Environmental monitoring of natural waters in the zone of impact of an enterprise producing explosives

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Abstract. Production of explosives, as part of chemical industry, has a significant anthropogenic impact on components of environment. The greatest negative impact due to water requirements of the industry enterprises have on hydrosphere. Generally pollutants of this group of enterprises are nitroesters – one of the most important components of products that determine energy properties of powders. In article considers the need for water quality monitoring of water bodies located in zone of influence of enterprises for contamination with nitroesters, in particular nitroglycerine (1,2,3-trinitrooxypropane). As a rule, such enterprises are located on the largest water bodies. Low solubility of the substance in water determines its risk to aquatic organisms and population. The Kama river was selected as the water object of the research in area of impact of the gunpowder production enterprise on territory of a large industrial and residential agglomeration of Perm. According to the results of environmental monitoring, which consisted in sewage and natural water, a significant excess of maximum permissible concentration of nitroglycerin in natural waters was detected, which is unacceptable for water bodies of the highest fishing category of water consumption. To reduce the anthropogenic impact on the water body, it is proposed to introduce a system for wastewater treatment from the source pollutant by ozonation of industrial wastewater with introduction of an alkaline reagent. The revealed high efficiency of the method of wastewater treatment to the content of nitroester at level of trace concentrations makes it possible to exclude the impact of the enterprise on the watercourse.

1 Introduction

The production of explosives contributes little to environmental pollution compared to other major industries, but wastewater discharges contain specific compounds that significantly affect aquatic ecosystems as well as humans. Water is used at all stages of the production cycle (technological needs, transportation of semi and finished products), as a result, sewage receives generally pollutants for this industry. These include ammonium ions, nitrates, nitrites, sulfates, chlorides, zinc and lead, and nitroglycerin (NG) [1].

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Detailed studies of the toxic effects of specific pollutants are reduced to the definition of substances that determine the energy properties of the final product, the main component of which for ammunition production enterprises are nitroesters, in particular nitroglycerin. However, contamination of natural waters by generally pollutants in the industry is not considered as widely as, for example, the impact on soils [1-4]. The substance has a significant toxic effect on organisms, including humans, which most affects the cardiovascular and nervous systems [5,6]. The human body can develop a tolerance to the substance, causing addiction [7]. As a result, there is a need for wastewater treatment from this contaminant of aquatic habitat.

Research in the faculty of monitoring the impact of enterprises in this industry is partly difficult due to the specifics of maintaining the secrecy of production necessary for their safety and the security of states. To assess the local impact of industry enterprises, it is necessary to conduct monitoring researches of the quality of natural environment components, especially water bodies where sewage is discharged. In addition, environmental monitoring allows us to prove the introduction or improvement of sewage treatment systems of factories to reduce impact on the natural environment and humans [8].

Currently, there are various methods of wastewater treatment from nitroesters, related to chemical, physical and biological methods [9-13]. The classic chemical method is hydrolysis of nitroesters, the introduction of various alkaline reagents [7]. Physical methods include adsorption processes, neutralization at high pressure and temperature, electrochemical methods, microwave destruction of NG [6,10,14-16], as well as a method for ozonating wastewater treated with a solution of caustic soda [17]. Biological methods for removing nitroesters using microbial strains in natural conditions, biofilters and bioreactors, as well as accumulation by aquatic vegetation are widely presented [4,18-22].

2 Material and methods

An industrial facility for the production of explosives for monitoring research is considered an enterprise located in the city of Perm that discharges effluent into the Kama river, which is an object of the highest category of fisheries significance.

To assess the state of the waters of the Kama river, provided that the discharge of wastewater is located within the administrative borders of Perm, the control traverse was installed at the point of discharge of effluent (p.3, Fig.1), the background traverse was installed at a distance of 500 m from the control traverse upstream of the Kama (p.2, Fig.1). In addition, samples were taken from the discharge waste water collector at the entrance to Oborino Bayou (p.1, Fig.1), which plays the role of an intermediate biological pond before the discharge of sewage into the river.

![Fig. 1. Map of the sampling.](image)

Sampling of sewage and natural water was carried out using a bathometer. For the analysis of samples for the metal cations content, samples were placed in a plastic opaque capacity, excluding oxygen access, and preserved with nitric acid to pH=2. Sampling to determine the content of anionic groups was performed in a plastic capacity, similarly without access to oxygen. All samples were transported to the laboratory chilled. Hydrogen ion exponent of the samples was determined on-site using a portable analyzer.
The determination of the studied components in the samples was carried out using the photometric method of analysis (sulfates, chlorides, nitrates, nitrites, ammonium nitrogen and total iron) – a spectrophotometer and the method of atomic absorption spectroscopy with electrothermal atomization (aluminum, lead, zinc, copper) – a atomic absorption spectrometer. The method of high-performance liquid chromatography was used to determine the content of nitroglycerin in wastewater and natural waters. [23]. Analysis of samples was conducted on the basis of Scientific and educational center for collective use of high-tech equipment «Center for collective use» of Saint-Petersburg mining University.

3 Results and Discussion

The results of analysis of samples of natural and waste waters in the area of release to the Kama river was summarized in table 1. Also were calculated contrast ratios as compared to maximum permission concentration (MPC) (for collecting water and controlling traverse) relative to background concentrations in the Kama (for control traverse, table 1).

| Indicator | Measurement result, mg/L | MPC, mg/L | Contrast ratio on MPC | Contrast ratio on background |
|-----------|--------------------------|-----------|-----------------------|-----------------------------|
|           | Sewage Background traverse | Control traverse | Sewage | Control traverse | Control traverse |
| Nitrites  | 1,73                     | 0,03      | 1,58                  | 0,08                        | 21,63                  | 19,75                  | 52,67                  |
| Nitrates  | 104,24                   | 3,17      | 137,36                | 40,0                        | 2,61                    | 3,43                    | 43,33                  |
| Ammonium  | 3,18                     | 0,06      | 2,06                  | 0,5                         | 6,36                    | 4,12                    | 34,33                  |
| Sulfates  | 207,4                    | 29,2      | 145,9                 | 100,0                       | 2,07                    | 1,46                    | 5,00                   |
| Iron      | 0,45                     | 0,44      | 0,50                  | 0,1                         | 4,50                    | 5,00                    | 1,14                   |
| Chlorides | 92,3                     | 13,6      | 78,1                  | 300,0                       | 0,31                    | 0,26                    | 5,74                   |
| Aluminum  | <0,005                   | 0,11      | 0,07                  | 0,04                        | 0,06                    | 1,75                    | 0,64                   |
| Zinc      | <0,005                   | <0,005    | <0,005                | 0,01                        | 0,25                    | 1,00                    | 1,00                   |
| Lead      | 0,008                    | 0,003     | 0,007                 | 0,006                       | 1,33                    | 1,17                    | 2,33                   |
| Copper    | 0,002                    | 0,003     | 0,003                 | 0,001                       | 2,50                    | 3,00                    | 1,00                   |
| NG        | 8,37                     | 0,006     | 8,19                  | 0,01                        | 837,00                  | 819,00                  | 1365,00                |
| pH        | 6,9                      | 7,7       | 7,6                   | -                           | -                       | -                       | -                      |

According to table 1, it is possible to draw conclusions about the excess of the MPC of a number of pollutants in effluent, as well as established control traverse. Besides, excess values for sewage components are also allocated relative to background values in the river.

The content of nitrites, ammonium, sulfates, lead, and NG relative to the wastewater coming out of the collector into the Oborinskaya Bayou is slightly reduced. Therefore, we can note, although insufficient, the role of the duct as an additional biological pond, where biological oxidation and bioaccumulation of pollutants occurs. The excess of total iron and copper in the control traverse mostly consists of a high background concentration of substances due to the local hydrogeochemical background caused by taiga-marshland landscapes in the water catchment area of the Kama river, as well as a secondary anthropogenic impact. A significant increase in the nitrate content in the control traverse is associated with the nitrification of ammonium ions and nitrites to nitrates, and the oxidation of NG in the habitat. The excess of nitrogen-containing compounds due to the use of nitric acid as a component of nitrating mixture from the receiving nitrocellulose (NC), which is the basis for the production of explosives, and the use of nitric acid during the esterification of alcohols in the generation of NG. Some of these compounds are formed during
wastewater treatment from NG, due to the oxidation and decomposition of it into simpler nitrogen-containing compounds. The increased content of these biogens may increase the eutrophication processes observed in the Votkinsk dam pond, which considerably affects the quality of water used for water withdrawers. The increased content of sulfates is formed due to the similar use of sulfuric acid in production of NC and esterification of alcohols.

In addition, a substantial contribution to the formation of high nitrate concentrations in the control traverse can play surface flow from the territory of the village of Oborino and infiltration to groundwater from its cesspool of households. The greatest excess relative to the MPC in the control traverse was found for NG (819 times), in addition, the MPC exceeds for this pollutant and in the sewage of the release (837 times). In the control traverse, excess background concentrations of the substance are 1365 times. Based on the above, there is a need to implement measures aimed at reducing the concentration of NG in sewage to reduce anthropogenic impact of the enterprise on the Kama river.

Currently, there are different methods of wastewater treatment from nitroesters, which include NG. However, chemical methods are expensive, they do not provide sewage treatment up to the MPC standards. Biological methods are expensive if the enterprise in question is located in a temperate climate. Based on a technical and economic comparison of methods, ozonation of sewage containing nitroesters is the most acceptable. The main advantage of the method is destruction of nitroester to the level of trace concentrations.

Ozone has a strong oxidizing effect and effectively destroys various organic pollutants, its redox potential in an acidic environment is 2.07 V, and in an alkaline environment - 1.24 V [24]. The proposed technology is based on hydrolysis of NG in an alkaline medium followed by the introduction of ozone [15]. A hydrolysis reaction occurs:

$$C_3H_5(ONO_2)_3 + 5NaOH \rightarrow NaNO_3 + 2NaNO_2 + CH_3COONa + HCOONa + 3H_2O$$  \hspace{1cm} (1)

Saponification promotes the oxidative decomposition of organic (sodium acetate and formate) and inorganic (sodium nitrate and nitrite) components. Generally, the interaction of ozone with nitroglycerin in an alkaline environment can be represented as:

$$C_3H_5(ONO_2)_3 + 6NaOH + 3O_3 \rightarrow 3NaNO_3 + 3NaHCO_3 + 3H_2O + O_2$$  \hspace{1cm} (2)

Thus, we can conclude that the decomposition of nitroglycerin into simple products-nitrates and bicarbonates, which are significantly less dangerous to the environment.

The general scheme of the proposed wastewater treatment (Fig.2) is to supply sewage pH=6 to accumulation tanks. Then the wastewater is fed to the chemical blender, where NaOH is introduced to pH=12, followed by holding the effluent for 3 hours with constant stirring. After holding in chemical blender, the sewage is fed to the contact case of the bubbling type, where an ozone-air mixture is introduced from the ozone generator with a concentration of 430 g/m³. Part of the residual ozone is removed to the destructor, where the ozone is decomposed to oxygen. After ozonation for 5 minutes, the water purified from nitroglycerin with a pH=12 enters the contact device for neutralization, where the necessary volume of the acidic waste mixture with a pH=3.2 is introduced. After neutralization, the treated wastewater with a pH=7 is discharged into sewage collector further into the Kama.

![Fig. 2. Proposed wastewater treatment system.](image)

The economic efficiency of the event is confirmed by the calculations (table 2).
Table 2. Economic benefit of the proposed event

| Index number                        | Sum, million rub. | Payback time |
|-------------------------------------|------------------|--------------|
| Capital input                       | 12,804           |              |
| Operating costs                     | 2,497            |              |
| Savings on payments for the discharge of pollutants | 4,499           |              |
| Annual benefits                     | 2,878            |              |
| Prevented environmental and economic damage | 537,593         | 4 years      |

4 Conclusions

1. Enterprises for production explosives have a significant negative impact on environmental components, especially on water bodies, which is due to the significant water requirements of the process flowsheet of these enterprises. As a result, there is a need for environmental monitoring of local hydrosphere objects located in the impact zone of it.

2. Monitoring researches conducted to assess the quality of natural waters of the Kama river, in the area of impact of enterprises producing explosives, revealed a significant level of anthropogenic impact of the enterprise on a large watercourse.

3. The largest contribution to technogenic pollution of natural waters of the Kama river is provided by the discharge of a generally for this industry pollutant-nitroglycerin. The excess in the control traverse was 819 times relative to the MPC of the substance and 1365 times relative to background concentrations of nitroglycerin in natural waters.

4. The research reviewed existing methods of wastewater treatment from nitroesters, in particular nitroglycerin, which resulted in the selection of a technology for ozonation of sewage with the previous introduction of an alkaline reagent required for hydrolysis of NG. The technological scheme of sewage treatment with neutralization of alkaline effluents formed after hydrolysis, mixture of acidic waste formed at the enterprise is justified.

5. Ozonation provides almost 100% of wastewater treatment from nitroester due to the high oxidative effect of ozone in alkaline environments, as well as the possibility of destruction of nitroester hydrolysis products: formates and acetates to simpler and less dangerous environmental chemical. Ozonation of nitroglycerine in an alkaline environment is also an economical environmental protection measure with a significant amount of prevented environmental and economic damage, as well as a noticeable reduction in fees for negative environmental impact. In addition, the event has a fairly short payback time – 4 years.

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