Biological treatment efficiency of wastewaters from a mining-processing plant by constructed floating wetland

Vladimir Myazin[1,2*], *Nadezhda* Fokina[3], *Aleksandra* Chaporgina[2], *Anastasia* Soshina[2], and *Elena* Latuk[4]

[1]RUDN University, Miklouho-Maklaya st., 6, Moscow, 117198, Russia
[2]Institute of North Industrial Ecology Problems – Subdivision of the Federal Research Centre Kola Scientific Centre of Russian Academy of Science, Akademgorodok, 14A, Apatity, 184209, Russia
[3]Sirius University of Science and Technology, Olympiyskiy Avenue, 1, Federal territory "Sirius", 354340, Russia
[4]RIVS Group of Companies, Zheleznovodskaya st., 11A, Saint Petersburg, 199155, Russia

Abstract. This paper presents the results of laboratory studies on the effectiveness of biological treatment of wastewater from a mining-processing plant for the removal of nitrogen compounds and phosphates. It was found that quarry wastewater and technological water are non-toxic or slightly toxic to plants and can be treated using constructed wetlands. Mine wastewater was toxic to the studied plants, making treatment impractical. Biological treatment with plants increased the removal of nitrate by 2.3-2.5 times, nitrite by 5.0 times, ammonium by 3.7-5.0 times, and phosphate by 16-30 times. Plants and microorganisms, growing in water and roots, were found to remove up to 86 mg nitrate, up to 2.25 mg nitrite, and up to 2.45 mg ammonium per 1 g of wet plant biomass per day. It has been calculated that a plant community on a 1 m^2 constructed floating wetland consisting of sedge (*Carex sp.*) and reed (*Phragmites australis*) can remove up to 35 g nitrate, 1.3 g nitrite, 1.0 g ammonium and 1.6 g phosphate from water per day.

1 Introduction

Mining using blasting typically results in the pollution of mine and quarry wastewaters with nitrogen compounds due to incomplete combustion of explosives. Drainage of mine and quarry water is a prerequisite for ore extraction. Open-pit mining results in the accumulation of large volumes of groundwater and precipitation during heavy rains and snowmelt. Polluted groundwaters from mine and quarry are pumped to the surface. Nitrogen compounds entering surface waters lead to eutrophication of water bodies, and must be removed from wastewater during treatment. All nitrogen compounds, with the exception of magnesium ammonium phosphate, are highly soluble in water and cannot be

* Corresponding author: myazin-va@rudn.ru

removed chemically. There are no universal solutions to this problem due to the volume and the composition of wastewater, and the specific characteristics of the process.

The most common processes for removing nitrogen compounds include ion exchange, catalytic oxidation, reverse osmosis, and biological treatment. Traditional approaches to wastewater treatment are constantly being improved through the introduction of new technologies and modern equipment. However, along with the pollutants removed, some of the main criteria for selecting of these technologies include capital and operating costs for water treatment, the complexity of maintenance, and climatic limitations of use. Therefore, an active search for, development, and implementation of the most effective, environmentally and economically feasible alternative methods continues. One of the solutions for improving traditional water treatment methods was to supplement them with a biological method using the plants and microorganisms [1, 2].

Biological treatment is based on natural processes occurring in landscape and aquatic ecosystems [3]. Constructed wetlands can purify wastewater from a wide range of pollutants – suspended solids, organic matter, nitrogen, phosphorus, sulfur, heavy metals and bacterial contamination with high efficiency [4]. It can be operated for a long time and does not require high costs for maintaining operation [5]. Nitrogen removal during treatment includes sedimentation, biodegradation, biological assimilation, nitrification, denitrification, anaerobic ammonium oxidation, plant uptake, adsorption and emission of nitrogen oxides [6].

Various approaches can be used for treatment, one of which is the creation of floating modules with plants – constructed floating wetland (CFW) [7]. The main advantage of CFW over traditional wetlands is the ability to cope with changing water depth [8], which allows the treatment system to be designed as a storage basin, to take large volume of runoff and slowly discharge it.

Plant uptake of nutrients and other elements may be higher in CFW. Plant roots are not in contact with sediments or soil and can only access elements and compounds in the water. Under the floating mat, plant roots become a surface for biofilm formation and the biochemical conversion of pollutants and physical processes such as filtration and sedimentation [9]. CFW were used to treat domestic wastewater [6], agricultural and industrial wastewater [7], and for reviving urban ecosystems [10, 11]. As a result of microbiological transformation, sorption, and uptake by plants, 0.5 to 5.8 g N/m^2, up to 0.5 g P/m^2, and up to 0.3 g K/m^2 per day are removed from water. During the growing season, a module with plants of 1 m^2 area can remove up to 580 g N, 50 g P, and 30 g K [12]. In Canada, a module with plants of 55.2 m^2 area removed 38.1 kg of N (or 16 g N/m^2 per day) from water in 42 days [13].

CFW have proven effective in treating wastewater of various pollutants and are used in the United States, Europe, and China. In Russia, these technologies are not widely used, primarily due to unfavorable climatic conditions. Therefore, the aim of this study was to assess the possibility of biological treatment of wastewater from a mining-processing plant using a CFW.

2 Materials and Methods

2.1 Sampling of wastewaters

Wastewater samples for laboratory experiments were collected during the summer period at several points within the mining-processing plant, taking into account the specifics of the technological process:

- quarry water in the settling pond;

- technological water in the tailings settling pond;
- mine water.

2.2 Chemical and physicochemical methods

In the field, pH, water temperature, and dissolved oxygen content in the surface water were measured at the work site. Portable instruments were used to determine the physicochemical parameters of the water: an HM Digital pH-80 (pH-meter, thermometer) and Milwaukee MW600 (dissolved oxygen sensor).

The ammonium (PND F 14.1:2:3.1-95), nitrite (PND F 14.1:2:4.3-95), nitrate (PND F 14.1:2:4.157-99), and phosphate (PND F 14.1:2:4.157-99) contents were determined in the water samples initially and during the experiment in the laboratory.

2.3 Phytotoxicity test of wastewaters

The toxicity of water samples was assessed based on changes in seedling height and root length of test plants: oats (*Avena sativa*), wheat (*Triticum aestivum*), and garden cress (*Lepidium sativum*) grown in Petri dishes with wastewater during 14 days [14].

Testing was in triplicate for each water sample. Seeds were placed in Petri dishes on filter paper and watered with the test water. The toxicity index (T) was determined based on the presence of significant differences between the control and test samples:

$$T = \frac{Xi - Xc}{Xc} \cdot 10o \quad (1)$$

where Xi is the test value for the wastewater sample, Xc is the test value for the control sample (nontoxic). A negative value T indicates toxicity, while a positive value indicates a stimulating effect. The following water toxicity classes were identified: $0 < T < 25$ (non-toxic), $26 < T < 50$ (slightly toxic), $51 < T < 75$ (toxic), $76 < T < 100$ (highly toxic).

2.4 Wastewater treatment

To wastewater treatment, two common plant species were used: reed (*Phragmites australis*) and sedge (*Carex* sp.). Reed is a hygrohelophyte, widely distributed in soils with shallow groundwater. Reed is common in swamps, overgrown lakes, floodplains, and river and lake shores. The plant is cold-resistant and frost-resistant, tolerates significant water salinity and grows in a variety of soil types. Sedge is a helophyte, growing in all climatic zones. Most species grow in the Northern Hemisphere, primarily in temperate and cold climates. Most sedge species prefer moist habitats – lake and river banks, ponds, marshes, coastal meadows, coastal and river sands, and marshy tundra; they sometimes grow directly in water.

For the laboratory study, mature plants taken from their natural habitat were used. In the laboratory, the plant roots were thoroughly rinsed under water and dried with paper towels. Plastic containers were filled with 1,000 mL of wastewater (quarry water and technological water), and the plants (biomass about 50 g) were placed inside. The water volume in the containers was maintained at a constant level. The experiment lasted 21 days.

3 Results and Discussion

3.1 Content of nitrogen compounds and phosphate in wastewaters

Wastewater pH values at the sampling site ranged from 7.6 for quarry wastewater to 10.0 for mine wastewater (Table 1). The pH values of technological water and mine wastewater exceeded the standard for fishery water bodies (Order № 296 "Water Quality Standards for Fishery Water, Including Standards for Maximum Permissible Concentrations of Pollutants in Fishery Water", 26.05.2025).

Dissolved oxygen in the surface water was within the standard (at least 6 mg/L). Dissolved oxygen in mine wastewater and technological water was slightly lower due to process conditions.

Phosphate in quarry wastewater was low (less than 0.25 mg/L), but higher in mine wastewater (up to 0.31 mg/L) and, especially, in technological water (1.74 mg/L), which is 9-12 times higher than the maximum permissible concentration (MPC) for oligotrophic water. Phosphorus compounds enter technological water as a result of the technological process.

The highest ammonium concentration during the sampling period was in mine wastewater (6.78 mg/L), while the lowest was in technological water (0.05 mg/L).

Nitrite concentrations in quarry and mine wastewaters exceeded the MPC. The highest nitrite content was in mine wastewater (4.10 mg/L). Technological water had a minimum nitrite (0.05 mg/L), which did not exceed the MPC.

The nitrate content in all the wastewaters exceeded the MPC during the sampling period. Mine wastewater and technological water had higher nitrate than quarry wastewater.

Table 1. Chemical indicators of wastewaters.

Type of wastewater	pH	Dissolved oxygen, mg/L	NH_4^+, mg/L	NO_2^-, mg/L	NO_3^-, mg/L	PO_4^{2-}, mg/L
Quarry water	7.6	12.7	0.72	0.25	46.1	<0.25
Mine water	10.0	8.7	6.78	4.10	80.7	0.31
Technological water	8.9	8.9	0.05	0.05	80.7	1.74
Standards (Order № 296, 26.05.2025)						
	6.5-8.5	Not less than 6	0.5	0.08	40	0.15

Quarry and mine wastewaters contain high concentrations of all nitrogen compounds, while technological water contains high concentrations of nitrate and phosphate. Mine wastewater had the highest pH, ammonium, and nitrite levels. Pollutants in mine and quarry wastewaters can enter natural water, while pollutants in technological water can accumulate during the production cycle, negatively impacting the technological process.

Water analysis results indicate the current wastewater treatment system is ineffective. Wastewater aeration provides a high degree of ammonium removal, but can also lead to the accumulation of nitrites and nitrates.

The large volumes of incoming wastewater make it difficult to treat using traditional methods, and the chemical and physical precipitation methods used are ineffective to remove nitrogen compounds.

A characteristic feature of wastewater is the unevenness of its inflow, which depends on the season and precipitation, as well as fluctuations in the pollutant content of the wastewaters. Under these conditions, CFW are the most effective method of wastewater treatment, as previously demonstrated for mining-processing plants in northwestern Russia [3]. And the first thing that needs to be done is to assess the toxicity of the wastewater, which should not inhibit the growth of the plants used.

3.2 Phytotoxicity of wastewater

Growing wheat seeds with wastewater resulted in a reduction in root length. Quarry wastewater and technological water were slightly toxic, while mine wastewater was toxic. Mine wastewater was also slightly toxic to oat roots. Mine wastewater and technological water resulted in a reduction in the weight of the garden cress (Table 2).

Table 2. Plant test reactions and wastewater toxicity.

	Quarry wastewater	Mine wastewater	Technological water	Clean water
Triticum aestivum				
Seedling height, cm	14.63±0.49	14.06±0.74	14.60±0.51	17.85±0.33
Root length, cm	12.59±0.58	10.09±0.68	12.75±0.68	20.54±0.49
Plants mass, g	0.24±0.01	0.25±0.01	0.27±0.01	0.31±0.01
T	slightly toxic	toxic	slightly toxic	-
Avena sativa				
Seedling height, cm	8.72±0.73	8.49±1.24	11.71±0.56	11.13±1.01
Root length, cm	8.08±0.71	6.32±0.73	8.01±0.84	9.70±0.59
Plants mass, g	0.37±0.02	0.36±0.03	0.40±0.04	0.36±0.02
T	non-toxic	slightly toxic	non-toxic	-
Lepidium sativum				
Seedling height, cm	2.57±0.17	2.59±0.19	2.96±0.25	2.93±0.09
Root length, cm	7.95±0.70	6.20±0.53	8.84±0.73	7.82±0.57
Plants mass, g	0.05±0.005	0.03±0.003	0.04±0.004	0.06±0.001
T	non-toxic	slightly toxic	slightly toxic	-

Thus, mine wastewater had a negative impact on all test plants, limiting the possibility of its direct treatment using CFW. The toxicity of mine wastewater is primarily due to its high pH (10 or higher), which inhibits root growth. Quarry wastewater and technological water were no toxic or only slightly toxic to the test plants, so they were used in the next stage of the study.

3.3 Efficiency of biotreatment of wastewater

3.3.1 Quarry water treatment

Without plants, the biological transformation of nitrogen compounds in wastewater occurs solely through the activity of bacteria and microalgae with optimal temperature and light conditions. During a 21-day experiment, nitrate in quarry wastewater decreased by 15%, ammonium – by 62%, and nitrite increased by 72%. The low number of nitrogen-transforming microorganisms in quarry wastewater prevents effective water treatment. Nitrite accumulation in the water is due to an imbalance in nitrogen compound transformation processes (inhibition of the second phase of nitrification).

Nitrogen removal processes in CFW include sedimentation, biodegradation, biological assimilation, nitrification, denitrification, anaerobic ammonium oxidation, plant uptake, adsorption, and nitrogen oxide release. Inorganic nitrogen is soluble in water and is represented by ammonium, nitrate, and nitrite. It is highly reactive and is primarily assimilated by algae and plants, converting into organic nitrogen in biomass [12]. Some nitrogen is converted into nitrogen oxides or nitrogen gas through nitrification and denitrification, anammox, and biodegradation [7]. The complete nitrogen removal is achieved only by microbial nitrification and denitrification, while plants provide temporary storage for nitrogen and phosphorus. After plant death, nitrogen is released back into the water, where it precipitates and accumulates in bottom sediments or is decomposed by microorganisms.

The efficiency of quarry wastewater treatment with plants increased by 2.3-2.5 times for nitrate, by 3.7-5.0 times for ammonium, and by 5 times for nitrite. Nitrate content was reduced below the MPC in 7-14 days, and nitrite and ammonium content - in 14-21 days (Figure 1).

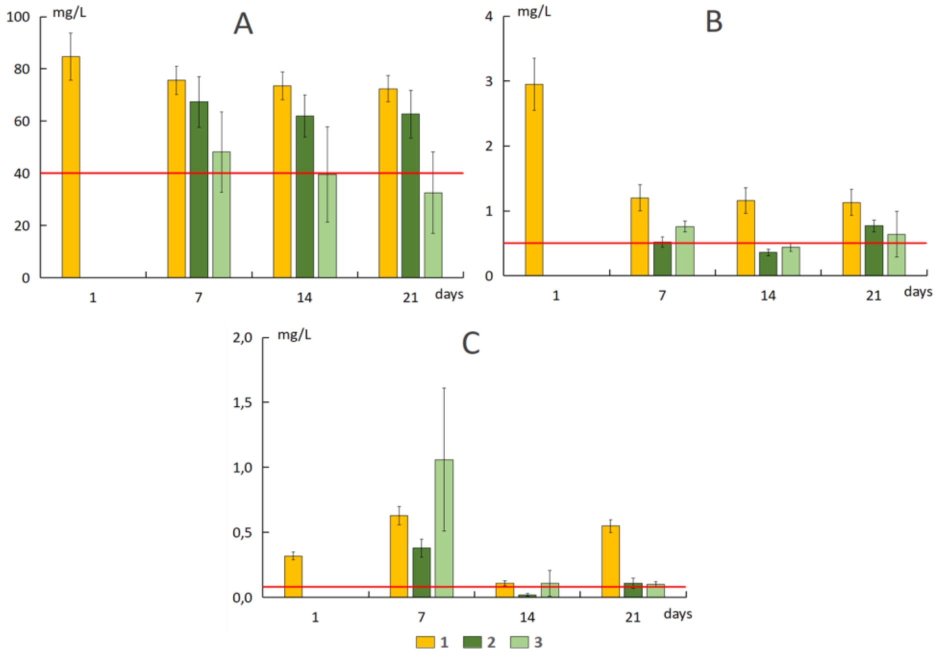

Fig. 1. Dynamics of nitrate (A), ammonium (B) and nitrite (C) during treatment of quarry water. 1 – without plants, 2 – *Phragmites australis*, 3 – *Carex sp*. The red line is the MPC value.

3.3.2 Technological water treatment

Over 21 days, the nitrate content in the technological water without plant decreased by 6%, but the nitrite and ammonium content increased by 2.6 and 4.6 times, respectively.

In the water treated with plants, nitrate content decreased below the MPC after 7 days, while ammonium content remained unchanged. As with quarry wastewater, nitrite in the technological water increased. However, nitrite content gradually decreased thereafter. Phosphate content in the water treated with plants decreased by 8-21 times to values close to the MPC for oligotrophic water (Figure 2).

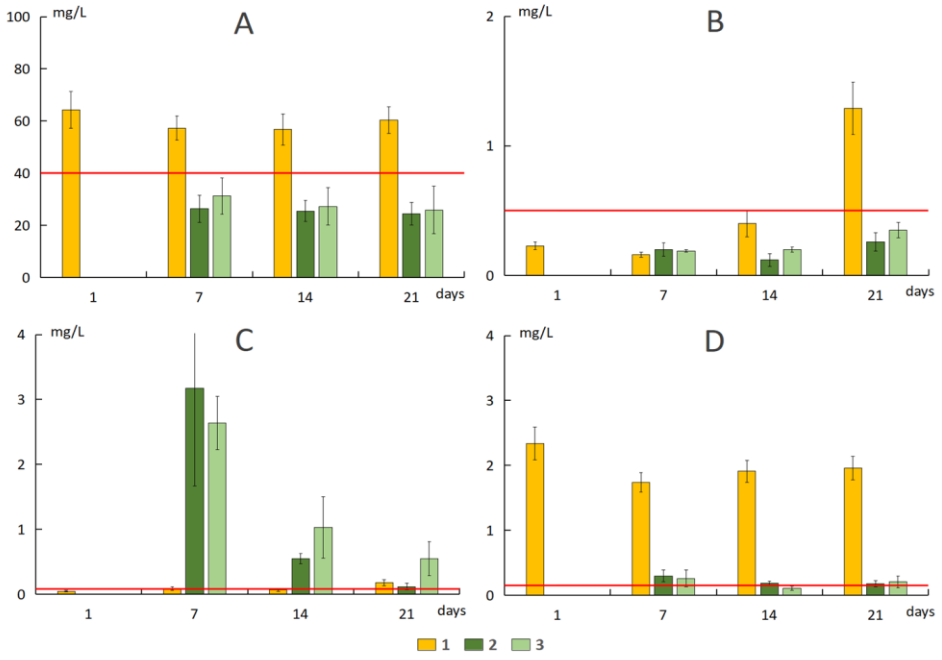

Fig. 2. Dynamics of nitrate (A), ammonium (B), nitrite (C), and phosphate (D) during treatment of the circulating technological water. 1 – without plants, 2 – *Phragmites australis*, 3 – *Carex sp*. The red line is the MPC value.

3.3.3 Wastewater treatment efficiency

The reduction in nitrogen compounds and phosphates in water is due not only to their uptake by plants but also to transformation in the biofilm of microorganisms developing on the roots.

Plants and microorganisms in water and root system removed up to 86 mg nitrate, up to 2.25 mg nitrite, up to 2.45 mg ammonium, and up to 2.23 mg phosphate per 1 g of wet biomass in 1 day. In addition, over 21 days, the reed biomass increased by 23-29%, and the sedge biomass by 33-45%, which corresponds to an increase in plant biomass of 0.92-11.60 g.

The maximum rate of nitrate, phosphate, and ammonium removal in the laboratory was during the first week, and nitrite removal – during the second week. No significant difference in removal efficiency was found between the plants (reed and sedge).

Coastal and aquatic plants have a high productivity. The green biomass of sedges (*Carex sp.*) reaches 2-3 t/ha (200-300 g/m^2), reed (*Phragmites australis*) – 5-6 t/ha (500-600 g/m^2). The raw biomass of pondweed (*Potamogeton sp.*), waterweeds (*Elodea sp.*), water milfoil (*Myriophyllum sp.*), hornworts (*Ceratophyllum sp.*) in the central zone of Russia reaches 3-4 kg/m^2, arrowhead (*Sagittaria sp.*) – 6-10 kg/m^2, water-soldier (*Stratiotes aloides*) – 2-13 kg/m^2, longroot smartweed (*Persicaria amphibia*) – 8-10 kg/m^2, bur-reed (*Sparganium sp.*) – up to 10 kg/m^2. In highly productive constructed systems with a constant presence of nitrogen compounds, the productivity of plant communities can be higher. The total biomass of various sedge species has been reported to reach 19.7 t/ha (1970 g/m^2), with an average biomass of 9 to 12 t/ha (900-1200 g/m^2) [15].

In our case, a 1 m^2 plant community of sedge and reed, as part of a constructed floating wetland, can extract from the water up to 35 g nitrate, 1.3 g nitrite, 1.0 g ammonium, and 1.6 g phosphate per day.

The average nitrogen compound content in quarry wastewater exceeded the MPC throughout the year. To achieve the required values, 4.16 g ammonium, 2.34 g nitrite, and 49.43 g nitrate must be removed from each m^3 of quarry wastewater before discharging it into a natural waterbody.

When treating technological water to remove nitrogen compounds, the less strict standards for domestic water sources (SanPiN 1.2.3685-21 "Hygienic Standards and Requirements for Ensuring the Safety and/or Harmlessness of Environmental Factors for Humans", 28.01.2021) can be used as a target (2 mg/L NH_4^+, 3.3 mg/L NO_2^-, and 45 mg/L NO_3^-). To achieve the required values, 0.35 g nitrite and 10.43 g nitrate must be removed from each m^3 of incoming water; ammonium removal is not required.

Considering that a plant community with an area of 1 m^2 can remove up to 35 g of nitrate, 1.3 g of nitrite, and 1.0 g of ammonium per day, the area of the CFW system should be at least 4000 m^2/1000 m^3 of incoming quarry wastewater and at least 300 m^2/1000 m^3 of incoming technological water.

The implementation of a CFW system for wastewater treatment at operating mining-processing plants is possible within existing treatment facilities, primarily in settling ponds, wastewater post-treatment basins, and drainage channels.

Plant biomass accumulated during the treating process can be efficiently processed to generate energy and fertilizer. The most efficient approach is to use the biomass to produce biogas (methane) through anaerobic digestion. This simultaneously produces green energy and a ready-to-use nitrogen-phosphorus fertilizer (digestate). Alternative methods include direct combustion for energy production, pyrolysis to produce syngas and biochar, and mulching and composting the biomass for application to the soil.

The main limiting factors for the effective use of CFW methods are high water flow rates, which reduce the contact time of polluted water with plant roots and microbial biofilm, as well as the short vegetation season for biological transformation of nitrogen compounds.

4 Conclusions

The study demonstrated the need and possibility of treating mining-processing plant wastewaters from nitrogen compounds and phosphate using CFW. The use of common plants (reed and sedge) significantly reduced nitrate, phosphate, and ammonium in the water within 7 days. Nitrite removal requires more time, but ultimately also results in a reduction of nitrite in the wastewater. The treatment efficiency of quarry wastewater increased by 2.3-2.5 times for nitrate, 5.0 times for nitrite, and 3.7-5.0 times for ammonium. In technological water, the use of plants increased the efficiency of nitrate removal by 3 times, and the concentration of phosphate decreased by 8-21 times during the treatment process.

A 1 m^2 plant community of sedge and reed, as part of a constructed floating wetland, can remove from the water up to 35 g nitrate, 1.3 g nitrite, 1.0 g ammonium, and 1.6 g phosphate per day, increasing biomass.

The implementation of a CFW system for wastewater treatment at operating mining-processing plants is possible within existing treatment facilities. Plant biomass accumulated during the treating process can be efficiently processed to generate energy and fertilizer.

The limitation of using CFW is water toxicity (which in our case is caused by high pH), high water flow rates and a short growing season.

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