Methods for reducing color and oxidability of natural waters

E V Nikolaenko, L M Arkhipova
Architecture and Construction Institute, South Ural State University, 76, Lenin Avenue, Chelyabinsk 454080, Russia

E-mail: ninkaenkev@susu.ru

Abstract. The qualitative indicators of natural waters of the open source of drinking water supply have been studied. The discrepancy with the regulatory requirements for such indicators as color and oxidability has been established. With the aim of reducing the color and oxidation of natural water, oxidative-sorption methods have been investigated. Based on the water quality indicators of the source, a non-reagent scheme of water treatment has been preliminarily proposed, including the filtration on sorption loads with preliminary chlorination of water with a dose within the limits of chlorine absorption. Such materials as quartz sand, granulated activated carbon of the brand "PUROLAT-ACTIVE", anthracite of the brand "PUROLAT-standard" and garnet have been investigated as possible loads for filtering plants. It has been established that effective reduction of water color in all considered periods of the year is achieved on a combined loading of "quartz sand - activated carbon". However, this loading has not shown the necessary reduction in oxidizability, in all series there has been an excess of regulatory requirements for this indicator. The best result for reducing water oxidation has been achieved on a two-layer load of "quartz sand - anthracite", which, according to the combined improvement of water quality indicators, has been recognized as the most effective.

1. Introduction

The composition of natural waters, concentrations and physical and chemical properties of impurities contained in them are fundamental when assessing the suitability of water for use by various categories of consumers. The hydrochemical regime of modern surface water sources is largely formed in conditions of intensive economic activity in catchment areas. In addition to traditional natural factors: geomorphological structure, climatic conditions, surface and soil cover, surface and groundwaters, the quality of water form scattered and point sources of anthropogenic and technogenic load. The combination of natural and anthropogenic factors forms bizarre combinations that provoke the total effects of the impact that affect the quality of water in the source. In order to ensure that the water treatment facilities serve as a reliable barrier preventing the inflow of pollution to consumers, in selecting water treatment technology, it is necessary to conduct an objective analysis of information on the variability of the quality of the source water in the water intake area.

2. Main part

The object of research is the water supply system of the Sport and Health Complex, located on the shore of Lake Bolshoy Sunukul. Water supply of the complex is currently carried out at the expense of groundwater. In connection with the increase in the number of holidaymakers in the summer and the
uneven water consumption throughout the year, there was a need for an additional source of water supply, for which the lake water can be used.

To determine the main technological processes and structure of water treatment plant facilities, water samples were taken at the proposed water intake point in the autumn-winter period, as well as during the spring high water. Analysis of the qualitative composition of the selected water, given in the table, showed that the quality of the water of the proposed source of water supply in these periods has similar quality indicators and does not meet the requirements of drinking water supply [1] for such indicators as color and permanganate oxidability.

The most effective methods to reduce oxidation and color of water are considered to be a strong oxidizer and sorption. Depending on the quality of the treated water, the composition and types of treatment facilities, various technological solutions for the use of the oxidation-sorption method of water purification can be adopted that will significantly expand the range of organic contaminants removed from the water. The sorption method is more reliable than the oxidative one, because it is based on the extraction of substances from the water, rather than on their transformation. As a sorbent, various filter materials can be used: granular and powdered activated carbon, activated anthracite, carbon fibrous materials and non-carbon adsorbents such as clinoptilolite, zeolites etc. Activated carbon is used in the form of powder (water carbonation) or in granular form as a charge filters, which is a more efficient method [2-6].

### Table. Indicators of the lake water quality for the periods of year.

| Indicator       | Units | Values in the autumn-winter period | Values in the spring period |
|-----------------|-------|-----------------------------------|----------------------------|
| Turbidity       | mg/l  | 0.85                              | 0.54                       |
| Color           | °     | 28                                | 28                         |
| Total hardness  | mg-eq/l | 5.2                             | 5.2                        |
| Calcium hardness| mg-eq/l | 1.6                             | 1.6                        |
| Alkalinity      | mg-eq/l | 6.6                             | 5.4                        |
| Ammonium ion    | mg/l  | 0.27                              | 0.27                       |
| Nitrites        | mg/l  | 0.0045                            | 0.0045                     |
| Oxidability     | mg/l  | 12                                | 11.2                       |
| Salt content    | mg/l  | 330                               | 330                        |
| Total iron      | mg/l  | Not detected                      | Not detected               |

Oxidizer must in all cases be introduced into the treated water before it enters the filtering load. The location of the oxidant input depends on the general tasks entrusted to the oxidizer, on the rate of its consumption and other factors. But in all cases it is necessary to ensure the presence of an oxidizer in the water entering the filtering load [7-9]. As a strong oxidizer, chlorine-containing reagents, ozone or potassium permanganate can be used. Reagents are used either alone or in combination with each other. The most widely used are chlorine-containing reagents, because of their prolonging effect. The chlorine dose is established in the process of technological analysis on the basis that in 1 ml of water supplied to the consumer, not more than 0.3 ... 0.5 mg of chlorine remains unreacted, which is an indicator of the adequacy of the accepted dose of the reagent [1]. In the conducted studies, the chlorine dose for preliminary chlorination was determined on the basis of the experimentally constructed chlorine absorption curve presented in Figure 1 and amounted to 1.5 mg/l in the autumn period and 2.3 mg/l in spring. Based on the water quality indicators of the source, a non-reagent scheme for water preparation was preliminarily proposed, including filtration with preliminary chlorination of water with a dose within the limits of chlorine absorption.

The correct choice of the filtering load and its parameters is important, as it is the main element of the filter structures. Such materials as quartz sand, granulated activated carbon of the brand "PUROLAT-ACTIVE", anthracite of the brand "PUROLAT-standard" and garnet were investigated as
possible loads for filtering plants. Downloads meet all the requirements for filtering materials and have a certificate for the right to use in drinking water supply.

The most effective and economical are the multilayer filters, which increase the efficiency of the filter due to the greater dirt capacity, longer filter cycle, high filtration rate and the quality of the filtrate at the outlet. The research was carried out on four possible combinations of loads: one-layer - from quartz sand and garnet; two-layer - anthracite and activated carbon in combination with quartz sand as the upper layer.

To study loads the process of filtering on fast filters was modeled in the laboratory. In the laboratory filter column, various filter materials were alternately loaded with a support layer of gravel. The height of the supporting and filter layers was calculated and amounted to 6 cm and 14 cm, respectively.

The initial water before filtration was treated with a strong oxidizing agent - chlorine, stirred and kept for 30 minutes. Next, samples were taken to determine the color and oxidability after treatment with a strong oxidizer. The water was then passed through the column at a flow rate of 6 ml/min, which corresponds to a linear rate of 5 m/h with a contact time of water with a load of 6 minutes. At the outlet, a filtrate was taken to determine the residual values of chromaticity and water oxidizability. The results of the experiments are presented in the form of diagrams in Fig. 2 ... 5.

![Figure 1](image1.png)

**Figure 1.** The curve of the chlorine absorptivity of Lake Bolshoy Sunukul in different periods of year: a - in the autumn-winter period; b - in the spring period.

The decrease in chromaticity was observed during all experiments with water in the autumn-winter period and water in the spring period. Most effectively, the colority decreased after filtering on the load, which is a combination of activated carbon and quartz sand (from 28° to 5.8° in the autumn-winter period and from 28° to 3° in the spring period).

Reduction of oxidizability to the standard of drinking-quality water was observed during the experiment on a multilayer load from quartz sand and anthracite. Oxidation decreased from 12 mg O₂/l to 4.9 mg O₂/l in the water of the autumn-winter period and from 11,2 mg O₂/l to 3,1 mg O₂/l in the spring water. The color at this loading was also brought to the standard of drinking-quality water and amounted to 10.5° in the autumn-winter and spring periods. During laboratory experiments, it was found that the reduction in color and oxidability during filtration on loads of quartz sand and garnet was not observed, compared to water samples after treatment with a strong oxidizer. When filtering through a combined loading of activated carbon and quartz sand, only the color index was reduced, and the oxidation was only slightly reduced by pre-chlorination. When filtering water in the spring period through loading of the garnet, a significant decrease in the oxidizability was observed, from 11,2 mg O₂/l to 8 mg O₂/l after treatment with chlorine and from 8 mg O₂/l to 5 mg O₂/l after filtering.
These experimental results can supposedly be explained by the different nature of the substances that determine the color and water oxidation indices in different periods of the year. The composition of organic substances in natural waters is formed under the influence of many factors. Among the most important are intra-biochemical processes of production and transformation, receipts from other water bodies, with surface and underground run-offs, with atmospheric precipitation. The organic substances formed in the body of water and incoming to it from outside are very diverse in nature and chemical properties, including resistance to the action of various oxidants [10-11].

**Figure 2.** Color indicators of the initial water of the autumn-winter period and the water after filtration at various loads.

**Figure 3.** Color indicators of the initial water of the autumn-winter period and the water after filtration at various loads.

**Figure 4.** Oxidation indicators of the initial water of the spring period and the water after filtration at various loads.
Figure 5. Oxidation indicators of the initial water of the spring period and the water after filtration at various loads.

The increased oxidation and color of surface water sources indicates the presence of impurities of natural organic substances - humic and fulvic acids.

Humic and fulvic acids, called humus acids, often constitute a significant proportion of organic pollution of natural waters and are complex mixtures of biochemically stable high-molecular compounds. The main source of humus acids in the natural waters are soils and peat bogs, from which they are washed by rain and thawed waters. A considerable part of humic acids is introduced into reservoirs together with dust and is formed directly in the reservoir during the transformation of living organic matter [11-16].

Humic acids in surface waters are in dissolved, suspended and colloidal states, the relationships between which are determined by the chemical composition of the waters, the pH of the solution, the biological situation in the reservoir, and other factors. The presence of carboxyl and phenol hydroxyl groups in the structure of fulvic and humic acids, amino groups promotes the formation of strong complex compounds of humic acids with metals. The chemical composition of the molecules of humic acids can be expressed by the gross formula C_{18}H_{15}O_{8}N. They are slightly soluble in water, with monovalent cations (K⁺, Na⁺, NH₄⁺) form water-soluble salts, and with divalent and trivalent cations (Ca²⁺, Mg²⁺, Al³⁺, Fe³⁺) easily precipitate. Humic acids have a branched molecular structure, which includes a large number of functional groups and active sites, they contain: nitrogen, potassium, phosphorus, etc. [17-20]

By elemental composition, fulvic acids differ markedly from humic acids, primarily higher oxygen content and less carbon. Fulvic acids are yellow-colored high-molecular nitrogen-containing organic acids. They are part of humic acids that do not precipitate when neutralizing organic substances extracted from peat and brown coals by alkali treatment. Fulvic acids are compounds of the hydroxycarboxylic acid type with a lower relative content of carbon and more pronounced acid properties. The good solubility of fulvic acids in comparison with humic acids is the reason for their higher concentrations and distribution in surface waters [11].

The obtained results indicate that the cause of the color of water in the source is fulvic acids, which are well sorbed on loading from activated carbon and anthracite. And increased values of oxidizability can be caused by a significant content of humic acids, the sorption of which is more effective on loading from anthracite of the brand "PUROLAT-standard".

Further research will be directed to a detailed study of these substances, and the patterns of their extraction from water by filtration and by treatment with a strong oxidant.

3. Conclusion
As a result of the conducted studies, it can be concluded that the water in the area of the proposed water intake in the autumn-winter - spring period has a stable quality that does not meet the current
norms for drinking water supply in such indicators as color and oxidizability. The most effective reduction in the values of these indicators was achieved by filtration on a combined charge of quartz sand and anthracite with preliminary chlorination of the dose within the limits of the chlorine absorption of water. According to preliminary results, filters with this loading are proposed as the main facilities for the technological scheme of water treatment of the sports and health complex.

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