Opoka in coagulation of slightly polluted surface water

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Abstract. The coagulation of low-water with reagent purification is difficult because of the low concentration of suspended solids. The increased consumption of coagulant in this case leads to an increase in the content of residual aluminum or iron in water leaving the treatment facilities of the water supply. Clapping can be intensified by adding mineral opacifiers to the water, the particles of which play the role of additional centers of flocculation, weigh the flakes and increase the degree of water purification due to sorption processes occurring on their surface. In the paper, the efficiency of using opoka for the turbidity of slightly contaminated surface waters is investigated. The composition of this rock contains a significant amount of silicon dioxide, which determines the sorption properties of this material. The study was carried out using the jar-test experiment, using the water of the Shershni reservoir on the Miass River. It was found that the use of the opoka is expedient with a two-stage water purification scheme "sedimentation-filtration". The opoka was dosed in the form of an aqueous suspension prior to the administration of the coagulant. The reduction of the residual aluminum content in the filtrate is more effective by 40% compared to the experiment without the opoka. It is noted that in the conditions of low temperatures the effect of opoka is more pronounced.

1. Introduction
Currently, coagulation remains one of the most common methods of treatment of surface natural waters for obtaining water of drinking quality. The efficiency of the coagulation process is influenced by factors such as the choice of coagulants and flocculants and their concentrations, the temperature of the water being treated, the pH, the ionic water composition, the mixing mode, the concentration of suspended solids, and others.

Low turbidity of water in the water source can cause unfavorable coagulation conditions, since in this case there is not enough flocculation centers, small flakes are formed, their settling is difficult. In the Russian Federation, according to the normative documentation, water with a suspended matter content of up to 50 mg·L\(^{-1}\) is considered undersized. Examples of such water sources are Pirogovskoe reservoir, used for water supply in Moscow, Shershni reservoir providing drinking water in Chelyabinsk, and others.

The increase in the doses of coagulant and flocculant to intensify the coagulation of low-water waters is ineffective and leads to an increase in the residual concentrations of these reagents in purified water.

One of the methods of intensifying coagulation of low-turbidity waters is the use of opacifiers. Opacifiers are finely dispersed substances, insoluble in water, whose particles play the role of additional centers of flocculation, weight the flakes and increase the degree of water purification due
to the sorption processes occurring on their surface. The process of flocculation is particularly accelerated when fine particles of less than 3 micron are added [1]. The most common opacifiers are clays, most often bentonite and kaolin, finely ground calcium carbonate, magnetite powder, fly ash. In addition, diatomite, modified waterworks sludge particles and other materials are used to intensify coagulation [2-7]. The authors of [8] propose the use of variable charge soil containing aluminum and iron oxides, which gives sorption properties to these materials. The nature of the sorption of the coagulant hydrolysis products on the turbidity particles is determined by the nature of the particles [9].

A promising additive for intensifying coagulation of low-humid natural waters can be an opoka - this is a light siliceous and microporous sedimentary rock of cristobalite-opal composition with an admixture of chalcedony, clay substance, sometimes silty particles and organic residues (skeletons of radiolarians, spicules of flint sponges, diatoms). According to the chemical composition, the opoka is close to montmorillonite, as indicated by a similar composition (SiO₂, Al₂O₃, Fe₂O₃). Opoka is widely distributed in the territory of south-eastern Europe and Russia, it is safe for human health, has a high porosity with considerable strength and possesses sorption properties that are enhanced by temperature treatment [10-14]. This allows using it for the removal of phosphorus, petroleum products, phenols, complex organic compounds, including dioxins, heavy metal salts and other pollutants [15-20]. In addition, the opoka is not flammable, not explosive and has a fairly low cost.

The main purpose of this work was to assess the possibility of using an opoka as a opacifier for intensifying the purification of low-water surface water springs.

2. Materials and method

2.1. Preparation of the opoka

In the experiment, the opoka of the Kamennoyarsky deposit of the Astrakhan region (Russia) was used. The averaged basic indicators of the chemical composition of the opoka according to the extractive company's data are as follows (%) SiO₂ – 86.20; Al₂O₃ – 4.15; Fe₂O₃ – 1.56; TiO₂ – 0.2; K₂O – 1.2; CaO – 1.00; MgO – up to 1.00; Na₂O – up to 0.5.

The opoka was fractionally shredded on a shaker and sieved through a sieve with a mesh size of 0.08 mm. To achieve the maximum homogeneity of the chemical composition, the residue on the screen is again ground and sieved. The size distribution of the opoka particles was studied on the MICROTRAC S 3500 analyzer.

The opoka was introduced into the test water as a 1% aqueous suspension prepared according to the following procedure: 1 g of dry matter is mixed in 100 ml of water and settled for 10 minutes, the top layer of the slurry was selected for the experiments. The dose of the opoka varied in the interval 5–15 mg L⁻¹.

2.2. Jar-test experiment

For the jar tests (trial coagulation), the natural waters of the Miass River (Shershnevo Reservoir) were used, and the color, turbidity and temperature of the initial water were determined. Coagulant aluminum sulphate (1% by Al₂O₃) was used, coagulant doses are calculated per alumina.

Trial coagulation was carried out in graduated cylinders with a volume of 0.5 L at a fixed temperature. The order of introduction of the reagents is as follows: opacifier, then coagulant. After the addition of the coagulant, intensive mixing was carried out by translational movements without air intake (10 seconds), then for 120 seconds slow stirring in circular motions to avoid the destruction of the flakes formed in the initial period. The kinetics of coagulation and settling were observed for 30 minutes, after which a supernatant was taken from each cylinder to determine the turbidity (by kaolin), the water colour index and residual aluminum content.

2.3. Modeling the operation of fast filters
After preliminary coagulation of the water with the introduced dose of the opoka and settling for 30 min, the supernatant layer was accumulated in a single vessel. The water was then passed through a charge of quartz sand. The diagram of the laboratory installation is shown in Figure 1.

The filtration rate corresponded to the recommended value for fast filters and was in the range from 8 to 10 m·h⁻¹. At the treatment facilities of the drinking water in Chelyabinsk, the filtration rate is from 5.5 to 10.0 m·h⁻¹. The filtration rate was preset on distilled water, then clarified water was supplied to the charge. The samples of the filtrate with a volume of 100 ml were selected to determine the quality indicators. The total volume of filtered water was 500 ml.

3. Results and discussion

The effectiveness of the opacifiers depends on their nature, particle size, suspended matter concentration, surface area and other factors. Specific consumption of coagulant increases with decreasing particle size of suspended matter [9]. According to the study of the sediment of a opoka, the maximum proportion falls on particles with a size of 4 to 7 microns, which is close to the recommended sizes in the literature [1].

Temperature is the most important factor affecting coagulation. In surface water sources, seasonal temperature fluctuations are significant, so studies were conducted in the winter and summer periods of the year. In addition, the water colour index and turbidity of water in the reservoir varies according to the seasons of the year. The initial water quality parameters are given in Table 1.

Investigation of the effect of the opoka on coagulation at an initial water temperature of 21.5 °C showed the following. Dosages of coagulant 2 and 5mg·L⁻¹ proved to be scarce (Figures 2-4). At such doses of coagulant, the turbidity after coagulation in the presence of the opoka in the amount of 5–15 mg·L⁻¹ substantially increases in comparison with cylinders without the opoka, which is a consequence of insufficient coverage of the surface of impurities, including particles of the opoka, by hydrolysis products. However, the dose of coagulant 7 mg·L⁻¹ allows to reduce the color and turbidity of water, as well as to a significant extent the residual aluminum content. However, the advantages of using the the opoka in the entire range of its concentrations compared to coagulation without the opoka were not observed. In addition, in all cases (Figure 2), the turbidity should be reduced to a drinking water standard of 1.5, which is 1.5mg·L⁻¹ (by kaolin).

| Sample  | Temperature, °C | pH   | Water colour index, degrees | Turbidity, mg·L⁻¹ |
|---------|----------------|------|---------------------------|------------------|
| Sample 1 | 21.5           | 7.50 | 20                         | 2.7              |
| Sample 2 | 1.2            | 8.10 | 12                         | 2.8              |
| Sample 3 | 1.0            | 7.80 | 42                         | 0.6              |
The results of coagulation of water with or without the opoka under low temperature conditions (Table 1, Sample 2) are shown in Figures 5 and 6. The water colour index after coagulation was 7–8 degrees in all cylinders. Obviously, the use of the opoka allows a significant reduction in the residual aluminum content (Figure 6): an average of 1.5-2.5 times to concentrations of 0.08–0.14mg⋅L\(^{-1}\).

On the other hand, a low temperature leads to a sharp increase in the viscosity of water, so in cylinders with opoka, a significant turbidity rise was observed (Figure 5) to values of 4.4–5.8mg⋅L\(^{-1}\) compared with cylinders without the opoka, where the turbidity was 2.2–3 mg⋅L\(^{-1}\). However, the turbidity does not exceed the normalized value of the turbidity after the stay of water in the sedimentation tanks (not more than 8-12 mg⋅L\(^{-1}\)). This allows you to feed water after turbidity on the fast filters with a load of quartz sand.
Further, a two-stage water purification (sedimentation-filtration) was investigated after opacification with an opoka to achieve a turbidity of 6.7 mg \( \cdot \) L\(^{-1}\) compared with the control without the opoka. The results are shown in Table 2.

**Table 2.** The efficiency of the opoka with a two-stage water purification scheme (Sample 3).

| Presence of an opacifier | After coagulation and sedimentation | After filtering |
|--------------------------|-------------------------------------|----------------|
|                          | Turbidity, mg\( \cdot \)L\(^{-1}\) | Water colour index, degrees | Turbidity, mg\( \cdot \)L\(^{-1}\) | Water colour index, degrees | Aluminum content, mg\( \cdot \)L\(^{-1}\) |
| With opoka               | 7.4                                 | 23.0            | 0.0                                   | 14.3                       | 0.16                        |
| Without opoka            | 2.8                                 | 31.0            | 0.0                                   | 18.4                       | 0.28                        |

At the settling stage, the turbidity in the case of using the opoka naturally increases to 7.4 mg \( \cdot \) L\(^{-1}\), however, the water colour index is reduced to 23 degrees, which is 25 % lower than without the opoka. At the same time, the filtering step allows not only to effectively reduce the water colour index, but also to achieve low concentrations of residual aluminum. At the same time, due to sorption on the opoka, it is possible to extract 42% more coagulant than without it.

**4. Conclusion**

Thus, dosing the opoka in the form of pulp before the introduction of the coagulant contributes to the intensification of coagulation of surface waters with low turbidity and water colour index in low temperature conditions (1.0 – 1.2°C).

Deficient doses of coagulant when combined with the opoka do not give a satisfactory result, because the degree of coating of particles with products of hydrolysis of the coagulant is insufficient.

The sedimentation after the introduction of the opoka and the coagulant does not sufficiently reduce the turbidity, therefore, a filtration step is additionally required which not only reduces the turbidity and water colour index, but also achieves lower concentrations of the residual coagulant due to sorption of the aluminum sulfate hydrolysis products on the flocculation particles.
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