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BIOLOGICAL DENITRIFICATION OF WASTE BATHS OF HIGH SALINITY IN A PACKED COLUMN

The work presents results of research on the possibilities of utilizing biological denitrification in a packed column (with an attached microbial heterogeneous culture) for treating wastewaters from browning. Such wastewaters contain nitrogenous pollutants (nitrates + nitrites) and sodium chloride in high concentrations. Operation of a laboratory denitrification model (12 dm³ volume) with both model and real wastewaters proved that at concentrations up to 30 g · dm⁻³ NaCl, long-term (for several months) denitrification proceeds with high efficiencies (> 98%).

1. INTRODUCTION

Biological denitrification carried out by suspended bacterial cultures is already quite widely spread even on industrial scale, but so far packed columns with attached biomass have been less utilized. The elimination of oxidative forms of nitrogen proceeds in accordance with well-known equations in the presence of a suitable carbon donor (carbonaceous substrate) and, of course, denitrification bacteria (e.g. [1]). Papers dealing with column denitrification in the presence of high concentrations of neutral salts are rather poorly represented in literature (compared to the wide range of papers on the denitrification in general). One of the interesting fields of applying removal of nitrates from drinking water due to a combination of ion exchange with biological denitrification was described by van der HOEK et al. [2]–[6]. After exhaustion of its exchange capacity, the ion exchanger was regenerated with a solution of sodium chloride or sodium hydrogen carbonate. The regenerative solution applied was subjected to biological denitrification and, on the replenishment of NaCl or NaHCO₃ to the concentrations

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required, was repeatedly used in the next stage of ion-exchanger regeneration. In paper [2], the nitrogenous pollutant of regenerative solution used for the ion exchanger was eliminated through usage of USB (upflow sludge blanket) reactors containing granulated denitrification sludge with influent concentration of nitrates in the range of $100\text{--}110\text{ g}\cdot\text{dm}^{-3}$. An unfavourable effect of high pH (8.2–9.2) on denitrification rate was not observed, this rate remained constant in the range of $400\text{--}500\text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}\text{ NO}_3\text{-N}$. At the concentration of $25\text{ g}\cdot\text{dm}^{-3}$ NaCl denitrification efficiency was 40% during the first 6–8 days of experiment, after 3 weeks it increased to 60%. A 75% efficiency was attained when $30\text{ g}\cdot\text{dm}^{-3}$ NaHCO_3 was employed.

In a similar experiment, STRNADOVÁ [7] used a biofilm reactor filled with activated carbon. Concentration of nitrates in the model wastewater treatment was $100\text{ mg}\cdot\text{dm}^{-3}$; concentration of ethanol, $3.7\text{ mg}\cdot\text{dm}^{-3}$; concentration of NaCl was gradually increased from $5\text{ g}\cdot\text{dm}^{-3}$ up to $18\text{ g}\cdot\text{dm}^{-3}$. NaHCO_3 at a concentration of $25\text{ g}\cdot\text{dm}^{-3}$ was applied as a further possible regenerative solution. The process proceeded at an average efficiency of 98% and even the increased concentration of HCO_3^- ions did not influence this efficiency.

Biological denitrification was also applied in the case of purifying waters coming from salmon farming [8]. Sea water of $18\text{ g}\cdot\text{dm}^{-3}$ salinity contained ammonia, which was oxidized to nitrates on aeration biological filters. Water thus treated, containing $68 \pm 10\text{ mg}\cdot\text{dm}^{-3}\text{ NO}_3\text{-N}$, was subjected to biological denitrification in a denitrification column (1.5 dm^3) and reapplied. When carbonaceous and nitrogenous substances were dosed at a $\text{C/N} = 1$ ratio, an almost 100% removal of nitrates was achieved in the laboratory column, but relatively high production of nitrites ($2\text{ mg}\cdot\text{dm}^{-3}\text{ NO}_2\text{-N}$) was observed. During experiments in a pilot-plant column of approx. 1 m^3 volume, the mentioned dosage ratio of $\text{C/N} = 1$ proved to be optimal, no nitrites were detected, production of $\text{NH}_3\text{-N}$ was low, and denitrification efficiency approached the 100% value.

A model process of purifying water from a desulfurization plant by means of biological denitrification carried out by a suspended microbial culture was applied by KRISTENSEN and JENSEN [9]. Polluted water contained $150\text{--}300\text{ mg}\cdot\text{dm}^{-3}$ nitrates, $10\text{--}30\text{ g}\cdot\text{dm}^{-3}$ chlorides, $1\text{--}4\text{ g}\cdot\text{dm}^{-3}$ sulfates at the temperature ranging from 40 to 50 °C. The water contained traces of heavy metals that had to be removed in advance by chemical precipitation. An acetate ($1445\text{ g}\cdot\text{dm}^{-3}$) was employed here as carbon donor. The study showed that production of nitrites increased with the increase in both temperature and concentration of chlorides. Laboratory experiments confirmed the possibility of utilizing biological denitrification even under these extreme conditions. No adverse effect of high sulfate concentration on the denitrification efficiency was observed.

2. EXPERIMENTAL

2.1. CHEMICALS AND SOLUTIONS

Chemicals of standard chemical and analytical purity were used. Composition of drinking water: $60\text{--}90 \text{ mg}\cdot\text{dm}^{-3} \text{ SO}_4^{2-}$, $6\text{--}36 \text{ mg}\cdot\text{dm}^{-3} \text{ Cl}^-$, $< 0.01 \text{ mg}\cdot\text{dm}^{-3} \text{ NO}_2^-$, $< 10 \text{ mg}\cdot\text{dm}^{-3} \text{ NO}_3^-$ and $< 0.05 \text{ mg}\cdot\text{dm}^{-3} \text{ NH}_4^+$.

Model Wastewater (MWW)

This was prepared from stored solutions of KNO_3 , NaNO_3 , NaNO_2 , $(\text{NH}_4)_2\text{HPO}_4$ and CH_3OH by diluting them with drinking water (source of trace elements). MWW was mixed with methyl alcohol solution prior to entering the denitrification column. The quantity of methyl alcohol required was calculated according to relation (1) where $K = 1.4$:

$$\text{mg CH}_3\text{OH} = (0.431 * \text{mg NO}_3^- + 0.348 * \text{mg NO}_2^-) * K. \quad (1)$$

Actual composition: $625 \text{ mg}\cdot\text{dm}^{-3} \text{ NO}_3^-$, $445 \text{ mg}\cdot\text{dm}^{-3} \text{ NO}_2^-$, $590 \text{ mg}\cdot\text{dm}^{-3} \text{ CH}_3\text{OH}$, $5 \text{ mg}\cdot\text{dm}^{-3} \text{ PO}_4^{3-}\text{-P}$ and $2.9 \text{ mg}\cdot\text{dm}^{-3} \text{ NH}_4^+$.

Synthetic Wastewater (SWW)

SWW was prepared analogously to MWW. Actual composition: $62 \text{ mg}\cdot\text{dm}^{-3} \text{ NO}_3^-$, $460 \text{ mg}\cdot\text{dm}^{-3} \text{ NO}_2^-$, $0.4 \text{ mg}\cdot\text{dm}^{-3} \text{ PO}_4^{3-}\text{-P}$, $0.46 \text{ mg}\cdot\text{dm}^{-3} \text{ NH}_4^+$ and $262 \text{ mg}\cdot\text{dm}^{-3} \text{ CH}_3\text{OH}$ ($K = 1.4$ in equation (1) if not given otherwise), variable amount of NaCl added (stated in text).

Real Wastewater (RWW)

Rinsing water from the browning of iron parts was prepared in the laboratory from an approx. 50% solution of Brunigal (91% NaOH + 9% NaNO_2) after its neutralization with hydrochloric acid and subsequent dilution to the concentration required (the same procedure as in technological process). It was mixed with the solution of methyl alcohol prior to entering the denitrification column. Actual compositions:

RWW 1: $345 \text{ mg}\cdot\text{dm}^{-3} \text{ NO}_3^-$, $456 \text{ mg}\cdot\text{dm}^{-3} \text{ NO}_2^-$, $590 \text{ mg}\cdot\text{dm}^{-3} \text{ CH}_3\text{OH}$ ($K = 1.86$ in equation (1)), $2 \text{ mg}\cdot\text{dm}^{-3} \text{ P}$. Concentration of NaCl adjusted to $29.8 \text{ g}\cdot\text{dm}^{-3}$.

RWW 2: The same as RWW 1 but without the complementing addition of NaCl . Concentration of NaCl was $5.82 \text{ g}\cdot\text{dm}^{-3}$.

RWW 3: $8 \text{ mg}\cdot\text{dm}^{-3} \text{ NO}_3^-$, $392 \text{ mg}\cdot\text{dm}^{-3} \text{ NO}_2^-$, $262 \text{ mg}\cdot\text{dm}^{-3} \text{ CH}_3\text{OH}$ ($K = 1.52$ in equation (1)), $2 \text{ mg}\cdot\text{dm}^{-3} \text{ P}$, $3.95 \text{ g}\cdot\text{dm}^{-3} \text{ NaCl}$.

2.2. ANALYTICAL METHODS

Determinations of pollutants were carried out according to usual standard procedures: PO_4^{3-} -P by the reaction with molybdate and ascorbic acid, NO_2^- with sulfanilic acid and N-(1-naphthyl)-ethylene diamine (or by isotachopheresis), NO_3^- was determined indirectly after its reduction by Devarda's alloy to ammonia (at lower salinities by the isotachopheresis technique), NH_4^+ after distillation by reaction with Nessler's reagent, Cl^- was determined by argentometry. Analyses were performed using standard laboratory equipment.

2.3. DENITRIFICATION COLUMN

This was a 1:10 model of an already completed industrial denitrification plant described in detail in [10]. The column is built out of a cast-iron cylinder of 207 mm inner diameter, 403 mm height, with wastewater inlet in the bottom of cylinder. 50 mm from the bottom, on a perforated partition, the column is loosely loaded with plastic packing of a 4.3 m^2 surface (specific surface is $360 \text{ m}^2 \cdot \text{m}^{-3}$). Free volume of the model was 12 dm^3 . Denitrification was carried out at laboratory temperature ($22 \pm 3 \text{ }^\circ\text{C}$).

3. RESULTS AND DISCUSSION

The initial stage of operating the column inoculated with biomass obtained from anaerobic digestion sludge tanks was its "running-in", i.e., bringing it to a regime displaying a high denitrification effect. This approx. 6 month operation was conducted in a manner analogous to that described in [10] for model wastewater (MWW, molar ratio of $\text{NO}_2^- : \text{NO}_3^-$ was approx. 1:1). During the second half of "running-in", an average efficiency of 99.7% nitrogen removal was achieved at a load of $8.9 \text{ g} \cdot \text{h}^{-1} \text{m}^{-3}$ nitrogen (NO_2^- -N + NO_3^- -N) and hydraulic load of $0.9 \text{ m}^3 \cdot \text{d}^{-1} \text{m}^{-3}$. Residual concentrations of NO_3^- and NO_2^- in effluent were oscillating about the values of $0.6 \text{ mg} \cdot \text{dm}^{-3}$ and $5.4 \text{ mg} \cdot \text{dm}^{-3}$, respectively.

The aim of the second stage of experiments was to establish the influence of increasing load of inorganic salt (sodium chloride) on denitrification biomass, and the effect of expected changes in alkalinity of environment on the efficiency of denitrification process and the "resistance" of the system to possible fluctuations in composition of waters being treated. During this stage the column was loaded with synthetic wastewaters (SWW) of various sodium chloride concentrations (gradually increasing); concentrations of nitrite and nitrate in SWW were chosen in accordance with the composition of real wastewaters (molar ratio of $\text{NO}_2^- : \text{NO}_3^-$ was approx. 10:1) and remained unchanged during this stage of experiments. The load based on total nitrogen fluctuations between 9.1 and $10.4 \text{ g} \cdot \text{h}^{-1} \text{m}^{-3}$, and hydraulic load was in the range of 1.3 – $1.5 \text{ m}^3 \cdot \text{d}^{-1} \text{m}^{-3}$.

Sodium chloride added to the SWW in the dose of $2.3 \text{ g} \cdot \text{dm}^{-3}$ and subsequently in the dose of $10 \text{ g} \cdot \text{dm}^{-3}$ had virtually no effect on denitrification efficiency; its initial values (at least 99.5%) were obtained even after approx. 3 months. When NaCl concentration was increased to $15 \text{ g} \cdot \text{dm}^{-3}$ the efficiency dropped within several days to the value as low as 63% and rose again after several days to the value higher than 99%. A further increase in NaCl content to $30 \text{ g} \cdot \text{dm}^{-3}$ led again to a reduced denitrification effect (85.8%), and after the same time (21 days) the denitrification efficiency reached at least 95%.

The above process of gradual loading the denitrification column with waters of increasing salinity (longer than 1 year) was several times interrupted (mostly for 3–4 weeks) for operational reasons. In subsequent restarts of operation it became evident that the decreases in denitrification efficiency as well as the extension of periods necessary to renew original values were proportional to the increasing salinity of SWW (from several days at a low NaCl content up to several weeks at the NaCl concentration of $30 \text{ g} \cdot \text{dm}^{-3}$).

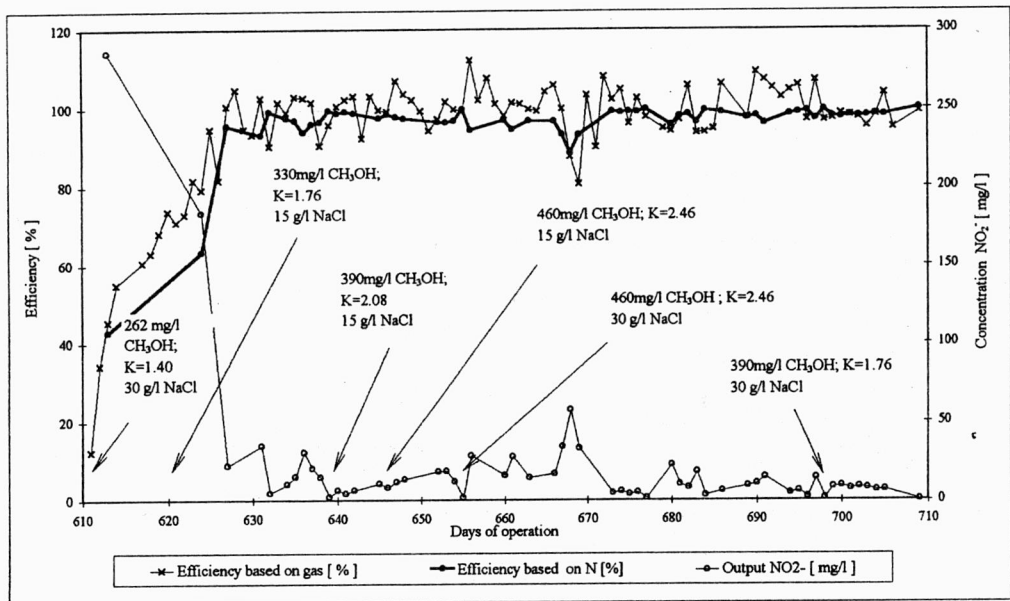


Fig. 1. The influence of sodium chloride and methyl alcohol concentrations on the efficiency of synthetic wastewater denitrification

The mentioned fluctuations in the efficiency of the process were not so considerable in experiments during which really continuous operation was maintained and only salinity of water under treatment or also the dosage of carbonaceous substrate (methyl alcohol) were being changed. Attention was given to the circumstances in the following period (610–710 days of operation); conditions of work (concentrations of methyl alcohol and NaCl in SWW and times of their changes)

are seen in figure 1. The very low initial denitrification efficiencies were caused by a preceding 52 day break in column operation. It is obvious from figure 1 that reasonable efficiency was renewed only after approx. 14 days. In further course of work, the column showed a relatively stable average 97% denitrification efficiency which did not change significantly even with changes in salinity or dosage of methyl alcohol (figure 1).

In these and other stages of the experiment, the efficiency was also assessed on the basis of the quantity of gas being generated (this was not corrected in such a way as to obtain normal conditions of temperature, pressure and water vapour tension). Although production of gas pulsated due to trapped gas bubbles (employing a honeycomb type of packing in the column would have been more convenient), this mode of observation was valuable for its fast information. When nitrogenous substances were analyzed, the response to the possible changes in the influent composition was decided by time of detention in the column (approx. 17 hours) and, of course, by time necessary for carrying out analyses.

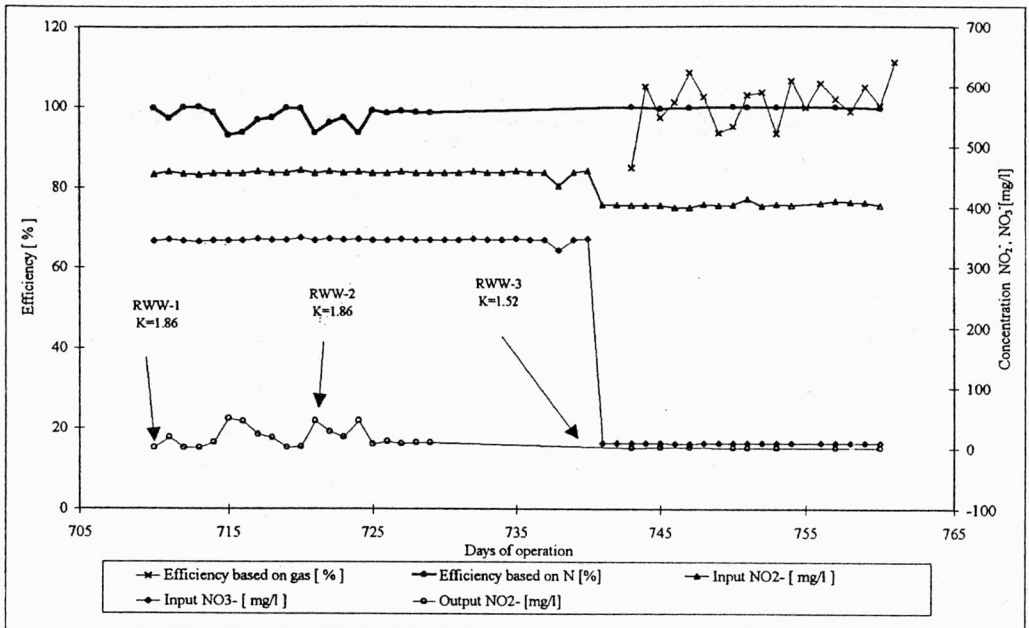


Fig. 2. The efficiency of real wastewater denitrification

An interesting correlation appeared between denitrification efficiencies observed by means of the balance of nitrogenous materials and of produced gas. In the case when gas was related to normal pressure, temperature and water vapour tension, a 6–8% drop in the efficiency of the gas production appeared. This “missing” nitrogen was probably used by biomass for assimilation. At the same time the

input-output balance showed a decrease in the concentrations of NH_4^+ (approx. $0.3\text{--}0.4 \text{ mg}\cdot\text{dm}^{-3}$) and of phosphorus ($0.1\text{--}0.2 \text{ mg}\cdot\text{dm}^{-3}$). A rise in the concentrations of these nutrients would probably (according to literature) bring about an increased denitrification rate, but also an undesirable increase of their concentrations in effluent.

Verification of the course of the process tested was carried out with the so-called real wastewaters (RWW) representing technological baths used in metal parts finishing by browning (figure 2). The composition of RWW did not exceed values defined by experimental conditions with SWW. At this stage, the wastewater was initially treated to have a concentration of $30 \text{ g}\cdot\text{dm}^{-3}$ NaCl (RWW 1). As figure 2 illustrates, an approx. 98% efficiency was reached at the given concentration despite the loading of column being more than 30% heavier ($12.7 \text{ g}\cdot\text{m}^{-3}\text{h}^{-1}$ of nitrogen) compared to the preceding operation. The efficiency was maintained even during following work with RWW 2 ($5.82 \text{ g}\cdot\text{dm}^{-3}$ NaCl) and rose to 99.7% with RWW 3 ($3.95 \text{ g}\cdot\text{dm}^{-3}$ NaCl, load merely $7.6 \text{ g}\cdot\text{m}^{-3}\text{h}^{-1}$ based on N). It may be said, therefore, that this type of denitrification of real wastewaters proceeded with no difficulties and gave perfectly satisfactory results.

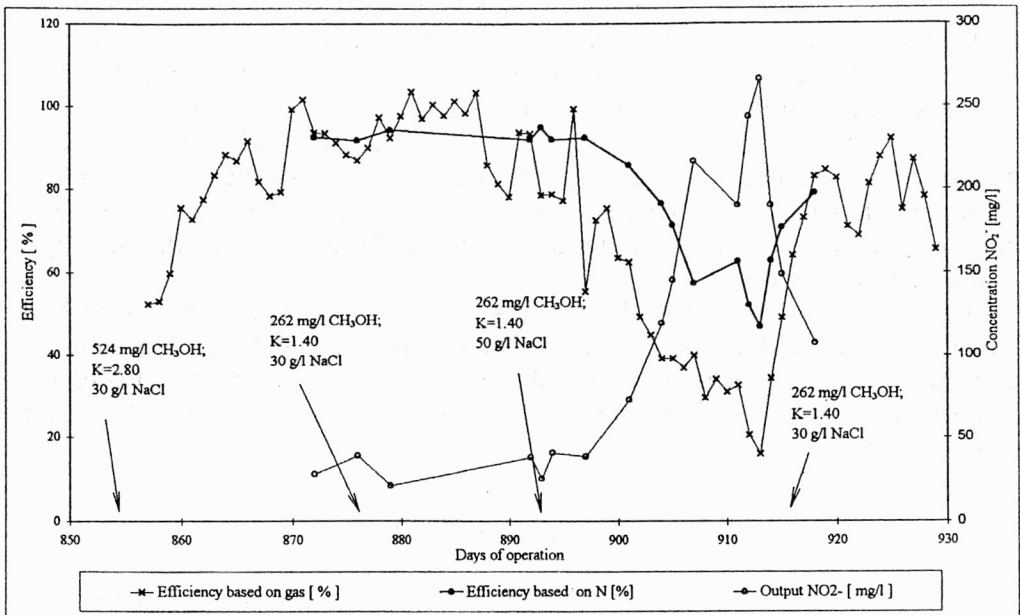


Fig. 3. The influence of extreme salinity of synthetic wastewaters on denitrification efficiency

Following a quarter-year break, the denitrification column was further operated with SWW of extreme salinity (figure 3). Activating the column again lasted about 20 days but only a 92% denitrification efficiency was obtained. After increasing

a salinity to $50 \text{ g} \cdot \text{dm}^{-3}$ NaCl a gradual pronounced decrease in efficiency appeared; it was as low as approx. 50%. When original conditions were renewed, the efficiency quickly increased again, however, without regaining initial values during the test. Nevertheless, based on facts stated it may be obviously claimed that a short-term increase in salinity ($50 \text{ g} \cdot \text{dm}^{-3}$) will be manifested itself only as a reversible efficiency decrease.

Due to high methanol additions to the medium of denitrification, the relatively high residual concentrations of methanol in effluents can be anticipated. As post-denitrification effluents in this case are to be aerobically post-treated, the residual concentrations of methanol (expressed, e.g., as TOC) were not investigated.

4. CONCLUSIONS

This work verified the possibility of utilizing denitrification biotechnology for removal of nitrogenous pollutants of waste baths from metalworks (containing high concentrations of nitrite and sodium chloride). This technology was tested in a laboratory model denitrification column with biomass loosely attached to plastic packing. During a 3-year operation a 98% denitrification efficiency was achieved at a salinity of $30 \text{ g} \cdot \text{dm}^{-3}$ NaCl. With lower contents of NaCl (below $15 \text{ g} \cdot \text{dm}^{-3}$) the efficiencies exceeded 99%. Temporary increase in salinity (for approx. 3 weeks) to $50 \text{ g} \cdot \text{dm}^{-3}$ NaCl did not cause destruction of the denitrification culture; the denitrification efficiency was quickly renewed after salinity had been reduced.

It was shown that interrupted operation of the model under conditions of increasing salinity has a longer-term impact on the decrease in the activity of denitrification biomass.

The denitrification described is applicable to the treatment of browning baths following suitable dilution. From the environmental point of view, however, chemical treatment (regeneration) of old baths is more expedient than loading the recipient with waters of increasing and unremovable salinity caused in this case by NaCl, NaHCO_3 and Na_2CO_3 .

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BIOLOGICZNA DENITRYFIKACJA KĄPIELI ODPADOWYCH O DUŻYM ZASOLENIU W KOLUMNIE Z WYPEŁNIENIEM

Przedstawiono wyniki badań dotyczących możliwości wykorzystania biologicznej denitryfikacji w kolumnie z wypełnieniem (z heterogeniczną kulturą bakterii) do oczyszczania ścieków powstałych podczas oksydowania. Takie ścieki zawierają zanieczyszczenia azotowe (azotany i azotyny) i chlorek sodu w dużych stężeniach. Działanie laboratoryjnego modelu denitryfikacyjnego (o objętości 12 dm³), w którym testowano zarówno prawdziwe, jak i modelowe ścieki, dowiodło, że dla stężeń do 30 g·dm⁻³ NaCl zachodzi długotrwała (kilkumiesięczna) i wysoce efektywna (> 98%) denitryfikacja.

