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BIOCHEMICAL REMOVAL OF NITROGEN COMPOUNDS FROM WASTEWATER

The results of investigations on the removal of nitrogen compounds from wastewaters by the nitrification and denitrification method using activated sludge were described. It has been shown that the optimal removal of nitrogen compounds from wastewater obtained by conventional technological systems is 35%. The results of tests of the intensification of nitrification process involving pure oxygen have suggested a two-way course of the nitrogen compound conversion (assimilation and nitrification of nitrogen compounds). The influence of some oxygen acceptors on the course of denitrification process was discussed including for the organic substances present in wastewaters and in activated sludge biomass, as well as the aliphatic alcohols. The modification of technological system to a more effective removal of nitrogen compounds, including the denitrification — nitrification — denitrification processes was assessed and the results were given.

1. INTRODUCTION

The removal of nitrogen compounds from wastewater is one of the current problems related to the abatement of stagnant water eutrophication phenomenon [10, 12, 14, 17, 19]. In the recent years more and more attention has been paid to this problem, mostly because the good quality water sources to meet the increasing demands of industry become limited.

The steel industry which is water consuming is seriously affected by the shortage of suitable quality water, mainly for the make up of losses in the cooling circuits [6]. Therefore there is a particular interest in new industrial water sources such as properly purified sewage and industrial wastewater. The reuse of treated wastewater depends on the possibility of biogenous constituents removal, first of all nitrogen compounds [1], [2].

2. DISCUSSION OF THE NITROGEN COMPOUNDS REMOVAL FROM WASTEWATER

In the treatment of wastewater for cooling purposes in the industry there is a tendency to reduce the ammonium ion concentration in order to prevent the acidification of water by the nitrification process products.

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This results from the following reactions [11]:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+,$$

$$H^+ + HCO_3^- \rightarrow CO_2 + H_2O,$$

$$5CO_2 + NH_4^+ + 2H_2O \rightarrow C_5H_7O_2N + 5O_2 + H^+.$$

The permissible ammonium ion concentration depends among others on the basicity of water. For the basity m 4 mval/dm^3, the concentration of ammonium nitrogen should not exceed 5 mg/dm^3 N_{NH_4}, and for the basicity m 2 mval/dm^3 — 2 mg/dm^3 N_{NH_4}.

The idea of nitrification is based on the biochemical oxidation of NH_3 to NO_3^- with the help of *Nitrosomonas* and *Nitrobacter* bacteria conducted in aerobic conditions. *Nitrosomonas* oxidizes NH_3 to NO_2^-, while the *Nitrobacter* continues the nitrification by the oxidation of NO_2^- to NO_3^-, the remining oxidation product — CO_2 is assimilated by the biomass [11]. The nitrification bacteria are sensitive to high loadings of activated sludge are applied in the aeration chamber, the nitrification process should be preceded by the biodegradation of organic compounds [1, 5, 15, 18, 191.

Microorganisms which can perform the enzymatic decomposition of nitrates to nitrogen are called denitrifiers and the process is the denitrification. This process takes place in anaerobic conditions and results in an increase of hydroxide ion concentration. The denitrification reactions can be illustrated as follows:

$$2NO_3^- \xrightarrow{+4H^+} 2NO_2^- + H_2O \rightarrow \begin{cases} \xrightarrow{+6H^+} N_2 + 2OH^- + 2H_2O \\ \xrightarrow{+4H^+} N_2O + 2OH^- + H_2O \\ \xrightarrow{+12H^+} 2NH_3 + 2OH^- + 2H_2O \end{cases}.$$

Technological systems for the biological removal of nitrogen compounds from municipa and industrial wastewater were tested by many researchers such as WUHRMAN [19], BRINGMANN [3], JOHNSON and SCHROEPFER [8]. In these systems the nitrification and denitrification processes are conducted seperately, and in some cases the activated sludge works in aerobic and anaerobic conditions alternatively, whereas in the other ones it operates in aerobic and anaerobic conditions separately. In some systems the denitrification process is activated by the addition of oxygen acceptor in form of untreated wastewater or selected organic compounds.

The conventional technological system applied to third stage of wastewater purification do not provide sufficient removal of nitrogen compounds, even at a low loading of activated sludge. A high variety of the degrees of NH_3 oxidation to nitrates occurring in the nitrification process [18] is due to the production of toxic NO in the activated sludge flocs. NO results from the reduction of NO_3, when the oxygen content is below 0.5 mg/dm^3 and is an inhibitor of respiration processes in microorganisms [9]. In these systems the effect of denitrification process — expressed by the loss of nitrates at the loading of activated sludge in the aeration chamber equal to 0.3 kg BOD_5/kg d.m. per day — does not exceed 35%. The addition of about 33% of untreated wastewater to the total wastewater

volume in a denitrification chamber [1], [3], [18] increases the denitrification effect by 20%; but the ammonia from untreated wastewater passes to the purified wastewater.

The model tests of the nitrification–denitrification systems have indicated that the nitrification process does not occur earlier than after the mineralization of organic compounds is completed. The high degree of wastewater mineralization required for the nitrification process has an unfavourable effect on the denitrification as because of the shortage of oxygen acceptors. Thus in a classical technological nitrification–denitrification system a complete nitrogen compounds removal is not possible unless an additional oxygen acceptor is present in the denitrification process.

3. INTENSIFICATION OF THE NITRIFICATION PROCESS

The nitrification process depends on the following parameters:

— wastewater temperature,

— wastewater reaction,

— oxygen concentration in the aeration chamber, activated sludge loading.

The wastewater temperature in the industrial installations depends on the ambient temperature. The effect of nitrification process deteriorates markedly, when the wastewater temperature falls below 10 °C. The pH value deviations from the optimum 6.8–7.2 can be corrected without any difficulties. The sludge loading in the aeration chamber equal to or smaller than 0.3 kg BOD_5/kg d.m. per day, the oxygen content over 1 mg/dm^3 and together with the optimum temperature and pH value assure a 90% efficiency of the nitrification process.

The theoretical oxygen amount needed to oxidize ammonia to nitrates is equal to:

$$1 \text{ mg } N_{NH_4^+} + 4.57 \text{ mg } O_2 = 1 \text{ mg } N_{NO_3^-} .$$

Our experiments were focused on the intensification of nitrification process. To this end a laboratory model was used (fig. 1). The experimental system was supplied with wastewater or the Rawa river water sample. Pure oxygen at increased pressure was directed into the nitrification chamber.

The results obtained for sample of wastewater (fig. 2) indicate that in the presence of easily decomposable fructose the course of nitrogen assimilation process is faster than the nitrification process. The nitrogen assimilated by bacteria passes to the activated sludge.

This last observation is of interest, as the sludge obtained in the biological wastewater treatment can be utilized in agriculture [2], [4], [16].

In the purification of Rawa river water containing a mixture of municipal and industrial wastewater, the nitrification dominates over the nitrogen assimilation. This is due to a high content of hardly decomposable pollutants in the wastewater (fig. 3).

Thus the microorganisms have to produce lyso-enzymes capable of breaking large organic compound molecules into smaller ones whose biodegradation is easier [7].

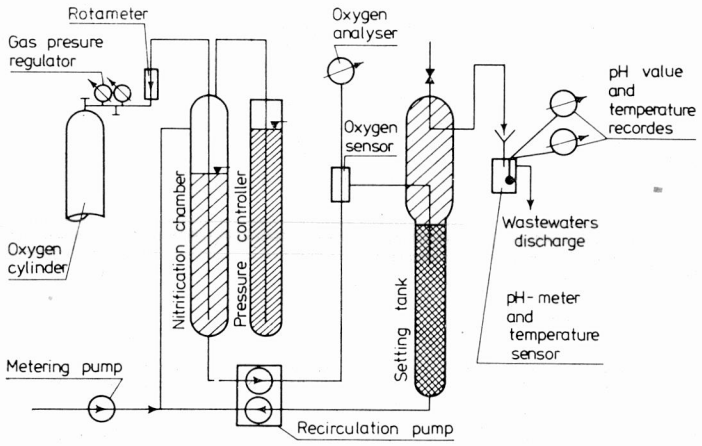

Fig. 1. The diagram of experimental installation model for the wastewater nitrification with the use of pure oxygen

Rys. 1. Schemat modelu aparatury doświadczalnej do nitryfikacji ścieków czystym tlenem

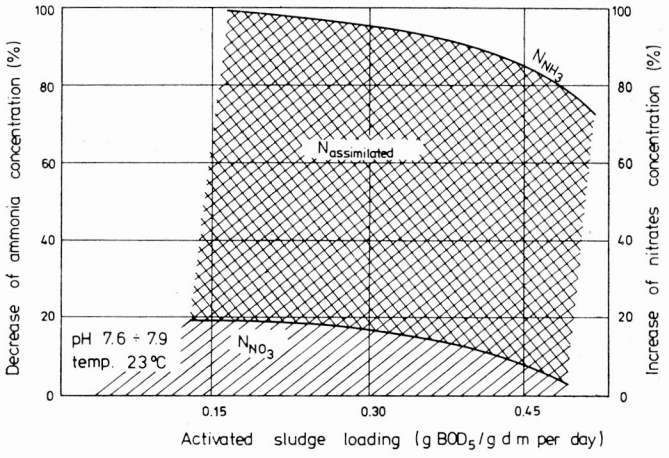

Fig. 2. The removal of ammonia and the increase of nitrates for a sample of wastewater vs. the activated sludge loading with the use of pure oxygen

Rys. 2. Eliminacja amoniaku i przyrost azotanów dla ścieków preparowanych w zależności od obciążenia osadu czynnego przy zastosowaniu czystego tlenu

4. DENITRIFICATION PROCESS INTENSIFICATION

The denitrification process consists in supplying the bacteria with free energy which in the assimilation process is consumed by the nitrates being the acceptors of hydrogen formed during the oxidation of cell parent substances.

The parent substances (oxygen acceptors) oxidized by nitrate oxygen in the denitrification process may comprise the reserve substances of bacteria, organic compounds contained in wastewater or other easily biodegradable compounds dozed into the denitrification chamber. From the technological viewpoint this problem is vast that is why we shall discuss here only the activity of the selected organic compounds as oxygen acceptors in the denitrification.

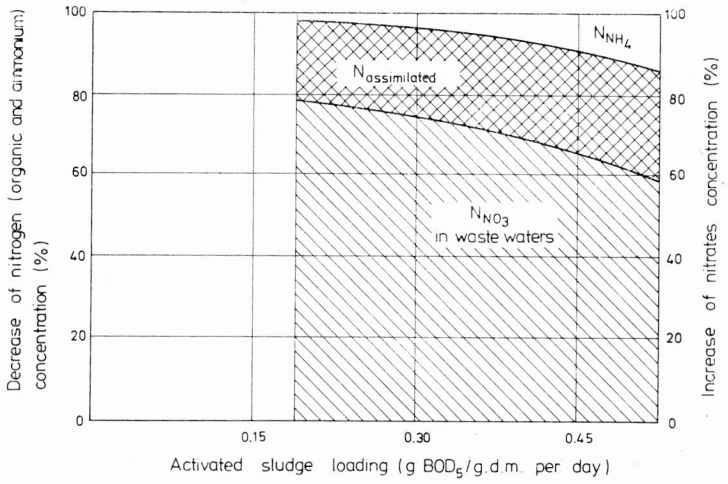

Fig. 3. The removal of organic and ammonium nitrogen and the increase of nitrates for wastewater from the Rawa river vs. the activated sludge loading with the use of pure oxygen

Rys. 3. Eliminacja azotu (organicznego i amonowego) i przyrost azotanów dla ścieków z rzeki Rawy w zależności od obciążenia osadu czynnego przy stosowaniu czystego tlenu

The investigations on the selection of oxygen acceptor have indicated that various organic substances, even these coming from the same compound group, have different effects upon the rate of the denitrification process. This is shown in figs. 4-7. The tangent slopes obtained from the experimental curves allowed to rank the oxygen acceptors investigated according to their efficiency:

- glycerol 45.75,
- ethyl alcohol 26.10,
- glucose 19.20,
- starch 9.20.

From the comparison of the coefficients calculated for the value $O_2 - NO_3/O_2$ — oxygen acceptor < 2.6 it can be seen, that glycerol has the most favourable effect on the denitrification process acceralation. The use of glycerol as the denitrification process modulator has been secured in patent [13]. The starch suggested for industrial use as an oxygen acceptor in the denitrification process [17] has a relatively small activity.

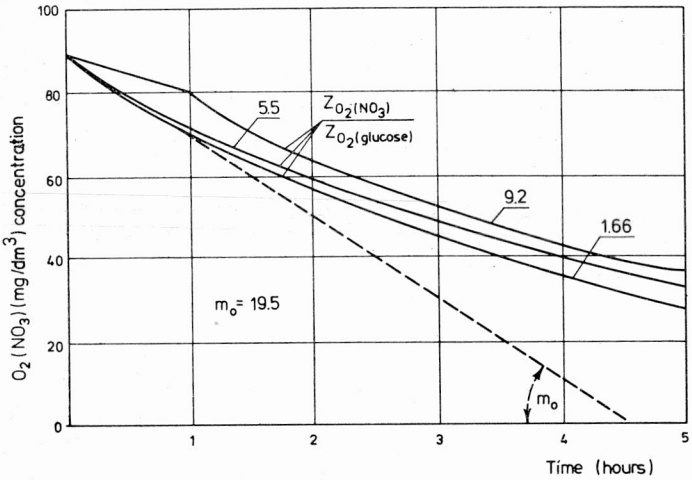

Fig. 4. The effect of glucose on the denitrification process rate

Rys. 4. Wpływ glukozy na prędkość przebiegu procesu denitryfikacji

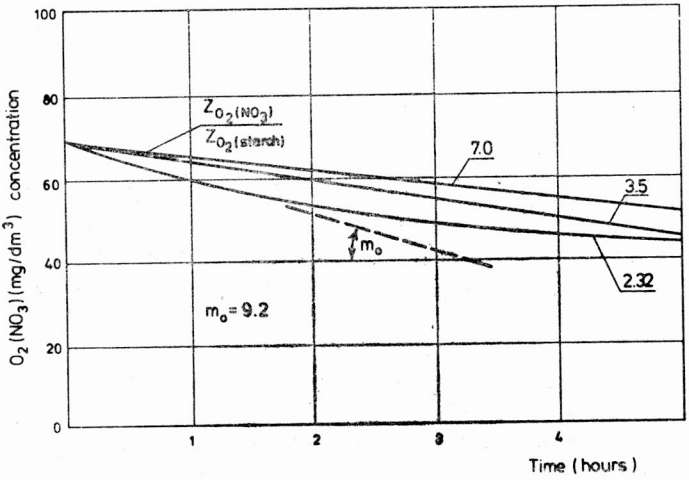

Fig. 5. The effect of starch on the denitrification process rate

Rys. 5. Wpływ skrobii na prędkość przebiegu procesu denitryfikacji

5. MODEL INVESTIGATIONS ON A NEW TECHNOLOGICAL SYSTEM FOR THE NITROGEN COMPOUNDS REMOVAL FROM WASTEWATER

The new technological system which has been elaborated, guarantees a high operational reliability and a complete removal of nitrogen compound from wastewater without detrimental effect on the purified wastewater quality [18]. It moreover allows an intergrated treatment of municipal and industrial wastewater containing nitrates.

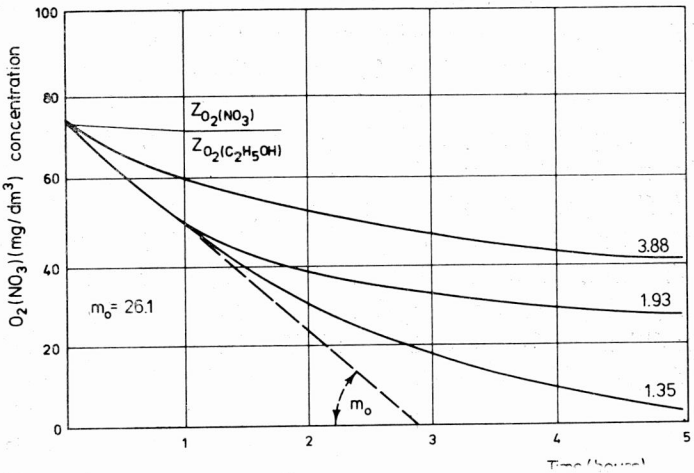

Fig. 6. The effect of ethyl alcohol on the denitrification process rate

Rys. 6. Wpływ alkoholu etylowego na prędkość przebiegu procesu denitryfikacji

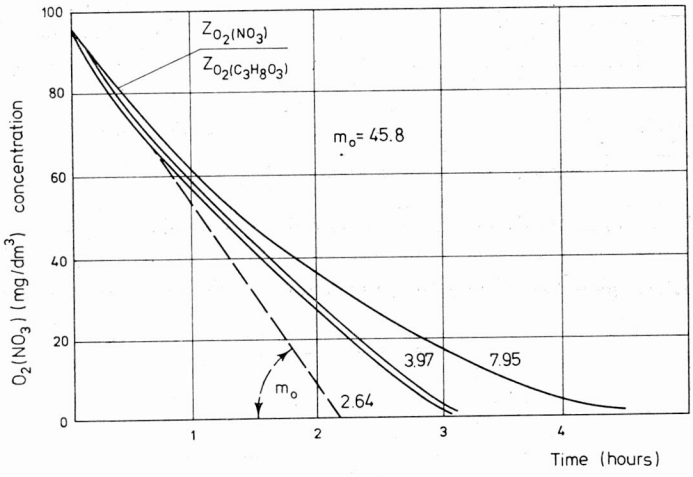

Fig. 7. The effect of glycerol on the denitrification process rate

Rys. 7. Wpływ gliceryny na prędkość przebiegu procesu denitryfikacji

In the technological system suggested the removal of nitrogen compounds is a three stage process (fig. 8). The denitrification process occurs in the first and the third stages. In the first stage the organic compounds present in untreated wastewater are used as oxygen acceptors, in the third stage, however, they must be supplied to the system. The second stage comprises ammonification process followed by the nitrification of the remaining amounts of organic and ammonium nitrogen present in the wastewater.

The investigations of the first treatment have indicated, that the reduction of organic

compounds expressed in BOD_5 depends on the BOD_5 to nitrate oxygen concentration ratio (fig. 9) and decreases nonlinearily with increasing BOD_5, the value of the latter being related to the nitrate oxygen concentration. The application of organic compounds containing organic and ammonium nitrogen to the denitrification process in wastewater treatment does not ensure a complete removal of nitrogen compounds. Nevertheless the results obtained from the experiments are very interesting from the point of view of technological feasibility. They indicate, that the nitrate oxygen may be used in biodegradation at the first stage of wastewater treatment, as the process efficiency is high. The sufficient wastewater detention time in the denitrification chamber is about 1 hour.

In the technological system investigated the stage of the second wastewater treatment under aerobic conditions leads to a complete nitrification process. For a relatively short (about 2 hours) detention time of wastewater in the nitrification chamber the ammonia

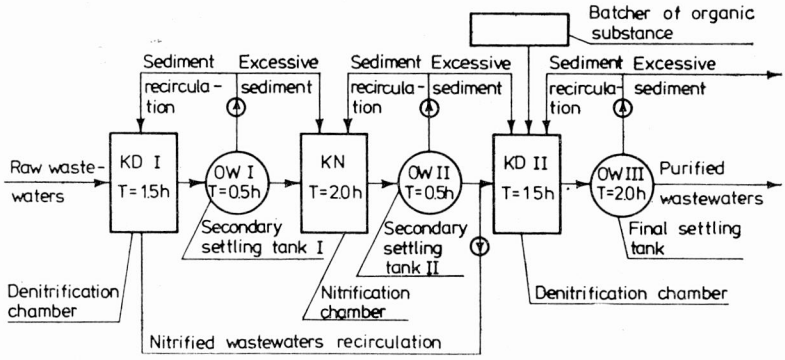

Fig. 8. The technological diagram of a modified system for the removal of nitrogen compounds from wastewater

Rys. 8. Schemat technologiczny zmodyfikowanego układu do eliminacji związków azotowych ze ścieków

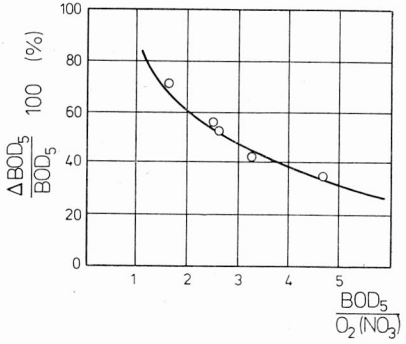

Fig. 9. The reduction of organic compounds in BOD_5 vs. the BOD_5 ratio to nitrate oxygen concentration in the nitrified wastewaters

Rys. 9. Redukcja związków organicznych wyrażonych w BZT_5 w zależności od stosunku BZT_5 do tlenu azotanowego ścieków znitryfikowanych

removal efficiency exceeded 94%, while the increase of nitrates concentration in relation to the ammonium nitrate, less the nitrate nitrogen, was from 87 do 114%. The values exceeding 100% should be noted as they indicate the biomas nitrogen oxidation to nitrates.

The phenomenon results from the nitrification process conducted at a very low loading of activated sludge organics (about 0.05 kg BOD_5/kg d.m. per day) and proves that the technological system has reached the activated sludge stability. In this case preliminary BOD_5 reduction in the first denitrification chamber is a contributing factor. Aparat from the above the wastewater buffering properties in the preliminary denitrification process favour the uniform run of nitrification process at the second treatment stage.

The investigations on the denitrification process in the third treatment stage with the use of additional oxygen acceptor have shown that a reduction of nitrates above 90% requires an excess of oxygen acceptor. In case of the ethyl alcohol this excess, expressed in the amount of oxygen necessary for oxidation of the oxygen acceptor to nitrate oxygen, is

$$5.2\ \frac{O_2(C_{org})}{O_2(NO_3)}\ ;\quad 1.48\ \frac{O_2(C_{org})}{O_2(NO_3)}$$

in the series of experiments, directly after using glycerol as oxygen acceptor. For methyl alcohol and glycerol these values are equal to 1.55, 0.91, respectively (fig. 10).

In the suggested technological system the industrial nitrate wastewater can be used for the preliminary treatment in the first stage of denitrification.

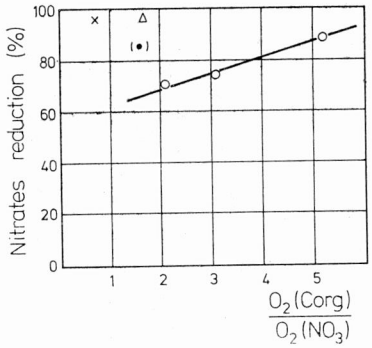

Fig. 10. The reduction of nitrates as a function of the ratio of theoretical amount of oxygen necessary for oxidation of the oxygen acceptor to the nitrate oxygen

o — ethanol,
x — glycerol,
△ — methanol,
(•) — ethanol after run with glycerol

Rys. 10. Redukcja azotanów w zależności od stosunku tlenu teoretycznego utleniania akceptora tlenu do tlenu azotanowego

o — etanol,
x — gliceryna,
△ — metanol,
(•) — etanol po serii z gliceryną

The proposed water treatment technology with a closed cooling cycle presented in fig. 11 shows the utilization of the denitrification process in "joint" technological systems applied in industrial practice. This system allows to match the treatment of cooling water in a closed circuit to the current requirements — make a better use of it and, consequently, to eliminate the additional wastewater salination. In the technology discussed, the cations are removed from circulating water by means of hydrogen ion exchangers, and the produced

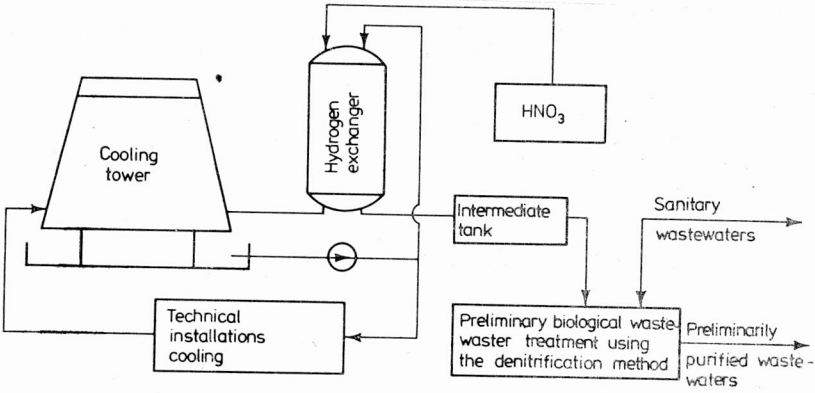

Fig. 11. The diagram of a joint technological system for the cooling circuit water treatment and the municipal wastewater treatment using the denitrification method

Rys. 11. Schemat skojarzonego układu technologicznego uzdatniania wody obiegu chłodzącego i oczyszczania ścieków sanitarnych metodą denitryfikacji

free organic acids are used for the correction of carbonate hardness in the same cooling system. Hydrogen ion exchanger, regenerated by the nitric acid, produces nitrate wastewater, which can be used for partial purification of municipal or other wastewater containing organic pollutants by the denitrification method. It can be seen that the acid used in the proposed technological process is formed from the atmospheric nitrogen, which is released again in the denitrification process and as a gas escapes to the atmosphere. This allows to eliminate biogenic compounds harmful for the surface waters.

6. FINAL CONCLUSIONS

1. Biochemical removal of nitrogen compounds by the activated sludge method is possible owing to the assimilation of nitrogen and of nitrification and denitrification processes.

2. To complete the nitrification and denitrification processes the loading of activated sludge organics at the nitrification chamber should be lower than 0.3 kg BOD_5/kg d.m. per day, and the nitrified wastewater in the denitrification chamber enriched with oxygen acceptors.

3. The application of technological system comprising a sequence of nitrification and denitrification processes without the usage of the reserve biomass substances allows to denitrify the purified wastewater up to 35%.

4. As oxygen acceptors in the denitrification process, either biochemically degradable organic substances present in wastewaters can be used or other organic compounds such as aliphatic alcohols can be introduced.

5. The economical factors of denitrification process can be improved by a maximal utilization of the oxygen acceptors present in the raw wastewater. This can be achieved by applying the technology consisting of a sequence of the denitrification — nitrification — denitrification processes.

6. In order to protect the natural environment against the excessive salinity of surface water it is advisable to introduce, wherever possible, the joint technological systems including the utilization of nitrate wastewater from the industrial cooling circuit water treatment for preliminary treatment municipal wastewater by the denitrification method. Therefore the location of municipal treatment plant in the vicinity of water consuming industries is fully justified.

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BIOCHEMICZNE USUWANIE ZWIĄZKÓW AZOTOWYCH ZE ŚCIEKÓW

Omówiono wyniki badań usuwania związków azotowych ze ścieków metodą nitryfikacji i denitryfikacji z udziałem osadu czynnego. Wykazano, że w klasycznych układach technologicznych optymalne eliminacje związków azotowych ze ścieków dochodzą do 35%. Wyniki badań nad intensyfikacją procesu nitryfikacji za pomocą czystego tlenu wskazują na możliwość dwukierunkowego przebiegu procesu przemian związków azotowych (asymilacja i nitryfikacja związków azotowych). Następnie omówiono wpływ niektórych akceptorów tlenu na przebieg procesu denitryfikacji, ze szczególnym uwzględnieniem substancji organicznych w ściekach i rezerwowych w biomasie osadu czynnego oraz alkoholi alifatycznych. Zaproponowano i przedstawiono wyniki badań zmodyfikowanego układu technologicznego dla efektywniejszego usuwania związków azotowych obejmującego kolejno proces denitryfikacji — nitryfikacji — denitryfikacji. Dla obniżenia kosztów eksploatacyjnych oczyszczanie ścieków sanitarnych w proponowanym układzie technologicznym wskazano na możliwość wykorzystania ścieków azotanowych pochodzących z poprawienia własności fizykochemicznych wód w zamkniętych obiegach chłodzących.

BIOCHEMISCHE BESEITIGUNG VON STICKSTOFFVERBINDUNGEN AUS ABWASSER

Besprochen werden die Versuchsergebnisse zur Beseitigung von Stickstoffverbindungen durch Nitrifikation und Denitrifikation im Belebtschlammverfahren.

Im klassischen Belebtschlammverfahren werden bis zu 35% der Stickstoffverbindungen beseitigt. Versuche zu einer mehr intensiven Nitrifikation mittels technischem Sauerstoff, zeigte die Möglichkeit eines in zwei Richtungen verlaufenden Abbaues von Stickstoffverbindungen auf (Assimilation und Nitrifikation). Anschliessend wurde der Einfluß einiger Sauerstoffakzeptoren auf die Nitrifikation besprochen; von besonderem Interesse sind hier die organischen Abwasserinhaltsstoffe, die Reservestoffe des belebten Schlammes sowie aliphatische Alkohole. Vorgeschlagen wird eine mehr effektive Verfahrenskette die sich aus der Denitrifikation → Nitrifikation → Denitrifikation zusammensetzt.

Eine Herabsetzung der Betriebskosten der Reinigung von Kommunalabwasser auf ein tragbares Niveau läßt sich dann erreichen, wenn das Nitrate beinhaltende Abwasser nach physikalisch-chemischen Nachreinigungsverfahren in Kühlkreisläufen verwendet wird.

БИОХИМИЧЕСКОЕ УДАЛЕНИЕ АЗОТИСТЫХ СОЕДИНЕНИЙ ИЗ СТОЧНЫХ ВОД

Обсуждены результаты исследований удаления азотистых соединений методом нитрификации и денитрификации с участием активного ила. Доказано, что в классических технологических системах оптимальные исключения азотистых соединений из сточных вод доходят до 35%. Результаты исследований по интенсификации процесса нитрификации с помощью чистого кислорода указывают на возможность двунаправленного протекания процесса превращений азотистых соединений (ассимиляция и нитрификация азотистых соединений).

Обсуждено также влияние некоторых акцепторов кислорода на протеакние процесса денитрификации с особым учётом органических веществ в сточных водах и запасных в биомассе активного ила, а также алифатических спиртов. Предложены и представлены результаты исследований модифицированной технологической сисстемы для более эффективного удаления азотистых соединений, охватывающих очерёдно процесс денитрификации — нитрификации — денитрификации.

Для снижения эксплуатационных расходов очистки санитарных стоков в предлагаемой технологической системе указывается на возможность использования нитратных сточных вод, происходящих от улучшения физико-химических свойств вод в замкнутых холодильных циклах.