sized ideal continuous stirred biofilm reactors (CSBR). The concept of CSBR was introduced by WIK [30].

The mass balance equations for dissolved substances over the bulk liquid in CSBR (WIK [30] and WIK et al. [31]) are as follows:

$$V \frac{dC_{if}}{dt} = Q(C_{if}^{in} - C_{if}) + AJ_i, \tag{11}$$

$$\varepsilon \frac{\partial C_i}{\partial t} = D \frac{\partial^2 C_i}{\partial x^2} - r_i. \tag{12}$$

The substrate flux can be calculated by differentiating the equations as follows:
• for the zero-order reaction and fully penetrated biofilm:

$$J_i = -D_i \frac{\partial C_i}{\partial x}\bigg|_{x=0} = \sqrt{\frac{n_i \mu_{\max} XL}{Y}}, \tag{13}$$

• for the zero-order reaction and partially penetrated biofilm:

$$J_i = -D_i \frac{\partial C_i}{\partial x}\bigg|_{x=0} = \sqrt{\frac{2n_i \mu_{\max} D_i XC_{if}}{Y}}, \tag{14}$$

• for the first-order reaction:

$$J_i = -D_i \frac{\partial C_i}{\partial x}\bigg|_{x=0} = C_{i0}\sqrt{\frac{\mu_{\max} n_i X}{YD_i K_{C_i}}} TANH\left(L \frac{\mu_{\max} n_i X}{YD_i K_{C_i}}\right). \tag{15}$$

To be applied in the Monod equations, the biofilm surface flux can be calculated from the following formula (GUJER, BOLLER [12] and CHEN, SYU [5]):

$$J_i = \sqrt{\frac{2\mu_{\max} n_i D_i X}{Y}\left(C_i + K_{C_i} LN\left(\frac{K_{C_i}}{K_{C_i} + C_i}\right)\right)}. \tag{16}$$

On the basis of equations (14) and (16) it is clear that the rate limiting substrate flux at the biofilm surface is approximately proportional to the square root of its bulk concentration.

Assuming the concept of the cascade of two continuous stirred biofilm reactors (CSBR) it is possible to express the mass balance for each reactor, taking account of the rate limiting substrate, as follows:

$$C_{if}^{in} - C_{if1} = \frac{ak\tau}{2}\sqrt{C_{if1}},$$

$$C_{if1} - C_{if2} = \frac{ak\tau}{2}\sqrt{C_{if2}}. \tag{17}$$

The substrate concentration from the reactor outlet can be calculated based on the formula:

$$C_{if2} = C_{if1} + \frac{ak\tau}{8}\left[ak\tau - \sqrt{16C_{if1} + a^2k^2\tau^2}\right]. \tag{18}$$

C_{if1} can be calculated as follows:

$$C_{if1} = C_i^{in} + \frac{ak\tau}{8}\left[ak\tau - \sqrt{16C_i^{in} + a^2k^2\tau^2}\right]. \tag{19}$$

In order to describe nitrification, the dispersion model was used as the alternative model.

The mass balance equation in the reactor can be written as follows (BURGHARDT, ZALESKI [4]):

$$\frac{1}{Pe}\frac{d^2\Gamma}{dz^2} - \frac{d\Gamma}{dz} - \frac{Ak\tau}{C_i^{in}}\sqrt{C_{if}} = 0 \tag{20}$$

with the boundary conditions:

$$\begin{cases} \Gamma - \dfrac{1}{Pe}\dfrac{d\Gamma}{dz} = 1 & \text{for } z = 0, \\ \dfrac{d\Gamma}{dz} = 0 & \text{for } z = 1, \end{cases} \tag{21}$$

where:

$$\Gamma = \frac{C_{if}}{C_{if}^{in}}, \tag{22}$$

$$z = \frac{h}{H}. \tag{23}$$

In a completely mixed reactor, the overall reaction rate per unit biofilm surface r_A for all filter media can be calculated based on the Stover–Kincannon model (GONZALEZ-MARTINEZ, DUQUE-LUCIANO [7]):

$$r_A = \frac{Q(C_i^{in} - C_{if})}{A} = \frac{(C_i^{in} - C_{if})}{a\tau}. \tag{24}$$

In two CSBR connected in series, the overall reaction rate can be calculated as follows:

$$r_A = \frac{k}{8}\left[\sqrt{16C_{if}^{in} + 3a^2k^2\tau^2 - 2ak\tau\sqrt{16C_{if}^{in} + a^2k^2\tau^2}} + \sqrt{16C_{if}^{in} + a^2k^2\tau^2} - 2k\tau\right]. \quad (25)$$

The nitrification rate greatly depends on the biofilm support material. The rate for the inert support material achieves the typical values obtained also by other investigators. For comparison, different rates are given in table 2.

T a b l e 2

Ammonia nitrogen removal rate

Biofilter type	NH$_4$–N removal rate (g N/(m^2·h))	Remarks	Reference
Polyethylene membrane reactor	$9.67\cdot10^{-2}$		KAZUAKI et al., 2000
Packed bed	$2.92\cdot10^{-4}$	cement ball carrier	KAZUAKI et al., 2000
Rotating disk reactor	$7.08\cdot10^{-4}$		OKABE et al. [21]
Fluidized bed reactors	$4.00\cdot10^{-3}$	nitrifying bacteria PVA-immobilized pellets	ARAKI et al. [2]
Fluidized bed reactors	$1.60\cdot10^{-3}$	nitrifying bacteria immobilized by macroporous cellulose carrier	MATSUMURA et al. [20]
Inner cylinder rotated reactor	0.26	influent ammonia concentration, 40 mg N-NH$_4$/dm^3	LIU et al. [19]
Inner cylinder rotated reactor	0.40	influent ammonia concentration, 60 and 82.5 mg N-NH$_4$/dm^3	LIU et al. [19]
Tricling filter	$2.50\cdot10^{-2}$	PVC specific surface area, 157 m^{2}m^{-3}	THÖRN et al. [27]
Tricling filter	$6.67\cdot10^{-2}$	PVC specific surface area, 226 m^{2}m^{-3}	THÖRN et al. [27]
Packed bed	$3.0\ 10^{-2}$	stone (inert material)	this paper
	$15.8\ 10^{-2}$	marble	this paper
Biofilters connected in series	$7.75\cdot10^{-2}$*	$t = 27$ °C	ZHU at al. [35]
	$7.17\cdot10^{-2}$*	$t = 20$ °C	ZHU at al. [35]
	$7.05\cdot10^{-2}$*	$t = 14$ °C	ZHU at al. [35]
	$6.92\cdot10^{-2}$*	$t = 8$ °C	ZHU at al. [35]

* R_{max} values.

Carbonaceous material used as the support medium allows the nitrification rate to be increased by approximately five times. Many authors confirm that carbonate addition significantly improves the nitrification efficiency in biofilm (BIESTERFELD et al.

[3], GREEN et al. [9]–[11], TARRE, GREEN [25], KOWALSKI, LEWANDOWSKI [14]) and activated sludge as well (LEWANDOWSKI [18], WETT et al. [29]).

On the basis of the experimental data the constant reaction rate k was calculated and the results were presented in table 3 and figure 7.

T a b l e 3

Nitrification constant rates in packed bed reactors for two different models

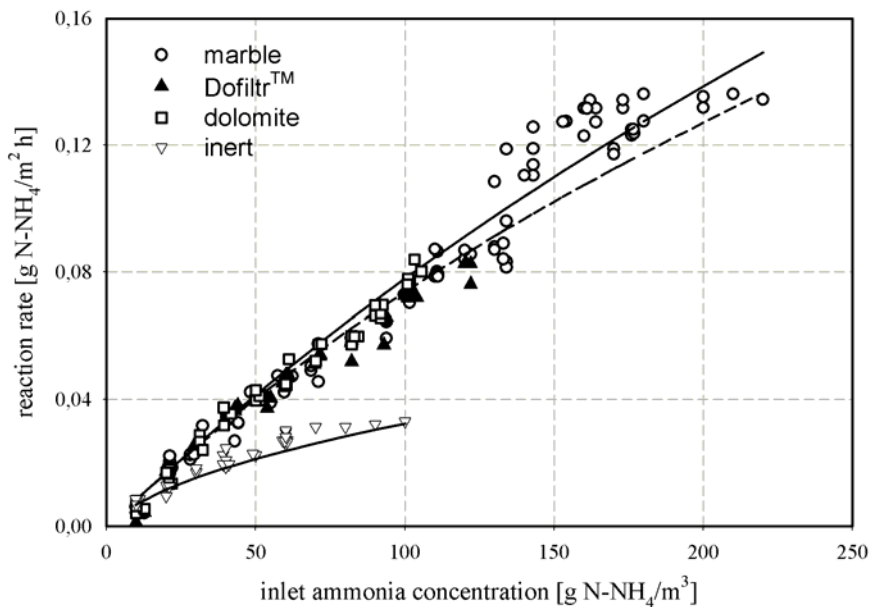| Reactors packing material	CSBR connected in series model	Dispersion model
	constant rate k (g N–NH$_4$$^{0.5}$ m$^{-0.5}$ h^{-1}) 10^2	
Inert	0.3866±0.0065	0.4128±0.0147
Dolomite	1.3893±0.0400	1.2834±0.0120
Dofiltr™	1.2104±0.02364	1.2493±0.02671
Marble	1.7322±0.05256	1.4473±0.04586

Fig. 7. Reaction rate for dispersion model (solid line) and that of the tanks connected in series (dotted line) for different support materials

In the dispersion model, the constant reaction rate was calculated numerically. For the inert support material, the constant rate of half order was $0.38 \cdot 10^{-2}$ g N–NH$_4$$^{0.5}$ m$^{-0.5}$ h^{-1}. The nitrification rate determined in the reactors with a carbonaceous material is approximately two to three time higher. The application of a carbonaceous material as

support assures the presence of bicarbonates inside biofilm, though all bicarbonates present in the bulk liquid are utilized.

5. CONCLUSION

The results of the investigations carried out confirm the concept that bicarbonates can limit the nitrification rate. Their concentration decreases proportionally to ammonia being oxidized (nitrified). If the bicarbonates present in bulk liquid are exhausted, the nitrification process on the inert support material is disturbed and ceases. Carbonaceous support material is applied to overcome this limitation. A decrease in proton concentration causes $CaCO_3$ dissolution and an increase of bicarbonate ion concentration inside the biofilm. Both low pH and alkalinity (bicarbonate ion concentration) of the bulk liquid do not affect the nitrification rate if bicarbonates are supplied from the support material in a sufficient amount. It is the self-acidity regulation mechanism that prevents overdosing which is of a practical importance. The reaction rate strongly depends on the type of the support material; the highest reaction rate is observed when marble is used as support. It can be stated that the nitrification rate depends on the carbonaceous material dissolving rate.

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