EFFECTIVE BIOLOGICAL TREATMENT OF TANNERY WASTEWATER FROM NITROGEN COMPOUNDS

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Even after using physico-chemical and biological methods, tannery wastewater still contains a large amount of nitrogen compounds, which reaches 90 mg/dm^3. The ingress of such wastewater into natural reservoirs leads to eutrophication. The goal is to determine the efficiency of nitrogen compounds removal during sequential wastewater treatment in anaerobic, anoxic and aerobic bioreactors with immobilized microorganisms. For the study, wastewater from a tannery, collected after cleaning in aeration tanks, was used. Model solutions with a concentration of 18.4 - 90 mg/dm^3 were obtained by dilution. 5 sequential bioreactors were used - anaerobic (2 stages), anoxic (2 stages) and aerobic (1 stage) with a capacity of 125 ml/h. Microorganisms were immobilized in each bioreactor on artificial carrier. The effects of organic nitrogen removal in anaerobic bioreactors were 58-66%, anoxic 51-70%, aerobic 57, 5%. A decrease in the concentration of nitrogen compounds occurs as a result of the formation of N_2, NH_3 gases and the use of nitrogen by microorganisms for biomass growth. It is proposed that sequential treatment of tannery wastewater in anaerobic, anoxic, and aerobic conditions with immobilized microorganisms made it possible to obtain a high degree of nitrogen removal. The method does not require chemical materials and is ecological.

Keywords: tannery wastewater, nitrogen compounds, biological treatment, immobilized microorganisms

INTRODUCTION

After the use of physical, chemical and biological treatment methods, the wastewater of the tannery still contains quite a large amount of nitrogen compounds even under the conditions of use involving natural ecological materials (Danylkovych *et al*., 2016). The concentration of these compounds in terms of total nitrogen reaches 80-90 mg/dm^3. A significant share is organic nitrogen, which forms ammonium compounds during decomposition. Under aerobic conditions, these compounds are oxidized by microorganisms to nitrites and nitrates in the process of nitrification. The discharge of such wastewater into a natural reservoir leads to the activation of the processes of flowering and eutrophication with the deterioration of water quality in them. Therefore, the removal of nitrogen compounds from tannery wastewater is an important problem.

Nitrification and denitrification methods are most often used to wastewater treatment from nitrogen compounds (Henze *et al*., 2008, Dytczak *et al*., 2008). Disadvantages of the nitrification-denitrification technology are high energy costs for nitrification and provision of the amount of organic matter required for denitrification, which is easily biodegradable (Sabliy *et al*., 2019).

The purpose of the work is to determine the efficiency of removal of nitrogen compounds in the proposed technology of sequential wastewater treatment in anaerobic, anoxic and aerobic bioreactors with immobilized microorganisms.

EXPERIMENTAL

Wastewater from a tannery was used for the study, collected after its treatment in aeration tanks. Model solutions with concentrations of 18.4-90 mg/dm^3 were obtained by diluting them. An installation of 5 consecutive bioreactors (Fig. 1) was used - anaerobic (2 stages), anoxic (2 stages) and aerobic (1 stage). Wastewater consumption through the installation was 125 ml/h.

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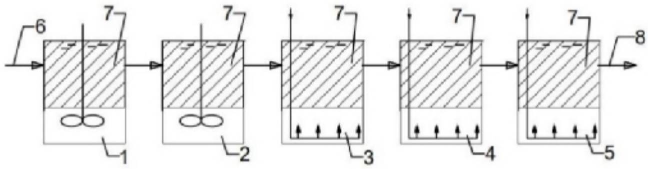
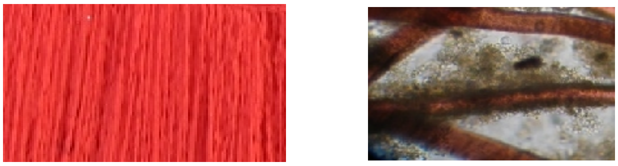


Figure. 1. Scheme of installation of bioreactors:
1 – anaerobic bioreactor of the I degree; 2 – anaerobic bioreactor of the II degree; 3 – anoxic bioreactor of the I degree; 4 – anoxic bioreactor of the II degree; 5 – aerobic bioreactor; 6 – the entrance of wastewater; 7 – fibrous carrier with immobilized microorganisms; 8 – the exit of wastewater.

Microorganisms were immobilized in each bioreactor on a fibrous kapron carrier (Fig. 2, a, b).



a) b)

Figure 2. Carrier for immobilization of microorganisms:
a) fibrous kapron; b) photomicrograph of carrier fibers with biofouling

The average thickness of the biological film on the fibrous carrier with a diameter of 3 mm – 1.5-3 mm was determined. Significant specific biofouling of the carrier was obtained - 32-38 mg/cm^2 (Fig. 2, b). Microscopy showed a great variety of bacterial species. In aerobic conditions, flagellated, free-swimming ciliates and conch rhizomes predominated among the protozoa. Multicellular organisms were represented by rotifers and roundworms. The high value of specific biofouling ensured the growth of biomass in the reaction zone of the bioreactor by 15-20 times compared to the activated sludge of aeration tanks and allowed to increase the efficiency of biological wastewater treatment.

RESULTS AND DISCUSSIONS

Wastewater analysis was carried out at the entrance and exit of each bioreactor according to the indicators: total nitrogen (N_{tot}); ammonium nitrogen (N_{NH4}), nitrites (N_{NO2}) and nitrates (N_{NO3}). Total nitrogen was determined by Kjeldahl, ammonium nitrogen, nitrites and nitrates were determined by colorimetric methods, respectively, with Nessler's reagent, Griess's reagent and salicylic acid, according to known methods. Organic nitrogen (N_{org}) was determined according to the formula (1):

$$N_{org} = N_{tot} – (N_{NH4} + N_{NO2} + N_{NO3}), mg/dm^3. \quad (1)$$

The effect of wastewater treatment was determined by various nitrogen compounds according to the formula (2):

$$E = (C_{en} – C_{ex})\cdot 100/C_{en}, \%, \quad (2)$$

where C_{en} - concentration of nitrogen compounds (for example, organic) at the entrance to this bioreactor (for example, anaerobic of the II degree), mg/dm^3; C_{ex} - concentration

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of nitrogen compounds (for example, organic) at the exit from this bioreactor (for example, anaerobic II stage), mg/dm^3.

The results of studies on the purification of model wastewater in anaerobic bioreactors are shown in Fig. 3 and 4. The effect of organic nitrogen removal in the anaerobic bioreactor of the first degree was 58-65%, in the anaerobic bioreactor of the second degree - 60-66%. In general, in two anaerobic bioreactors, the amount of organic nitrogen decreases by 83-88%, which indicates a high degree of decomposition of nitrogen-containing compounds in bioreactors with immobilized microorganisms, compared to methane tanks (54%) (Danylkovych *et al*., 2016). In anaerobic conditions, with the participation of heterotrophic microorganisms, organic nitrogen is broken down to form ammonia - the concentration of ammonium nitrogen at the exit from bioreactors increases. The decrease in the concentration of total nitrogen (~ by 17%) is associated with the release of N_2, NH_3 gases and the consumption of nitrogen for the growth of the biomass of microorganisms.

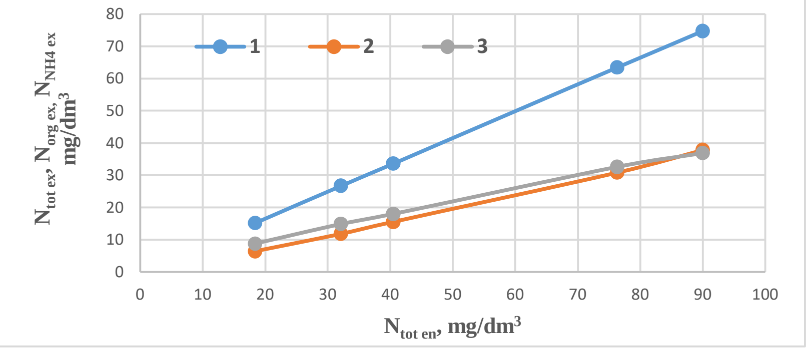

Figure 3. Graphs of dependence N_{tot}, N_{org}, N_{NH4} in an anaerobic bioreactor of the I degree: 1 - $N_{tot\ ex}$ concentration at the outlet from the concentration at the inlet $N_{tot\ en}$, 2- $N_{org\ ex}$ concentration at the outlet from the concentration at the inlet $N_{tot\ en}$, 3- $N_{NH4\ ex}$ concentration at the outlet from the concentration at the inlet $N_{tot\ ex}$

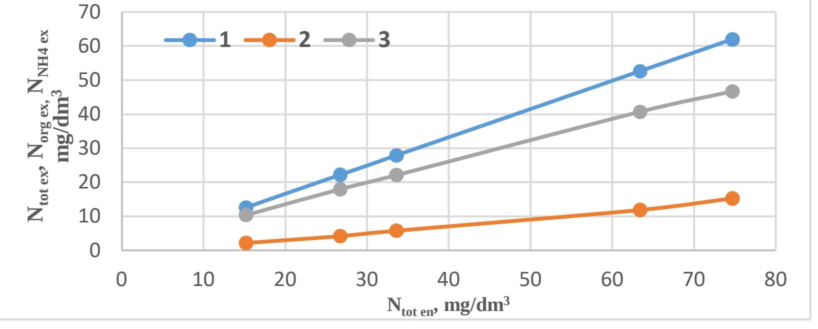

Figure 4. Graphs of dependence N_{tot}, N_{org}, N_{NH4} in an anaerobic bioreactor of the II degree: 1 - $N_{tot\ ex}$ concentration at the outlet from the concentration at the inlet $N_{tot\ en}$, 2- $N_{org\ ex}$ concentration at the outlet from the concentration at the inlet $N_{tot\ en}$, 3- $N_{NH4\ ex}$ concentration at the outlet from the concentration at the inlet $N_{tot\ ex}$

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The results of research in anoxic bioreactors are shown in Fig. 5 and 6. The effect of decomposition of organic nitrogen in the anoxic bioreactor of the 1st degree is 52-60%, in the anoxic bioreactor of the 2nd degree - 51-70%. In general, the amount of organic nitrogen decreases by 77-82% in two anoxic bioreactors. In anoxic conditions, with the participation of heterotrophic microorganisms, the decomposition of organic nitrogen continues with the formation of ammonium, which is partially oxidized to nitrites and nitrates by nitrifying microorganisms in the presence of a limited amount of oxygen (oxygen concentration 0.1-0.2 mg/dm^3). Ammonium in anaerobic conditions in the thickness of the biofilm is oxidized to gaseous nitrogen by anammox bacteria, which use the nitrogen of nitrites formed as a result of nitrification. The decrease in the level of total nitrogen to 32% in each stage of anoxic treatment and to 52% in both stages is associated with the release of N_2 gases (in the anammox process), NH_3 and the consumption of nitrogen for the growth of the biomass of microorganisms.

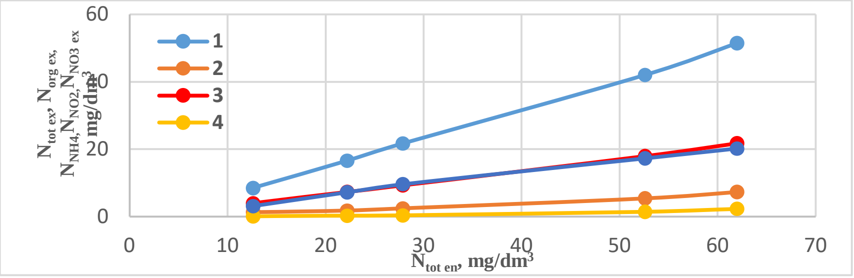

Figure 5. Graphs of dependence N_{tot}, N_{org}, N_{NH4}, N_{NO2}, N_{NO3} in an anoxic bioreactor of the I degree:

1 - $N_{tot\ ex}$ concentration at the outlet from the concentration at the inlet $N_{tot\ en}$, 2- $N_{org\ ex}$ concentration at the outlet from the concentration at the inlet $N_{tot\ en}$, 3- $N_{NH4\ ex}$ concentration at the outlet from the concentration at the inlet $N_{tot\ ex}$, 4- $N_{NO2\ ex}$ concentration at the outlet from the concentration at the inlet $N_{tot\ ex}$, 5- $N_{NO3\ ex}$ concentration at the outlet from the concentration at the inlet $N_{tot\ ex}$

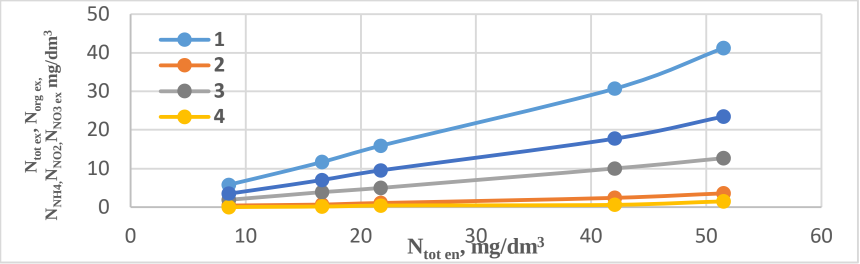

Figure 6. Graphs of dependence N_{tot}, N_{org}, N_{NH4}, N_{NO2}, N_{NO3} in an anoxic bioreactor of the II degree:

1 - $N_{tot\ ex}$ concentration at the outlet from the concentration at the inlet $N_{tot\ en}$, 2- $N_{org\ ex}$ concentration at the outlet from the concentration at the inlet $N_{tot\ en}$, 3- $N_{NH4\ ex}$ concentration at the outlet from the concentration at the inlet $N_{tot\ ex}$, 4- $N_{NO2\ ex}$ concentration at the outlet from the concentration at the inlet $N_{tot\ ex}$, 5- $N_{NO3\ ex}$ concentration at the outlet from the concentration at the inlet $N_{tot\ ex}$

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In fig. 7 shows the results of research in an aerobic bioreactor - the last stage of anaerobic-aerobic treatment. The efficiency of ammonia oxidation reaches high values - 86-95%. The effect of decomposition of organic nitrogen reaches 57.5%. In aerobic conditions, with the participation of heterotrophic microorganisms, the residual organic nitrogen contained in the wastewater at the exit from the anoxic bioreactor of the II degree is decomposed, with the formation of ammonium compounds. These compounds are oxidized to nitrites and nitrates by nitrifying microorganisms in the presence of oxygen (oxygen concentration in the bioreactor is 1.5-2 mg/dm^3). The decrease in the content of total nitrogen to 19% is associated with the release of gaseous N_2 in the denitrification process, which occurs in the thickness of the biomass of overgrowths on the supports, and the consumption of nitrogen for the growth of the biomass of microorganisms.

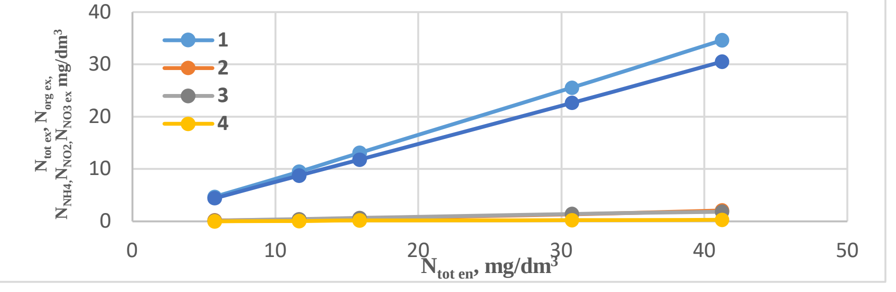

Figure 7. Graphs of dependence N_{tot}, N_{org}, N_{NH4}, N_{NO2}, N_{NO3} in an aerobic bioreactor: 1 - $N_{tot\ ex}$ concentration at the outlet from the concentration at the inlet $N_{tot\ en}$, 2- $N_{org\ ex}$ concentration at the outlet from the concentration at the inlet $N_{tot\ en}$, 3- $N_{NH4\ ex}$ concentration at the outlet from the concentration at the inlet $N_{tot\ ex}$, 4- $N_{NO2\ ex}$ concentration at the outlet from the concentration at the inlet $N_{tot\ ex}$, 5- $N_{NO3\ ex}$ concentration at the outlet from the concentration at the inlet $N_{tot\ ex}$

CONCLUSIONS

As a result of wastewater treatment at the exit from the aerobic bioreactor, the purified water contains ammonium nitrogen in a concentration of up to 0.5-1.8 mg/dm^3, nitrites - up to 0.03-0.25, nitrates - up to 5-31 mg/dm^3. This indicates the high efficiency of wastewater treatment from nitrogen compounds in bioreactors with immobilized microorganisms.

The originality of the technology is a significant decrease in the concentration of nitrogen compounds in the wastewater of a tannery when using biomass of nitrogen compound-destroying microorganisms immobilized on a fibrous carrier in successively created anaerobic, anoxic and aerobic conditions of the purification process.

Sequential treatment of tannery wastewater in anaerobic, anoxic, aerobic conditions with microorganisms immobilized on an artificial fibrous carrier is proposed. The high value of the specific biofouling of the carrier ensures the growth of biomass in the reaction zone of the bioreactor by 15-20 times compared to the active sludge of aeration tanks and allows to increase the efficiency of biological cleaning. The use of technology has shown the possibility of obtaining a high degree of removal of nitrogen compounds. Thus, for organic nitrogen, the overall cleaning effect reached 98-99%, for ammonium nitrogen - 86-95%. Thanks to this, low concentrations of ammonium nitrogen, nitrites

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and nitrates in purified water were obtained. The wastewater treatment method does not require chemical materials, is characterized by lower electricity consumption compared to the aerobic method due to the use of anaerobic and anoxic processes, and is environmentally friendly.

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