Nanofiltration to Purify Drinking Water from Cyanobacteria and Microcystins in Water Supply Systems

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Abstract. The pollution of a surface water supply source (Kuibyshev reservoir) with cyanobacterial metabolites under the conditions of the increased biogenic load has been estimated. During the period of mass growth of Cyanobacteria, the reservoir water quality deteriorates in some indicators, including the smell, taste, and content of organic and toxic substances. Among the wide range of cyanotoxins, microcystin-LR, the permissible concentration of which in drinking water should not exceed 1 μg/dm³, poses the greatest threat to the population. Global warming creates favorable conditions for the rapid growth of Cyanobacteria, therefore, the issue of providing the population with high-quality drinking water will further become aggravated.

Conventional process lines at municipal water treatment plants are ineffective in removing intracellular and extracellular cyanotoxins. The best and safest barrier against the ingress of cyanotoxins into drinking water can be membrane technologies that allow ultrafiltration of bacteria-l cells without mechanical damage and nanofiltration of cyanotoxins dissolved in water.

1. Introduction

The issue of providing the population with high-quality drinking water from surface water supply sources with a decelerated water exchange under the conditions of the increased biogenic load is gradually becoming aggravated. Excessive ingress of nitrogen and phosphorus to reservoirs from the point and diffuse pollution sources activates the mass growth of Cyanobacteria or blue-green algae (Cyanophyta), which leads to the emergence of toxic metabolites - cyanotoxins in the water [1-5]. A risk of ingesting toxic substances with drinking water by humans arises. The World Health Organization (WHO) has established that among cyanotoxins, microcystin-LR, the permissible concentration of which in drinking water should not exceed 1 μg/dm³, poses the greatest threat to the human health and life. Global warming creates favorable conditions for the rapid growth of Cyanobacteria, therefore, the issue of providing the population with high-quality drinking water will further become aggravated.

Large reservoirs of the Middle and Lower Volga are the centralized water supply sources for many Volga cities. Long-term observations at the Kuibyshev, Saratov, and Volgograd reservoirs show that the mass growth of Cyanobacteria (water blooming) disturbs the hydrochemical and gas regime of reservoirs and deteriorates water quality in some indicators, including taste, smell, and content of organic and, probably, toxic substances [6-8].
Under the conditions of the mass growth of Cyanobacteria, conventional water purification process lines preparing drinking water for the centralized water supply of Volga cities, including clarification, discoloration, and disinfection, are ineffective in removing toxins, as well as the off-flavor and smell of water [9]. Therefore, the real threat of toxic pollution of the Volga reservoirs as surface water supply sources should be estimated. As the research object, the largest in the Volga-Kama cascade – the Kuibyshev reservoir has been chosen.

As part of the study, it is planned to estimate the scale and intensity of the mass growth of Cyanobacteria in the Kuibyshev reservoir and determine the risks of contaminating the water supply source with cyanotoxins. A technique for purifying natural water from cyanotoxins should be chosen and a way to improve the existing water treatment process line in the Volga cities based on the implementation of membrane technologies for ultrafiltration and nanofiltration proposed.

2. Results and discussion
According to long-term observations, it has been established that the mass growth of Cyanobacteria in the Kuibyshev reservoir occurs annually during the summer low-water period. The scale, intensity, and duration of the process depends on hydrometeorological conditions, biogenic load, and the aqueous run-off regulation mode. In the reservoir water area, the process is characterized by spatial heterogeneity. The process proceeds more intensively in shallow water, bays, and estuaries of tributaries, which are virtually free of run-off current. Here, the cyanobacterial biomass may reach 100-150 mg/dm³. The wind surges form extensive water blooming spots, in the surface layer of which the cyanobacterial biomass can reach 400 and 2,000 mg/dm³ in the channel part and the floodplain, respectively. In the lower reservoir part, where the Togliatti water intake is located, the cyanobacterial biomass and population vary within 3 to 43 mg/dm³ and 23 to 80 mln. cells/dm³, respectively [10-13].

With an increase in the cyanobacterial biomass, the water acquires a smell, an increased color index, and an alkaline reaction. In the surface layer of the reservoir, the oxygen content increases sharply, and in the bottom layer, its deficiency is observed. The content of organic substances in the water increases. The highest organic matter concentration by permanganate oxidizability (PO) is observed at the peak of water blooming. Due to the mass growth of Cyanobacteria, PO increases by 10-15 %. Herewith, the contents of biogens, primarily, nitrates and phosphates in the water decrease. When the phosphate concentration reduces to zero, the growth of Cyanobacteria stops [14-16].

The Cyanobacteria Microcystis, Anabaena, and Aphanizomenon genera can produce toxins such as microcystins. Currently, more than 80 structural variants of microcystins are known, the most toxic of which is microcystin-LR consisting of 7 amino acids. The linear length of a single amino acid residue in the polypeptide chain is 0.35 nm [1, 3].

Research performed by the Kazan State University in 2014-2016 has shown that in the channel part of the reservoir (Zelenodolsk) and near Kazan, the content of microcystins exceeds the WHO-prescribed permissible concentration and is within 6-9 and 5-12 μg/dm³, respectively. More significant microcystin concentrations amounted to 200-470 μg/dm³ have been detected in the reservoir floodplain. It has been established that the microcystin concentration grows with an increase in the population and biomass of Cyanobacteria. When the bacteria population is over 21 mln. cells/ dm³, the microcystin concentration may exceed the permissible limit, i.e. 1 μg/dm³ [17].

Estimating the ecological state of the Kuibyshev reservoir has shown that during the period of mass growth of Cyanobacteria, the water quality deteriorates in the taste, smell, and content of organic substances; an actual threat of toxic pollution of the surface water supply source emerges. Therefore, special treatment techniques are required to purify natural water from organic and toxic biogenic substances.

In the Volga cities, to purify natural water to meet the standards for the drinking water quality, as a rule, process lines are used designed for class II surface water supply sources, which include disinfection by chlorination or ultraviolet radiation (UVR), clarification, discoloration, and chlorination of water supplied to the municipal network. The most controversial issue is the use of
UVR at the initial water treatment stage since radiation kills bacteria, and intracellular toxins enter the water.

The use of chlorination under the conditions of the mass growth of Cyanobacteria causes some concerns about cell rupture and the release of toxins. Chlorine water treatment at the water treatment inlet creates the risk of destruction of bacterial cells. Also, chlorination at a high organic content may lead to the formation of by-products during drinking water treatment, including organochlorine substances.

Some researchers believe that the listed conventional water treatment stages to one degree or another lead to partial removal of cyanotoxins contained in the source water. On the contrary, others believe that like algae toxins, the substances giving taste and smell to the water have never been removed by coagulation and flotation. Therefore, additional natural water purification stages based on sorption and membrane techniques are required.

The purification techniques should be chosen and the process lines developed to remove cyanotoxins, considering the two toxin occurring levels, i.e. extracellular and intracellular [18-22]. Intracellular toxins are contained in the bacterial cell and released by excretion, dissolution, or destruction of cells, whereupon toxins enter the water and become extracellular ones. Removal of intracellular toxin will be effective if the bacterial cells themselves are removed since the bulk of toxins (95%) are contained within the cell. The strategy of water purification from extracellular cyanotoxin is completely different and similar to water purification from natural organic substances.

**Intracellular cyanotoxins should be removed** without damaging the bacterial membranes of unicellular, filamentous, and colonial microorganisms. The unicellular bacteria diameter exceeds 500 nm. They can be removed using membrane techniques that allow filtering cells without mechanical damage. Two membrane filtration types are suitable: microfiltration and ultrafiltration. Porous microfiltration membranes have a pore size of 50 to 5,000 nm. Ultrafiltration membranes have a smaller pore size within 1 to 50 nm. They let through almost all dissolved forms but retain solid particles, protozoa, bacteria, and most viruses and macromolecules.

Given the minimum size of Cyanobacteria, it can be assumed that microfiltration and ultrafiltration will be effective in removing intact cyanobacterial cells, provided the water is pretreated to reduce membrane fouling. Mass cyanobacterial growth in the water supply source requires more frequent backflushing to reduce the risk of toxins entering the water.

**Removal of extracellular toxins** is achieved using membrane nanofiltration or activated carbon adsorption. When choosing a technique to purify natural water, it is recommended to perform experimental studies since the removal efficiency depends on the membrane and activated carbon pore size distribution and the water quality.

Membrane plants include the following main elements: mechanical filters, pumps, membrane units, and automation devices. Mechanical pre-filters are placed at the process line input. For this purpose, mesh or coarse-grained filters can be used to protect the membrane elements from damage and clogging with coarse impurities. Then, a pump is installed, the main task of which is maintaining the system pressure required. If the pressure is too low or too high, there is a risk of membrane damage.

Downstream, a unit of membrane devices in a cylindrical housing and automation devices are installed.

The unit of membrane devices requires continuous care and regular maintenance. The nanofiltration membrane is a thin two-layer film of inorganic materials. The outer membrane layer is a thin layer of solid material participating in activated diffusion. The inner membrane layer in the form of a substrate is a coarse porous material and is intended to strengthen the outer membrane layer. Nanofiltration membranes are negatively affected by various oxidants such as chlorine, which corrodes its thin layer.

By the operating mode, nanofiltration plants are divided into continuous and intermittent modules, and by the stage number, into single-stage and multistage ones. A stage is a set of modules or cascades. The module cascades are installed in parallel within a single stage and united by common source water, permeate, and concentrate collectors. In this case, a prerequisite is using identical
membrane modules. Stages are formed of one or more cascades, while the concentrate formed in the previous cascade serves as feed water for the next one. Multistage schemes are used to increase the hydraulic efficiency of the plant.

The membrane module may consist of one to several elements sequentially passed by the water to be purified. Since at each element, the run-off recommended should not exceed 15 % of the feedwater flow rate, several elements installed in series may significantly increase the hydraulic efficiency of the entire water treatment plant. A scheme should be chosen, which will allow achieving the required filtrate yield at the rated water purification degree.

The extracellular toxin can be removed from water by adsorption on activated carbon with high adsorptive capacity with less than 1 nm pore size. Activated carbon with similar properties is obtained by thermal treatment of a carbonaceous material — usually wood, coal, coconut shells, or peat. As a result of such activation, a porous material is formed with a large surface area within 500-1,500 m²/g and a high organic matter removal efficiency. The resulting activated carbon is used in a powder or granular form to remove organic substances, which deteriorate the water's taste and smell. There are reasons to believe that activated carbon is effective in absorbing microcystin. However, the removal efficiency depends on the toxin concentration, various structural microcystin variants, and the activated carbon dose and origin. The microcystin removal efficiency is improved if the carbon filters are replaced on time or regenerated with a high TOC breakthrough. Re-treatment may be required to completely remove microcystins.

It is quite obvious that to prevent the ingress of cyanotoxins into drinking water, the water treatment should be improved. During the period of mass growth of Cyanobacteria, the Volga water should be processed at a special process line including preliminary microfiltration and ultrafiltration, UVR, coagulation, precipitation, and activated carbon or nanofiltration. Almost complete microcystin removal may only be achieved using membrane technologies.

3. Conclusion

Estimating the ecological state of the Kuibyshev reservoir has shown that during the period of mass growth of Cyanobacteria, the quality of water in the surface water supply source deteriorates in taste, smell, and content of organic substances; an actual threat of contaminating the Volga water with cyanotoxins emerges, the concentration of which exceeds the WHO-prescribed permissible limits. Against the background of global warming, the issue of contaminating the surface water supply sources with cyanotoxins will further become aggravated. Therefore, research of the water quality change regularities under the conditions of mass growth of Cyanobacteria should be performed, cyanotoxin monitoring arranged, and their domestic MPCs in drinking water reservoirs determined.

Currently, conventional process lines installed at water treatment plants in the Volga cities to purify surface water supply sources are not focused on removing cyanotoxins, therefore, there are risks of toxic substances entering drinking water. The existing water treatment process lines should be improved, and new ones designed considering the implementation of microfiltration and ultrafiltration to remove bacterial cells and nanofiltration to remove extracellular cyanotoxin.

4. References

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