Comparison of the effectiveness of mineral and mixed coagulants in the lightening of water from a surface source

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Abstract. The results of experimental studies of the coagulation treatment of the Sura River water in the autumn period and during high water with the use of mixed coagulants based on aluminum sulfate (AS), polyaluminum chloride “AQUA-AURAT 18” (PACl) and organic coagulant FL 4540 are presented. When treating river water with a low temperature, the use of mixed organic and mineral coagulants allows for a more significant reduction in the turbidity of the settled water compared to mineral coagulants AS and PACl at the same doses. Mixed coagulants with a weight ratio of FL 4540: AS (or FL 4540: PACl) equal to 1:4 have a greater efficiency of action compared to coagulants with a ratio of organic and mineral parts equal to 1:1. When treating low-turbidity water with a low temperature in the autumn period, the highest effect of clarification by settling was obtained using mixed coagulants based on PACl and FL 4540. At a standard mixing time of the initial river water with coagulants of 2 min, the use of a mixed coagulant K3 based on PACl and FL 4540 allows getting the same lightening effect as when using only PACl, but with doses lower by 30%. Experimental data on the coagulation treatment of the source water with low alkalinity and increased turbidity during the flood showed the greatest effectiveness of the mixed coagulant K1 based on AS and FL 4540, the use of which, with a mixing time of 2 minutes with the source water, reduces the dose of AS by 10% with the same settling effect. Increasing the mixing time with water to 15 minutes increases the effectiveness of the mixed coagulants, which in this case can reduce the doses of AS and PACl by 1.6-2 times without compromising the quality of clarified water by settling.

1. Introduction

The coagulation of natural water impurities is carried out using mineral or organic coagulants. Aluminum-containing mineral coagulants are widely used in water treatment plants in Russia and abroad for the reagent treatment of natural surface waters. The most commonly used coagulant in national water treatment plants is aluminum sulfate (AS). As an alternative to AS, pre-hydrolyzed polyaluminum chloride (PACl) has been used for many years, the properties of which have been studied by many authors \cite{1-9}. Studies showed that the coagulation mechanisms of the reagents AS and PACl are different. After dosing into water, AS is hydrolyzed, and then the processes of aggregation of impurities and precipitation occur. The aluminum hydroxide Al(OH)\textsubscript{3} formed as a result of the hydrolysis of AS has a low solubility at neutral pH values and can remove impurities from water due to their capture by precipitating flakes and adsorption. PACl also forms flakes at sufficiently high pH values, but the polymer structure of PACl destabilizes impurities faster and allows it to retain on its surface a solid phase of water impurities of various nature with a wider range of characteristics, electrophoretic mobility and solubility compared to Al(OH)\textsubscript{3} \cite{3}. The experience of operating water treatment plants in Russia has shown that at low temperatures of natural water, the hydrolysis of AS
occurs slowly with the formation of small and light flakes of Al(OH)$_3$, which leads to a deterioration in the sedimentation processes of suspended substances. In such conditions, the use of PACI may be more appropriate, as this coagulant is able to work effectively in a wide range of natural water temperatures [10, 11].

In recent years, synthetic organic coagulants in the form of melamine formaldehyde, epichlorohydrin dimethylamine (or epiDMA) and deallyldimethyl ammonium polychloride (or PolyDADMAC) have been used in water treatment practice [11, 12]. Organic coagulants have a cationic charge and a molecular weight of $10^4$ to $10^5$, and their use is advisable in the purification of natural surface waters from fine suspended solids and colloidal particles with a low zeta potential due to the action of the bridge coagulation mechanism [12, 13]. The disadvantages of organic coagulants when used independently include the need for prolonged and intensive mixing with the source water (at least 20 minutes) to achieve a high clarification effect by settling [14, 15] and a sharp deterioration in the quality of the settled water, even with a slight deviation from the optimal dose of the coagulant in the direction of increase [16].

In some cases, when conducting experiments or industrial tests, it is noted that a single organic coagulant cannot provide the required quality of clarified water in comparison with a mineral coagulant [17], therefore, the joint use of both types of coagulants is of some practical interest.

Regardless of the type of coagulant, the rate of change in the numerical concentration of water impurity particles during the formation of coagulation structures (aggregates) and their destruction can be represented by the following balance equation [18, 19, 20]

$$\frac{dN_i}{dt} = N_{i-1} \sum_{j=1}^{l_{max}} 2^{j-1} \alpha_{i-1,j} \beta_{i,j} N_j + \frac{1}{2} \alpha_{i-1,i} \beta_{i,i} N_i - N_i \sum_{j=1}^{l_{max}} \alpha_{i,j} \beta_{i,j} N_j - S N_i + \gamma_{j} S_{j} N_{j} \tag{1}$$

where $N_i$ – numerical concentration of particles in the $i$-th elementary volume of a liquid; $N_j$ – numerical concentration of particles in the $j$-th elementary volume; $t$ – coagulation time; $\beta$ – particle collision frequency factor; $\alpha$ – particle collision efficiency factor; $S$ – the constant of the specific rate of destruction of aggregates; $\gamma$ – function that characterizes the degree of destruction of aggregates; $l_{max}$ – the maximum number of elementary volumes of liquid in which the entire range of sizes of coagulated particles is located; $l_{max2}$ – the maximum number of elementary volumes of liquid, during the transition from which to the adjacent volume, the resulting aggregates are destroyed.

In orthokinetic coagulation (due to artificial mixing), the collision frequency factor of the coagulated particles is determined by the formula [21, 22]

$$\beta_{i,j} = C \cdot G \cdot (\sqrt{E_{i,j} r_i} + \sqrt{E_{j,i} r_j})^3, \tag{2}$$

where $G$ – mixing speed gradient; $C$ – coefficient equal to 1.33 for laminar mixing and 1.23 for turbulent mixing; $E_{i,j}$ – efficiency of the agglomeration process due to the hydrodynamic effect on particles or aggregates; $r_i$ and $r_j$ – radii of particles or aggregates in the $i$-th and $j$-th elementary volumes.

The collision efficiency factor $\alpha$ is exponentially dependent on the total energy of the interaction of particles and is inversely proportional to the square of the distance between the centers of the interacting particles. The total energy of the interaction, in turn, depends on the pH and temperature of the water, the concentration of dissolved salts, and the type and dose of the coagulant. When organic or mixed organomineral coagulants are added to water, the electrochemical properties of the surfaces of the impurity particles are modified, which leads to a change in their total energy, primarily due to the formation of bridging bonds. Thus, the presence of high-molecular coagulants in water can change the nature of the dependence of the intensity of formation and destruction of aggregates on external factors (the gradient of the mixing rate and time, temperature, pH).

The aim of the research, the results of which are presented in this paper, was to compare the effectiveness of mixed organomineral coagulants and individual aluminum-containing coagulants in the lightening of natural water with a surface source with low turbidity under different conditions of changing the mixing time of coagulants with water.
2. Materials and methods

The water of the Sura River with low temperature and low turbidity (typical for the autumn period), as well as with low temperature and increased turbidity during the flood period, was studied. During the flood period, river water was characterized by the following indicators:

- temperature 2.2 -2.3 degree;
- turbidity 67-70 mg/l;
- alkalinity 1.3-1.4 mmol/l;
- pH=7.22-7.24.

When conducting experiments in the autumn period (November) the river water quality indicators were within the following limits:

- temperature 3.8 -4.0 degree;
- turbidity 22-23 mg/l;
- alkalinity 2.5-2.6 mmol/l;
- pH=7.98-8.04.

As reagents for the preparation of mixed coagulants, we used:

- aluminum sulphate (AS) in the form of a 10% solution containing aluminum oxide in the commercial product 16%;
- polyaluminum chloride “AQUA-AURATE 18” (PACl) in the form of a 10% solution containing aluminum oxide in the commercial product 18%;
- organic cationic coagulant FL 4540 of the “FLOQUAT” series with a very high charge density in the form of a gel.

The concentration of the active substance PolyDADMAC in the coagulant FL 4540 reached 20%, the molecular weight of the reagent was in the range of 3×10^5.

In the experiments, 4 types of mixed organomineral coagulating compositions were used, the characteristics of which are presented in Table 1.

| Numbers of mixed coagulants | Percentage of mineral coagulant | Percentage of organic coagulant |
|-----------------------------|--------------------------------|--------------------------------|
| K1                          | 80% AS                         | 20% FL 4540                    |
| K2                          | 50% AS                         | 50% FL 4540                    |
| K3                          | 80% PACl                       | 20% FL 4540                    |
| K4                          | 50% PACl                       | 50% FL 4540                    |

In addition, separate coagulants AS and PACl were used in the experiments.

The laboratory test program provided for the treatment of samples of the initial river water with the studied coagulants at the values of the mixing rate gradient with a laboratory agitator G=180 s⁻¹. In the first series of experiments, the time of mixing the coagulants with water was 2 minutes, in the second series – 15 minutes. The agitator was then switched to slow mixing for 15 minutes at a speed gradient of G=20 s⁻¹. After the end of mixing, the samples were poured into glass cylinders with a capacity of 1 l each and settled for 40 minutes. Further, samples of clarified water were taken from the upper parts of the cylinders and analyzed for the content of residual turbidity, determined by the photometric method. In addition, in each series of experiments, the pH values of the settled water were determined.

The efficiency of lightening by settling of natural water treated with mixed and mineral coagulants was determined by the formula

\[ E = \frac{C_0 - C_1}{C_0} \cdot 100\% , \]  

where \( C_0 \) – turbidity of the source water, mg/l; \( C_1 \) – turbidity of water after settling, mg/l.
The doses of coagulants in the flood period ranged from 40 to 60 mg/l, in the autumn period – from 12 to 24 mg/l.

3. Results and discussion
In Fig. 1a and 1b are graphs of turbidity of settling water during high water treated with mixed and mineral coagulants. When the initial river water was mixed with coagulants for 2 minutes, the most significant decrease in its turbidity after settling occurred when using mixed coagulants K1 and K2 based on AS and FL 4540 with a dose of $D_c = 60$ mg/l (see Figure 1a). The efficiency of water sedimentation when treated with the coagulant K1 was 92% ($C_1 = 5.7$ mg/l), while when using only AS, the value of E did not exceed 89%. The same lightening effect as for AS with a dose of 60 mg/l (about 90%) was obtained when using the coagulant K1 with a dose of 50 mg/l.

Mixed coagulants based on PACl and FL 4540 (K3 and K4) also achieved a higher water settling efficiency (E = 82-84%) compared to using only one PACl coagulant, which showed an efficiency of 80.5%. The coagulation threshold for the mineral reagents AS and PACl was observed at a dose of 50 mg/l, and when using mixed coagulants – at a dose of 45 mg/l.

Increasing the mixing time to 15 minutes allowed increasing the effectiveness of the mixed coagulants. The value of the settling effect of suspended solids when using coagulants K1 and K2 with a dose of 60 mg/l was 93 and 92% with turbidity $C_1$ of the settled water of 4.8 and 5.6 mg/l (see Figure

![Graphs of the dependence of the settled water turbidity ($C_1$) on the coagulant doses ($D_c$) at the mixing time of the source water of increased turbidity with the coagulants: a – t=2 min, b – t=15 min: 1 – AS; 2 – PACl; 3 – K1; 4 – K2; 5 – K3; 6 – K4.](image-url)
1b). The effectiveness of mixed coagulants K3 and K4 at $D_c = 60 \text{ mg/l}$ rose to 85.7 and 84%, respectively. Mineral coagulants, on the contrary, showed less effectiveness ($E = 80.7\%$ for AS and $E = 78\%$ for PACl). The data obtained are in good agreement with the results of studies to determine the efficiency of mixing aluminum-containing coagulants with turbid water [23], which showed that an increase in the duration of mixing of coagulants with water to 10 minutes or more at $G = 184 \text{ s}^{-1}$ leads to the destruction of coagulation structures.

When using mineral coagulants with doses higher than 55 mg/l, the pH values of the settled water were 6.5–6.6 for the AS coagulant and 5.8–6.0 for the PACl “AQUA-AURAT 18” coagulant. In experiments with mixed coagulants K1 and K2, the pH values of lightened water were 6.74–6.77 at doses above 50 mg/l, and for coagulants K3 and K4, the pH values were 6.3–6.32 at the same doses.

The experimental data obtained during the treatment of river water with coagulants in the autumn period are shown in Fig. 2a and 2b.

![Figure 2](image1.png)

**Figure 2.** Graphs of the dependence of the settled water turbidity ($C_1$) on the coagulant doses ($D_c$) at the mixing time of the low-turbidity source water with the coagulants: a – $t = 2 \text{ min}$, b – $t = 15 \text{ min}$: 1 – AS; 2 – PACl; 3 – K1; 4 – K2; 5 – K3; 6 – K4.

In the first series of experiments with a mixing time of $t = 2 \text{ min}$, the best turbidity values for the settled water were obtained using mixed coagulants K3 and K4 based on PACl and FL 4540. The highest lightening effect was observed when mixed coagulant K3 was added to water at a dose of 24 mg/l ($C_1 = 6.3 \text{ mg/l}$, $E = 71.4\%$, see Figure 2a). For K4 and PACl coagulants, the settling efficiency was
69 and 66%, respectively, with the same dose. Mixed coagulants K1 and K2 based on AS and FL 4540 showed lower efficiency (52.7 and 51%, respectively), and when using only AS at Dc=24 mg/l, the settling efficiency was the lowest (E=44.5%).

In the second series of experiments, where the mixing time of the source water with the reagents was 15 minutes, the best results for water lightening (C<sub>1</sub>&lt;6 mg/l,) were obtained using the coagulants K3 and K4. The efficiency of turbidity removal at the dose of these coagulants Dc=24 mg/l was in the range of 73.6-77% (see Fig. 2b). The coagulants K1, K2 and PACl had the worst performance indicators (60, 52 and 49%), and the use of the coagulant AS under these mixing conditions gave an efficiency of 29%. The threshold of coagulation in mixed organomineral coagulants occurred at doses of 15 mg/l, and for mineral aluminum-containing coagulants it was observed at 18 mg/l. The pH value of the settled water in the case of the use of coagulants K3 and K4 with doses above 18 mg/l decreased to 7.35-7.4, and for the coagulants K1 and K2 it was in the range of 7.82-7.86. The addition of AS coagulant to water with doses above 21 mg/l reduced its pH value to 7.6-7.72, and the use of PACl coagulant gave a pH value of clarified water from 7.08 to 7.2.

The analysis of the obtained experimental data allowed drawing the following conclusions:

1. The use of mixed organomineral coagulants based on AS, PACl and FL 4540 for the treatment of low-temperature Sura water provides a higher turbidity removal effect compared to the use of only mineral coagulants AS and PACl with the same doses. Mixed coagulants with a weight ratio of organic and mineral parts equal to 1:4, to ensure a high quality of water lightening, are more preferable than mixed coagulants with a ratio of organic and mineral parts equal to 1:1.

2. When treating low-turbidity water with a low temperature, the highest effect of lightening by settling is obtained by using mixed coagulants based on PACl and FL 45 40. When the mixing time of the initial river water with coagulants is 2 minutes, the use of the mixed coagulant K3 with doses of 17-18 mg/l allows to achieve the same level of residual turbidity of the settled water as when it is treated with the coagulant PACl “AQUA-AURAT 18” with a dose of 24 mg/l. Increasing the mixing time with water to 15 minutes increases the effectiveness of the mixed coagulants, the use of which allows reducing the required dose of PACl by more than 2 times without compromising the quality of lightened water.

3. When treating river water with low temperature and high turbidity (flood), mixed coagulants based on AS and FL 4540 showed the greatest efficiency. The doses of the mixed coagulant K1 at the mixing time with the source water of 2 min can be reduced by 10% (from 60 to 54 mg/l) compared to the dose of AS without worsening the settling effect, and at the mixing time of 15 min – by 1.6 times (from 60 to 40 mg/l) while maintaining the same quality of lightened water.

The decrease in the effectiveness of PACl and mixed coagulants based on it during the flood can be explained by the fact that for the successful use of this coagulant, a sufficiently high alkaline reserve of the treated water is required.

4. **Summary**

The conducted experimental studies have shown the possibility of using mixed organomineral coagulants based on AS, PACl and FL 4540 for the treatment of Sura water in periods of low temperatures in order to reduce the doses of aluminum-containing coagulants when they are used independently. Mixed coagulants with a weight ratio of organic and mineral parts equal to 1:4 show the greatest effectiveness in clarifying water by settling, while their coagulating effect increases with increasing mixing time with the original river water. For the treatment of low – turbidity water with low temperature, mixed coagulants based on PACl and FL 4540 can be recommended, and for cold water with high turbidity, coagulants based on AS and FL 4540 can be recommended.
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