Research of the Dimethylamine Influence on Removal of Organic Pollution and Nitrogen in Wastewater

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ABSTRACT
The research was carried out because of a survey of wastewater treatment plant of a chemical factory, which is planned to receive the dimethylamine-containing wastewater flow. It was essential to investigate the influence of dimethylamine and removal on organic pollutants and nitrogen compounds as well as to determine the limiting concentration of dimethylamine. There were variable concentrations of dimethylamine (20–500 mg/L) under investigation in several simultaneous laboratory benches. The results showed that the dimethylamine concentration lower than 40 mg/L showed almost no impact on wastewater treatment; meanwhile, the growth of concentration up to 300 mg/L (and above) dropped the treatment efficiency by times.

Keywords: wastewater treatment; dimethylamine; DMA; sequence batch reactor; SBR; BOD; nitrogen

INTRODUCTION
The research was carried out after the technological inspection of wastewater treatment plant (WWTP) of a chemical factory. A mixture of domestic wastewater and aniline-containing wastewater from the production of aniline enters the accumulation tank of the treatment facilities, and then is pumped to sequencing batch reactors (SBRs) for biological treatment. Three SBRs installed are similar to each other, with a cylindrical shape, the diameter of 19 m, the height of 4 m, and the working depth of 3.5 m; hydraulic retention time (HRT) in SBRs is 16 to 18 hours. This value of HRT is quite high due to the lower flow comparing to the designed value. Normal HRT should around 8 hours.

The SBR has a typical sequence of operation, which is based on a cyclic change of wastewater treatment processes occurring in a single reactor. Each reactor is sequentially filled with 200–220 m³ of wastewater. At the same time, active sludge and a residual layer of purified (nitrate) water are constantly present in the reactor. After filling the reactor, the aeration process is performed with air, then the aeration is turned off for the sedimentation process. The treated effluents are subsequently drained and the activated sludge is regenerated as necessary.

After biological treatment, water goes to the reservoir of treated wastewater, where it is disinfected with a solution of sodium hypochlorite. In order to intensify the mixing of biologically purified water with sodium hypochlorite, air is supplied from compressors through the hole pipes installed at the bottom of the tank. From the reservoir of biologically treated wastewater, the decontaminated wastewater flows by gravity to the reservoir of treated and decontaminated wastewater, followed by pumping to the storage pond.

The storage pond is intended for receiving and accumulating conditionally clean, stormwater and biologically treated wastewater of the enterprise. During the accumulation process in the storage pond, the influent wastewater is averaged and clarified (Table 1). The clarified waste water is used for irrigation of green spaces of the enterprise. In order to maintain the water level in the storage pond, excess wastewater is pumped to a third-party treatment facility.
As far as SBR are concerned, one of them was used for a full scale experiment to estimate the effect of DMA on the quality of biological treatment. The technological parameters of this test reactor are shown in Table 2.

An additional stream containing dimethylamine (DMA) with a mass concentration of 250 mg/L at the inlet of the treatment facilities is planned to be added to the existing influent wastewater. The amount of DMA-Containing wastewater is specified after the launch of the new production line of the enterprise.

During the survey of treatment facilities, the results of quantitative chemical analyses (QCA) of the wastewater samples taken at the treatment facilities for 3 months were evaluated (June-September 2020). In addition to the QCA results, the technological parameters of the treatment system were also analyzed – the amount of dissolved oxygen (DO), the amount of activated sludge (mixed liquor suspended solids (MLSS)), and the HRT.

The average concentration of DO in the reactor was about 5 mg/L, the average MLSS value was 4.4 g/L, and the mean HRT was 17 hours. At the same time, the results of QCA showed that overall, it was not possible to achieve the so-called simultaneous nitrification and denitrification (SND).

An important indicator of ensuring deep removal of nitrogen from wastewater is the ratio of the concentration of organic pollutants (in Russia, it is most common to express it with BOD) and nitrogen compounds in the wastewater coming to treatment. To date, the influence of the BOD/N ratio on the efficiency of biological nitrogen removal has been studied and the optimal range of values equal to 8–11 gBOD/gN has been determined [Jimenez et al. 2013, Li et al. 2014, Choi and Valentine 2002], at which it is possible to ensure denitrification with sufficient efficiency (total nitrogen removal is at the level of 85–90%). At the same time, many researchers [Duan et al. 2010, Hatt et al. 2013, Mitch and Sedlak 2002, Pehlivanoglu-Mantas et al. 2006, Dakkoune et al. 2020] note that in most cases this coefficient is in the range of 3.5–4.0 gBOD/gN, which hinders the efficient implementation of the denitrification process (the efficiency of removing total nitrogen at the level of 60-65%) due to the lack of energy (carbon feed) for the transition of nitrogen to another form. In addition, low BOD/N ratio leads to an imbalance of nitrification and denitrification [Weiqing Huang et al. 2017, Rikmann et al. 2018]. At the same time, higher BOD/N ratio (at the level of 10) was a condition for effective SND for studies of treatment of various wastewater compositions, including those containing DMA.
Another important parameter that provides an effective SND is the concentration of dissolved oxygen in water. It was noted that the efficiency of total nitrogen removal at a high level in most cases was achieved by maintaining dissolved oxygen at the level of 0.5–1.5 mg/L with the simultaneous use of chemically bound oxygen. At high concentrations, oxygen – as an inhibitor of denitrification – significantly inhibits the flow of this process.

The experience of SBR operation in terms of cleaning cycle time was also studied. In most cases, the mode with the cleaning cycle duration of 8 hours was considered optimal. Another option for the intensification of these structures may be the alternation of anoxic (mixing by agitators or submersible pumps in the presence of chemically bound oxygen) and aerobic mode of operation (aeration). The dose of activated sludge in most studies was maintained at the level of 3–4 g/L, which corresponds to the traditional scheme of wastewater treatment. The recommended sludge retention time (SRT) is in the range of 20–25 days. The following results of the wastewater treatment plant inspection may be considered as prerequisites for bench-scale research:

1) The operation of biological treatment facilities (SBRs) is now in the mode of complete oxidation with sufficient removal of organic pollutants, partial nitrification and denitrification processes. The standard treatment efficiency was not reached.

2) It was noted that the processes of nitrogen removal (ammonia nitrogen, nitrite and nitrate) remained unstable. It was found that the oxidation of ammonium nitrogen does not always reduce the concentration of NH₄ to the values required by regulatory documents. At the same time, in most cases when complete oxidation of ammonium nitrogen was observed, the concentration of nitrogen nitrates in the treated water significantly exceeded the standard values, which indicates that the processes of denitrification (reduction of nitrogen nitrates to nitrogen gas) were incomplete. A possible reason is the insufficient amount of carbon nutrition in the system, that is, the ratio of organic pollutants (BOD and COD) and nitrogen compounds in the influent water differs from the optimal one (BOD/N = 8–11) for complete simultaneous nitrification and denitrification. A lower ratio causes an imbalance in the nitrification and denitrification processes.

3) Additionally, the reason for the imbalance of nitrification and denitrification processes is the relatively high content of dissolved oxygen in the reactor. The studies on simultaneous nitrification and denitrification have shown its effectiveness at a concentration of dissolved oxygen at the level of 0.5–1.5 mg/L.

4) The SBR operation when DMA was added (concentration of 36–45 mg/L) does not have strong impact on the treatment quality.

5) The ongoing biological processes in biological treatment facilities are unstable in time, poorly regulated by technological parameters and maintained at a certain fairly constant level due to the high-quality operation of treatment facilities.

MATERIALS AND METHODS

Dimethylamine ((CH₃)₂NH) is a secondary amine, an ammonia derivative in which two hydrogen atoms are replaced by methyl radicals. It constitutes a colorless gas with a sharp specific “fishy” smell, easily liquefied when cooled into a colorless liquid. It is combustible; its melting point is 92.2 °C, whereas boiling point is 6.9 °C. Specific weight is 670 kg/m³.

Dimethylamine is soluble in water and organic solvents, forms crystalline salts with acids, is acylated, alkylated, nitrosated, etc. The substance belongs to the organic compounds which are hard to oxidize. Dimethylamine is formed when protein substances rot; in industry, it is obtained (with an admixture of trimethylamine) from methyl alcohol and ammonia, as well as from formaldehyde and ammonium chloride. Dimethylamine is used in organic synthesis (Mannich reaction), for the production of medicinal substances (dicaine, aminazine, etc.), rocket fuel (dimethylhydrazine), vulcanization accelerators, etc.

There were three goals established before the research:

- Assessment of the influence of the DMA value on organic pollution removal
- Assessment of the influence of the DMA value on nitrogen removal
- Determination of borderline concentration of DMA for deterioration of treatment efficiency

The research was performed at the laboratory of wastewater treatment in Moscow state university of civil engineering. The bench of
sequencing batch reactor (SBR) was made of polyethylene with total volume of 20 L (Fig. 1). The bench was equipped with mixer and aeration device; hydraulic retention time was variable throughout the research.

There was a synthetic wastewater on the peptone basis used. The composition of peptone was as follows (per 1 L): enzymatic peptone – 110.0 g; sodium chloride 68.8 g; potassium nitric acid – 1.2 g; soda ash – (16 ± 2) g. There were also calcium acetic acid (Ca(CH₃COO)₂) and potassium phosphoric acid, double-substituted (K₂HPO₄) added to achieve the values similar to real wastewater. Active sludge supplied from real wastewater treatment plant was added to synthetic wastewater in order to create mixed liquor that is similar to real wastewater in biological reactors.

There were following parameters under control: biological oxygen demand (BOD), suspended solids (SS), ammonium (NH₄), nitrites (NO₂), and nitrates (NO₃), dissolved oxygen (DO). Active sludge was examined from the point of view of mixed liquor suspended solids (MLSS) and sludge index (SI). The samples of wastewater were investigated manually, in accordance to standard techniques.

RESULTS AND DISCUSSION

First stage of experiment

The research initially was not separated into stages; however, after the start, two stages were introduced to make the results more clear and obvious. The first stage research lasted for 30 days.

It was urgent to establish and maintain the conditions, which would be close to real values at the WWTP of chemical plant. Moreover, it was essential to obtain a wide scope of data for future analysis. To this end, there was not one but six bench-scale models under operation with variable DMA concentration: 20 mg/L (bench 1); 40 mg/L (bench 2); 60 mg/L (bench 3); 80 mg/L (bench 4) and 100 mg/L (bench 5). The bench 6 has zero DMA concentration to compare the overall influence of DMA. The HRT was approx. 8 hours, DO value was in a range from 1.5 to 2 mg/L, MLSS was 3-4 mg/L in all 6 benches.

Figure 2 shows mean values of BOD concentrations in our benches that highest efficiency of BOD removal (90%) was achieved under the condition of zero concentration of DMA (bench 6) that may witness the negative impact of DMA on treatment processes. However, benches 1 and 2 showed about 5% reduction of efficiency that may be estimated as inaccuracy within the analysis of samples. On benches 3 and 4, the achieved efficiencies were 79% and 74%, respectively. For bench 5 (with DMA concentration of 100 mg/L) an efficiency drop by one third (61%) may be seen. In overall, DMA concentration in wastewater less than 40 mg/L had almost no impact on treatment efficiency, and this value may be considered as limiting point for normal removal of organic pollutants.

Figures 4 and 5 show the removal of ammonium in bench models in absolute values and efficiency of treatment. Here, much lower influence of the DMA presence on treatment efficiency is seen. When the DMA concentration increased up to 100 mg/L, the removal efficiency dropped only...
by 10%, comparing to reference sample; nevertheless, it still reduced.

Taking into account the values obtained, the ammonium oxidation rates were calculated (Fig. 6), which lay in the range between 0.9 and 1.2 mgNH₄/gVSS*h. The bench-scale results were then compared to values obtained at full-scale wastewater treatment plant of chemical facility (Fig. 7). In total,
the results were analogous, which speaks in favor of similarity of the experimental and real values. Slightly higher values (closer to the maximum industrial values) and a smaller spread of values for laboratory conditions can be explained by fewer factors affecting the cleaning efficiency (and a greater ability to maintain stable conditions), but in general, the data can be called comparable. The ratio of the purified NH$_4$ and NO$_3$ concentrations in the purified water was also considered (Fig. 9).

As can be seen, as the content of ammonium nitrogen in treated water increases, the concentration of nitrogen nitrates decreases, which indicates that the processes of nitrification and denitrification are inhibited, or the nitrogen group in wastewater increases as organic matter (DMA) is broken down into inorganic components.

If we briefly analyze the results presented in Figures 5–9, we can conclude that the presence of dimethylamine in wastewater at a concentration of more than 40 mg/l has a negative impact on the wastewater treatment processes, which is manifested in a decrease in the efficiency of removing organic pollutants and nitrogen compounds.

**Second stage of the experiment**

After receiving these data, it was decided to expand the range of studies. For the next 20 working days, the plant operated in the same temporary mode – 8 hours of stay in the variable-action reactor, but the influent concentrations were increased so that it was possible to study the possibility of reducing the concentration of nitrogen compounds under heavy loads for organic compounds. BOD concentrations were increased to 350–450 mg/L (to keep BOD/N balance between 8 and 11), and the concentrations of ammonium nitrogen in the influent water were kept at the same level, which allowed monitoring the nitrification process.
During this stage, the research was conducted in a similar way as before. There were also 6 installations of variable-action reactor models in operation. The changes affected the concentrations of DMA in wastewater received for treatment. It was decided to investigate the cleaning efficiency at the following dimethylamine concentrations: unit 1 – 40 mg/l, unit 2 – 80 mg/l, unit 3 – 100

Figure 7. Specific oxidation rates (ammonia) at real WWTP

Figure 8. Mean values of specific oxidation rates (ammonia) at bench-scale and full-scale experiment

Figure 9. NH$_4$/NO$_3$ ratio in the effluent
mg/l, unit 4 – 300 mg/l and unit 5 – 500 mg/l. The sixth installation, as before, was a control one.

The specified concentration range was selected for the following reasons. The initial concentration of 40 mg/dm³ was chosen because it had previously produced the results comparable to the control sample, that is, in the absence of DMA. The concentrations of 80 and 100 mg/dm³ were selected to track the dynamics of current results and compare them with the existing ones. The DMA concentrations of 300 and 500 mg/L were selected to study the system operation under the conditions of multiple discharge of wastewater containing a large amount of DMA.

During the tests, plentiful foaming, swelling and dying of biomass were observed visually on the water surface of installations No. 4 (Fig. 10) and No. 5 (Fig. 11). This was not noticed on other installations. The amount of foam decreased as it was processed, but the presence of foam was maintained on the surface.

After the research, the key results were analyzed. As before, the dynamics of reducing the concentration of pollutants was studied, and the cleaning efficiency was compared at different concentrations of DMA in the source water. Fig. 12 and 13 show the graphs of reducing the concentration of pollutants for BOD and ammonium nitrogen in laboratory benches.

Figure 14 shows an analysis of the efficiency of removing contaminants for BOD and ammonium nitrogen. It is noted that, as before, the best efficiency is observed in the control unit, that is, the presence of DMA in the water generally slows down the cleaning processes. For a DMA concentration of 40 mg/l in the source water, the efficiency of BOD treatment is approximately 10% lower than in the control unit, but the efficiency of reducing the concentration of ammonium nitrogen is comparable to the control one. Thus, we can conclude that the results of the first part of the study were confirmed – the concentration

Figure 10. Foam in the bench 4

Figure 11. Foam in the bench 5
of DMA 40 mg/dm³ has little effect on the cleaning efficiency, since in general, the results can be called comparable. The following features can be noted for the operation of installations #2 and #3. If the removal efficiency of organic pollutants by BOD remained at the level of plant No. 1 (40 mg/L), the removal efficiency of ammonium nitrogen decreased by 30% at a concentration...
of DMA in the feed water of 100 mg/L. It can be noted that at a DMA concentration of 40 mg/L, the quality of cleaning is generally stable, and as it increases, the cleaning processes are destabilized and there is a significant decrease in efficiency. When considering the efficiency of benches No. 4 and 5, there is a sharp decrease in the efficiency of pollution removal – the effect of BOD cleaning does not exceed 20%, the effect of removing ammonium nitrogen does not exceed 10%, that is, the cleaning processes are almost completely stopped.

Observation of the benches operation showed that the activated sludge of the first four plants is standard, after the cleaning process, it restores its properties and continues to work. The active silt of the fifth and sixth installations is almost destroyed; the biomass is small and swollen. Restoration of microflora in this case is not possible in the structure.

In addition, the specific oxidation rate for ammonium nitrogen was calculated again, which is shown in figure 15. This diagram can be divided into three parts. The specific oxidation rate for the installations containing no more than 80 mg/L is at the level of 0.75–0.9 mgNH₄/gVSS. This value is lower than during previous studies, which can be explained by a higher load on the system for BOD. At the same time, these values are closer to the average values obtained when processing the results of real treatment facilities, that is, the convergence of the results is quite clearly traced here, despite the different values of the concentrations of pollutants in untreated wastewater (Fig.16). Then, when the concentration of DMA in the source water is 100 mg/L, the specific oxidation rate is almost halved and is approximately 0.45 mg NH₄/gVSS. When the concentration of DMA in the source water is 300 and 500 mg/L, the specific oxidation rate...
rate drops to the values close to 0.1 mgNH₄/gVSS, that is, the oxidation of ammonium nitrogen compounds is almost completely stopped.

Figure 17 shows the ratio of nitrogen of ammonium and nitrates in effluent at different concentrations of DMA in the source water. As can be seen, the processes of nitrification and denitrification are also inhibited. When analyzing the results obtained, it can be concluded that the possible salvo discharges of concentrated wastewater (with a high content of DMA) can significantly disrupt the normal functioning of treatment processes.

Long-term exposure to high concentrations of DMA (300 and 500 mg/L) has not been studied in the research. It this viewpoint, it may be possible that in the case of long-term discharge of wastewater under constant high DMA content, the biological system will be able to adapt to the current conditions with a gradual increase in the quality of treatment. However, at the same time, considering the overall quality of the cleaning is observed unacceptably low.

Since the results were generally clear, but the cleaning efficiency was lower than the required standard values, it was decided to study the operation of the system with an extended residence time of 16 hours (Fig. 18). The presented graphs show that the results were generally similar, that is, a two-fold increase in processing time did not lead to a noticeable increase in efficiency, while the oxidation rate decreased (Fig. 19). However, there is a slight habituation of biomass to DMA, which is shown by experience with a concentration of 80 mg/L.

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**CONCLUSIONS**

After the research, the following issues may summarize the overall results:

1. Studies conducted in parallel mode on laboratory benches at different concentrations of dimethylamine (DMA) have shown that the presence of DMA in wastewater reduces the removal efficiency of organic pollutants, as well as nitrogen. However, when the concentration of DMA is up to 40 mg/L, the decrease in efficiency is about 5%, which can be regarded as an acceptable error.

2. These values are obtained at a BOD/N ratio in the range of 5–10, but when the ratio in the feed water reaches the value of BOD/N=10, the treatment efficiency decreases by about 20%, while an increase in HRT (from 8 to 16 hours) has a very slight practical effect on the increase of treatment efficiency.

3. If the DMA concentration in the feed wastewater increases from 100 to 300 mg/L, there is a sharp deterioration in efficiency, up to almost complete shutdown of the treatment processes.

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