REMOVAL OF NITROGEN FROM MUNICIPAL WASTEWATER - THE EFFECT OF THE ADDITION OF CARBON SOURCES ON BIOLOGICAL DENITRIFICATION

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ABSTRACT

In this work was used activated sludge from the WWTP (wastewater treatment plant), in which with technique accumulation nitrificants and denitrificants, were prepared mixed bacterial cultures which showed the ability nitrification of ammonia- nitrogen to nitrate, as well as the ability of denitrification of nitrate nitrogen to gaseous nitrogen in municipal wastewater. As carbon source in the process of biological denitrification was used sodium acetate, in the ratio C/N=1 and C/N=2. Activity of mixed microbial cultures for removal components with nitrogen was determined by measuring the concentration of organic matter, expressed as COD, ammonia-nitrogen, nitrite, nitrate, pH, concentration dissolved oxygen, and the concentration of microbial biomass.

Keywords: municipal water, activated sludge, nitrogen removal

INTRODUCTION

The most widely used procedure for the treatment of municipal wastewater is an aerobic process with activated sludge. The activated sludge system with balance between different types of bacteria is essential to ensure effective removal of pollutants, good sedimentation of sludge and low levels of suspended particulate matter (Mesquita et al. 2009). Biological nitrogen removal from wastewater is achieved by applying the process of aerobic ammonia oxidation, or autotrophic aerobic nitrification and anoxic (facultative-anaerobic) denitrification. Ammonia oxidizing bacteria (AOB), such as *Nitrosomonas*, *Nitrosospira* and *Nitrosococcus*, converted ammonia to nitrite.

Nitrate oxidizing bacteria (NOB), such as *Nitrobacter*, *Nitrosospira, Nitrococcus* and *Nitrospina,* further converted nitrite to nitrate (Henze et al. 2002). During denitrification process nitrates are exceeding into the nitrogen gas. Nitrogen gas is released into the air, and in this way removed from the wastewater. These two processes depend on several factors, such as temperature, pH, dissolved oxygen, alkalinity, toxicity, etc. (Metcalf & Eddy, 2003; Jeyanayaga, 2005; Gerardi, 2002).

The main objective of this study was to define the working conditions of removal nitrogen compounds process of nitrification and denitrification in municipal wastewater, with the addition of heterotrophic carbon source, and to determine the conditions for quality water treatment in accordance with current regulations.

MATERIAL AND METHODS

In the research was used activated sludge from the WWTP (wastewater treatment plant). In the activated sludge is, with a technique accumulation nitrificants and denitrificants, prepared mixed bacterial cultures, which showed the ability of nitrification ammonia nitrogen to nitrate, and the ability of denitrification of nitrate nitrogen to nitrogen gas. The enrichment of mixed microbial culture was performed in Erlenmeyer flasks (500 mL, with working volume of 100 mL) on rotary shaker and room temperature, with municipal wastewater as a source of ammonium nitrogen (15-147 mg NH4+-N L^{-1}). After of cultivation, the biomass as inoculum was prepared and used in all experiments.

Activity of the microbial culture for the removal of nitrogen compounds was determined by measuring the concentration of ammonia nitrogen, nitrite, nitrate, pH, dissolved oxygen concentration and the concentration of the microbial biomass. Nitrogen removal in oxy/anoxia conditions, as well as all the experiments that preceded: autotrophic and heterotrophic nitrification with adding an external carbon source for nitrification, were conducted in a laboratory reactor working volume of 2 liters. Denitrification is carried out in conditions without aeration, with stirring the reactor contents with the help of the mixer placed in the reactor. The reactor is equipped with gauges of pH, dissolved oxygen and temperature.

All analytical data were determined by the methods prescribed by APHA (APHA, 1998): the concentration of organic substances, expressed as COD-value, BOD, NH_4-N, NO_3-N, NO_2-N, pH, temperature, dissolved oxygen concentration, dry matter, suspended solids and biomass concentration.

RESULTS

Experiments were carried out by gradually increasing the concentration of NH_4-N, 15 mg/L to 147 mg/L, which is the same concentration of ammonia in municipal wastewater. In experiments was monitored microbial activity with the addition of sodium acetate as a carbon source in an external ratios C:N=1:1, C:N=2:1. Once the technique of enrichment and adaptation prepared microbial cultures which showed the ability of biodegradation, in experiments is added municipal wastewater and is accompanied by its biodegradation. Below are shown the most important results.

Table 1. Chemical and physical indicators of quality of municipal wastewater

Parameter	**Value**
Color	gray-brown
Smell	typical
Temperature (°C)	14,7
pH	8
Conductivity (µS)	816
Oxygen saturation (%)	7,2
Dissolved oxygen (mg/L)	3,4
Sediment matter (ml of sediment)	5
Evaporated residue (mg/L)	754,48
Annealed rest (mg/L)	231
Suspended solids (mg/L)	1014
Nitrites (mg/L)	0,41
Nitrates (mg/L)	1,1
Ammonia (mg/L)	147
COD (mgO_2/L)	284
BOD5 (mgO_2/L)	245

Sludge from the treatment of wastewater NaAc was added as an external carbon source in the ratio of C:N=2:1, and the concentration of NH_4-N addition to the initial 50 mg/L. The total volume of the reactor is 2L.

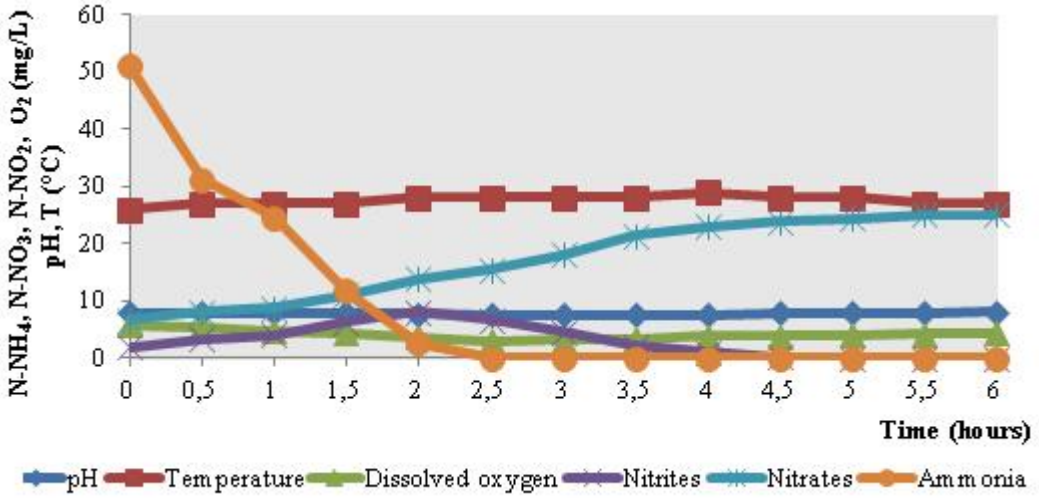

Figure 1. NH_4-N, NO_3-N, NO_2-N and dissolved oxygen concentration, pH and temperature determined during the process of nitrification

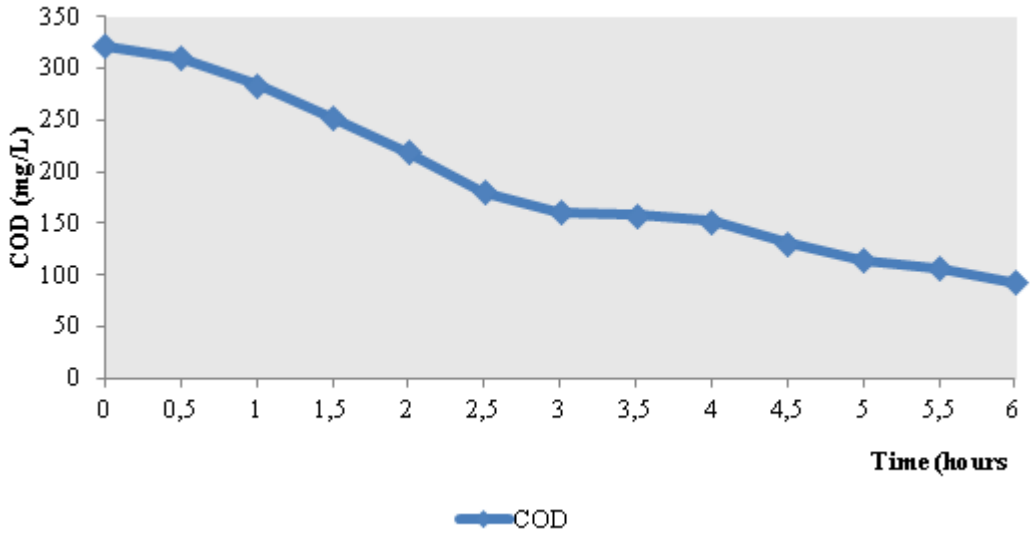

Figure 2. The concentration of organic substances, expressed as COD

In the enriched microbial culture was added a municipal wastewater in an amount so that the concentration of NH_4-N is set to the initial 70 mg/L. As an external carbon source was added sodium acetate at a ratio of C:N=1:1. The experiment was carried out with alternating nitrification and denitrification. Nitrification is carried out in the oxy and denitrification in anoxia conditions, with stirring. Oxy/anoxia conditions during the process of alternating nitrification/denitrification maintained by the dynamics: 0.5 hours of anoxia conditions, then 1 hour oxy conditions, then again 0.5 hours of anoxia conditions and again oxy conditions. The total volume of the reactor is 2L.

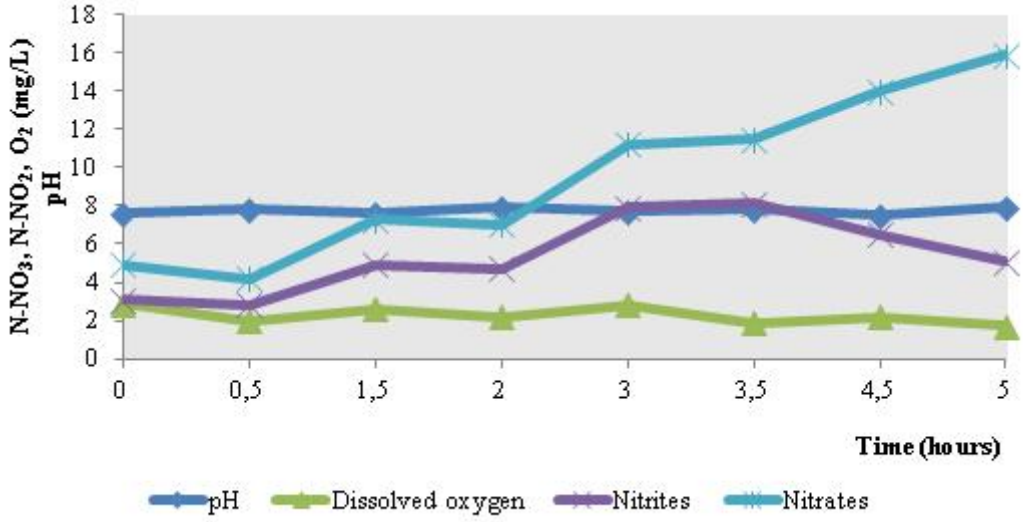

Figure 3. NO_3-N, NO_2-N and dissolved oxygen concentration and pH value determined during the biodegradation process of wastewater

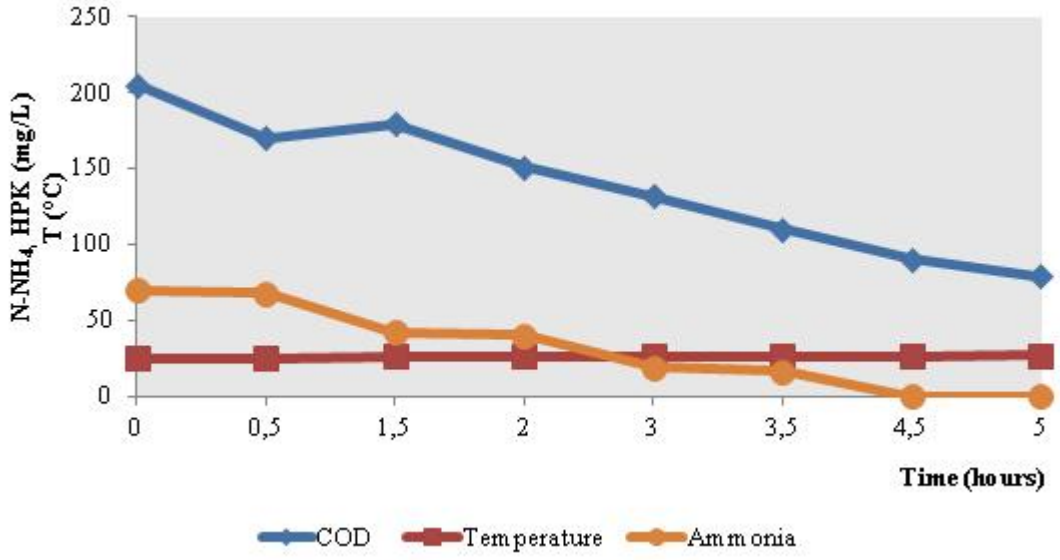

Figure 4. The concentration of organic substances, expressed as COD and NH_4-N during the biodegradation of wastewater

After the technique of adaptation and enrichment, it was prepared microbial culture capable of biological degradation, and in the sludge is added municipal wastewater and the NH_4-N concentration of 147 mg/L. The total volume of the reactor is 2L.

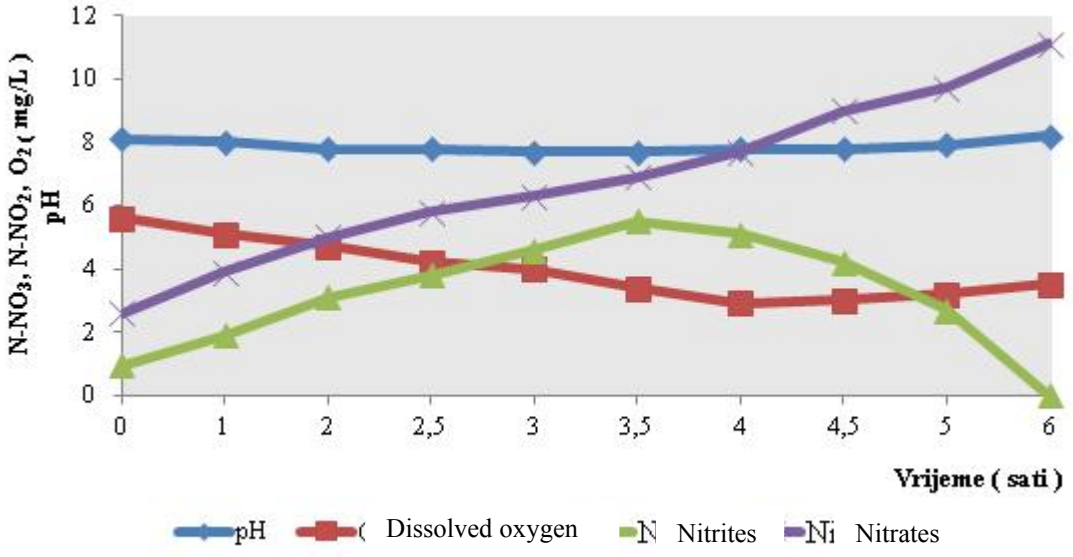

Figure 5. NO_3-N, NO_2-N, dissolved oxygen concentration and pH during the biodegradation process of wastewater

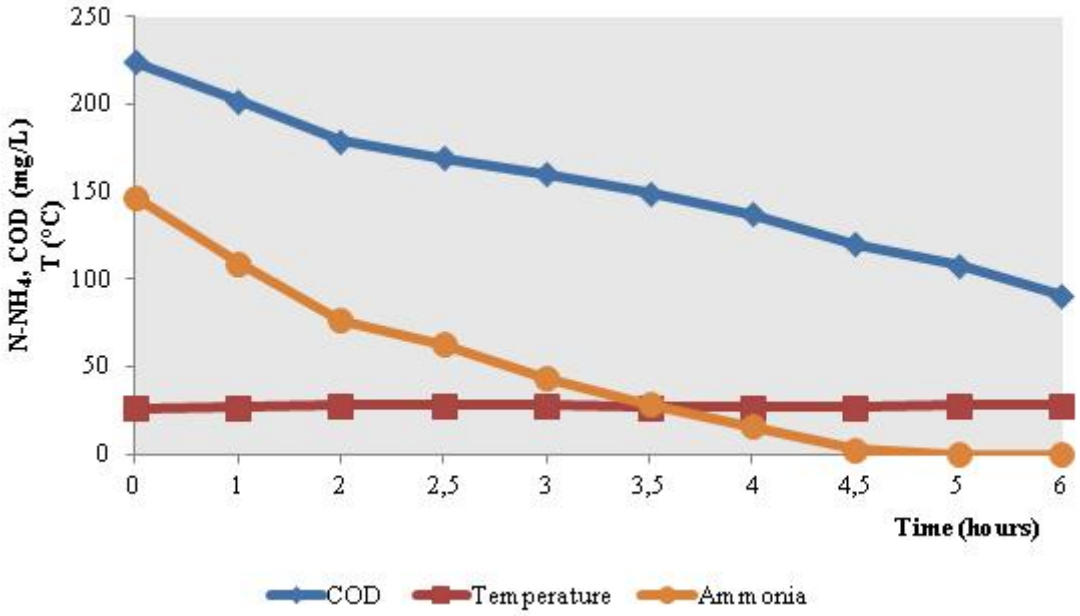

Figure 6. The concentration of organic substances, expressed as COD, NH_4-N, and the temperature

All previous nitrification processes were carried out under aerobic conditions. After nitrite nitrogen completely oxidized, after 6 hours, into nitrate nitrogen, investigate the ability of microbial cultures for the denitrification. Denitrification is carried out under anoxic conditions, only by stirring. As a carbon source was used municipal wastewater. Parameters were monitored every 3 hours, and 24 hours. The volume of the reactor is 2L.

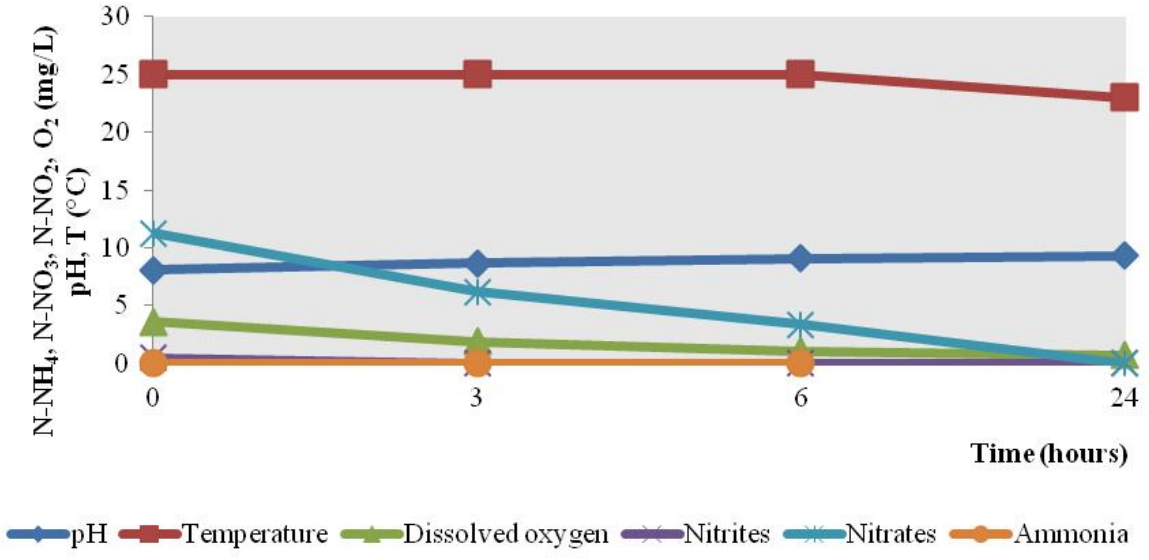

Figure 7. NH_4-N, NO_3-N, NO_2-N and the concentration of dissolved oxygen, pH and temperature during the process of denitrification

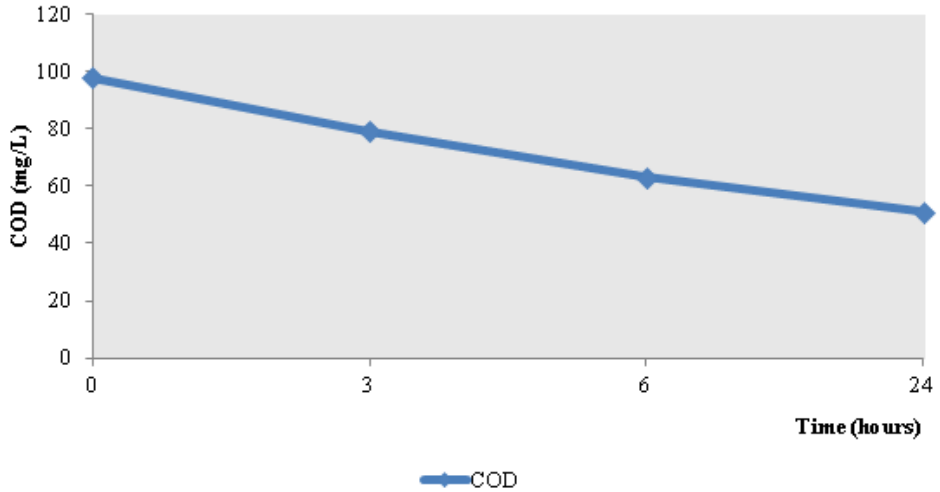

Figure 8. The concentration of organic substances, expressed as COD

DISCUSSION

In the experiment in the heterotrophic nitrification, where the organic compound as a source of added sodium acetate in a 2:1 ratio, and the initial concentration of NH4-N 50 mg / l, nitrification is done for five hours (Figure 1). Oxidation of ammonia (ammonia converted into NO3 -N and NO 2-N) is followed by decomposition of organic matter (COD) in the beginning of the process, as well as the accumulation of nitrite and nitrate (see Figures 1 and 2). Extended aeration for a further three hours, all the NO_2-N is converted to NO_3-N. From the first hour until the end of the process, NO_3-N has accumulated (Figure 1). In the experiment, heterotrophic nitrification rate of oxidation of ammonia was 19.4 mg NH_4-N removed/L,h. The highest concentration of nitrite of 8 mg/L was determined after two hours of nitrification, when all the NH_4-N was converted to NO_3-N and NO_2-N (Figure 1) and the pH of the lowest point is reached, known as "ammonium valley" (7, 6). This "valley ammonia" pH profile can be used as an indicator of the end of nitrification - accumulation of nitrite. For a further three hours of aeration nitrite is oxidized to nitrate, and the pH is slowly started to rise (7.8 and 7.9), (Figure 2). It was observed a decrease of pH during nitrification due to reduced buffering capacity as well as reaching the lowest value of pH in point of nitrification and dissolved oxygen. These profiles of pH (decrease of pH during nitrification due to reduced buffering capacity as well as reaching the lowest pH in point of nitrification) and dissolved oxygen (oxidation of ammonia during the process of low dissolved oxygen concentrations and a progressive increase in dissolved oxygen concentration when ammonia is almost completely oxidized) during the removal process nitrogen described by other authors (Chang & Hao, 1996; Paul et al. 1998).

Experiment alternating nitrification/denitrification was carried out at an initial concentration of NH_4-N 70 mg/L NO_3-N 4.9 mg/L and COD 205 mg O_2/L, with the addition of NaAc in a ratio C:N=1:1 (Figure 3 and 4). Oxy/anoxia conditions during the process of alternating nitrification/denitrification maintained by the dynamics: 0.5 hours of anoxia conditions, one hour of oxy conditions, 0.5 hours of anoxia conditions, then again oxy conditions. In the experiment was added sodium acetate at a ratio of C:N= 1:1 as the source of the carbon for denitrification. Oxy conditions are achieved airing content in the reactor (air intake) and denitrification is carried out in conditions without ventilation (auto aeration) but stirring the contents of the reactor (by using the mixer). In experiments is added municipal wastewater. During the first 0.5 hours of anoxic conditions increases the pH and reduces the concentration of organic substances, expressed as COD value (see Figures 3 and 4). During denitrification

reduces the concentration of NO_3-N and slightly decreases the concentration of NH_4-N (see Figures 3 and 4). The concentration of dissolved oxygen in the denitrification ranged was from 1.9 ± 0.2 mg/L. After completing the first stage of denitrification (0.5 hours anoxia conditions) the aeration is included and under the oxy conditions nitrification is carried out for one hour. In doing so, it reduces the pH value with the accumulation of NO_3-N and NO_2-N. Then follows the second denitrification, which caused a significant reduction in COD values. And this follows the denitrification reduction of NO_3-N and a slight decrease in residual NH_4-N (see Figures 3 and 4). Denitrification again accompanied by an increase in pH (Figure 3). After finishing second denitrification, aeration was included and conducted the experiment nitrification. Over the next two and half hours, a process of nitrification was through accumulation of NO3-N and NO2-N in the first three and a half hours the process, followed by further aeration oxidation of NO2-N to NO3-N. In these experiments of nitrification it was observed a decrease in pH value, which achieved the lowest value in the point of nitritation, after which the pH value increases slightly by the end of the process. COD value does not change significantly during the process of nitrification. In the experiment of alternating nitrification/denitrification, dissolved oxygen concentration is reached 2 mg O2/L during the first half hour of anoxia conditions; 2.6 mg O2/L during the first hour of the oxy conditions and 2.2 mg O2/L in the next half hour anoxia conditions. During the last phase of nitrification in this experiment, there was a slight increase in the concentration of dissolved oxygen (Figure 3). Rate of oxidation of ammonia in the experiment alternating nitrification/denitrification is 11.95 NH4-N/L,h. Rate of accumulation of nitrate in the experiment alternating nitrification/denitrification was 2.2 mg NO3-N/L,h during all phases of the observed processes. The experiment of removing substances with nitrogen from municipal wastewater was carried out with a previously prepared mixed microbial culture and municipal wastewater. NH_4-N concentration is reached 147 mg/L (see Figures 5 and 6). Complete nitrification was achieve d for six hours. In this work the oxidation of the ammonia is achieved for five hours, and to the accumulation of nitrate and nitrite. Extended aeration for one hour nitrite is completely converted into nitrate. The rate of removal of ammonia was 28.82 mg NH4-N/L, h. The highest concentration of nitrite was 5.5 mg/L. In the fifth hour all the NH4-N is converted to NO3-N and NO2-N. The concentration of dissolved oxygen in the course of these experiments (Figure 5) shows a pronounced oxygen consumption during the oxidation of NH4-N with accumulation and NO3-N and NO2-N. Shortly after graduating nitritation (accumulation of nitrite) concentration of dissolved oxygen begins to grow until the end of the experiment. After complete nitrification concentration of NO3-N amounted 11.1 mg/L The experiment was conducted under conditions of temperature 26±2. Concentration of organic ingredients is expressed as COD value, and the speed of decomposition of organic substances, expressed as COD value was 22.16 mg/L,h. Concentration of sludge dry matter amounted to 3.5 g/L.

All previous nitrification processes were carried out under aerobic conditions. After nitrite nitrogen completely oxidized, or after six hours passed into nitrate nitrogen, experiment was set out to investigate the ability of microbial cultures for the implementation of denitrification. Denitrification was carried out under anaerobic conditions, only stirring. Parameters were monitored every three hours, and 24 hours. Dry matter was 3 g/L. The concentration of NH4-N during denitrification process has not changed, and amounted to 0 mg/L. The concentration of nitrite and nitrate is reduced during the process of denitrification. Nitrates are from the initial 11.3 mg/L after 24 hours of completely oxidized to nitrogen gas. Dissolved oxygen is consumed in the process of denitrification, and after 24 hours the dissolved oxygen concentration was 0.7 mg/L. The process of denitrification, nitrate reduction, follow the increase in pH. The pH of the initial value of 8.1 after 24 hours the process was 9.3. Speed degradation of organic substances, expressed as COD value was 1.95 mg/L,h (see Figures 7 and 8).

CONCLUSION

Based on the obtained results and conducting discussion may be adopted the following conclusions:

- Biological processes with activated sludge achieved very efficiently removal of nitrogen from wastewater.
- Wastewater investigated in this work is a municipal wastewater in which the ingredients are organic biodegradable, as evidenced by the results of research.
- The activated sludge from the WWTP (wastewater treatment plant), which is used in research, with technique of accumulation nitrificants and denitrificants, was prepared as a mixed microbial culture that has the ability to process simultaneous nitrification and denitrification of nitrogen compounds in municipal wastewater.
- Removal of nitrogen from wastewater is achieved by the process of denitrification, where the process must ensure the existence of anoxic conditions. Many studies have confirmed that controled nitrogen in the used water can be achieved in the most efficient processes with a combined nitrification and denitrification (Stefancic, 2003, Dong et al. 2006).
- In the experiment of heterotrophic nitrification, with addition of sodium acetate as an external carbon source at a ratio of 2:1 and a pH of 7.8, the rate of oxidation of ammonia was 16.4 mg NH_4-N removed/L,h.
- Rate of oxidation ammonia in the experiment alternating nitrification/denitrification amounted to 11.95 mg NH_4-N/L,h.
- Mixed culture has shown the ability for a higher degree of nitrification at higher pH values from 7.7 to 8.8 and a temperature of 27-30°C in municipal wastewater in which is presented ammonia nitrogen source.

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