COMPARATIVE ANALYSIS OF EFFECTIVENESS OF POLVAK 15/72 AS A COAGULANT FOR DRINKING WATER PRODUCTION

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ABSTRACT

New coagulant Polvak 15/72 consisting of aluminum hydroxychloride with a pure Al_2O_3 content of at least 15.3 wt % was investigated as a possible highly effective agent for discoloration, clarification, and cleaning the natural freshwater to produce high-quality drinking water.

Water was taken from the river of Dnipro during the winter-summer period of 2022. A 20 mg dm^{-3} coagulant concentration showed sufficient water cleaning effectiveness, and brought its chromaticity, turbidity, permanganate oxidizability, aluminum and iron contents within the sanitary limits. This result has been achieved using a coagulant that does not consist of Fe (for which the toxicity is higher than that of Al) and less Al than in the widely used Polvak-68. The effectiveness of removing trihalomethanes (THM, mostly chloroform) by Polvak 15/72 is insufficient, and additional non-polar adsorbent or the use of a chlorine-free water disinfection technology is required to keep the content of THM within the sanitary limits.

Keywords: drinking water production, coagulation, discoloration, turbidity, permanganate oxidizability, Polvak coagulant.

INTRODUCTION

As available water resources become scarcer, the problem of high-quality drinking water production gains more and more topicality and acuteness [1, 2]. In many regions, this resource is deficient, which pushes the local population and authorities to look for alternative water sources such as desalination, the use of highly mineralized deep artesian water, and others [3 - 5]. Numerous approaches are used to bring the water quality parameters within the sanitary limits, and coagulation can be mentioned among them as an effective and multipurpose method of water treatment, which facilitates the elimination of suspended particles together with various toxic agents adsorbed on them: bacterial and chemical.

Coagulation requires the special agents, coagulants, to be added to the raw water. Since the particles suspended in natural water usually have a negative grain charge, the most effective coagulation can be performed by the small-size multicharged cations. Taking into account general toxicity, solubility, residual agent concentration, price, and some other reasons, various water-soluble compounds of Al^{3+} and Fe^{3+} are the most popular coagulants. Traditionally, they are used as "Alum" and "Ferric" - mixed hydroxychlorides or hydroxysulfates with variable composition. Their coagulating activity depends on the chemical composition, the suspended particles' nature, the granulometric size of the coagulant's particles, and some other parameters. When performing the coagulation of drinking water, the coagulant's influence on the organoleptic properties of water (color, taste, and odor), its toxicity, and water acidification because of partial hydrolysis of Al^{3+} and Fe^{3+} compounds should also be considered. In general, the coagulating effectiveness of the Ferric-based compositions is considered higher than that of the Alum-based ones, though the toxicity, residual coagulant concentration, and negative influence on the water pH and organoleptic properties of the former is worse [6 - 8]. That is why extensive efforts are still taken in the search for new effective compositions of the traditional Ferric and Alum coagulants as well as in the investigation of other organic and inorganic coagulation agents [6 - 10].

Even though Alum and Ferric materials have long been used as coagulants, their potential is not exhausted yet. Both compounds undergo partial hydrolysis upon contact with water, forming a complex combination of non-stoichiometric hydroxy salts and polymeric species [11, 12]. Thus, the adverse impact of pH shifting, water colorization (especially in the case of Fe^{3+}-based agents), and the presence of residual coagulant on the water quality can be diminished by using some preliminarily prepared compositions of hydroxy sulfates or hydroxy chlorides of Fe^{3+} or Al^{3+} instead of the pure salts.

When performing the coagulation treatment of water from open sources like rivers, it should be taken into consideration that the raw water quality may vary widely depending on the weather conditions, river flow rate, and some other parameters. Sometimes, the water quality may deteriorate significantly, which requires additional amounts of coagulants and other reagents to bring it within the sanitary limits. This imposes other requirements and restrictions on the potential coagulant's toxicity and its effect on the organoleptic parameters of water.

This article represents the results of the investigation of the coagulation activity of a new Alum-based agent, Polvak 15/72. It is a mixed composition of aluminum hydroxy chlorides with the general formula $Al_2(OH)_nCl_{6-n}$, consisting of at least 15.3 wt % pure aluminum oxide. This agent can be classified as a representative of the PAC (polyaluminumchloride) class of water coagulants.

EXPERIMENTAL

All investigations were carried out with the water samples taken during the winter-summer seasons of 2022 from the river Dnipro near the water intake points of the municipal water supply company of the city of Cherkasy, Ukraine, and the samples taken from the water cleaning equipment of the company. Raw river water samples were taken directly from the water intake pipeline, and the treated water samples were taken to determine their quality after preliminary coarse filtration, addition of a coagulant, settling, and secondary fine filtration, but without any additional disinfection.

The following water quality parameters were controlled: chromaticity, turbidity, permanganate oxidizability, residual chloroform, iron, and aluminum contents. All but the last parameters reflect the effectiveness of elimination of the unwanted components present in the source water that should be removed during its cleaning, while the last one represents the safety of the given coagulant, which brings some extra agents required for the coagulation that should be removed from the final product together with other pollutants before supplying water to the municipal network.

The chromaticity was determined in conventional degrees by the standard chromium-cobalt scale [14]: the reference solutions consisting of some particular amounts of $K_2Cr_2O_7$, $CoSO_4$, and sulfuric acid were used to build the calibrating graph of the solution absorbance at the wavelength 413 nm (against distilled water) vs conventional degrees. Then, the sample's absorbance was measured and converted into conventional degrees using this graph.

Water turbidity was determined as a mass of dry residue after complete evaporation of 1 dm^3 of water. Permanganate oxidizability was determined in mg O dm^{-3} according to [15]: same volumes of a solution consisting of an exactly known amount of $KMnO_4$ and H_2SO_4 were added to the experimental and control water samples. The samples were boiled for 2 h, and the concentration of $KMnO_4$ was determined in both mixtures. Oxygen consumption (as permanganate oxidizability) was calculated by a decrease in the concentration of $KMnO_4$ in the experimental solution due to the oxidation of various compounds in it, with the account of its natural decrease because of thermal decomposition as determined in the control sample.

Residual chloroform, iron, aluminum contents were determined in μg dm^{-3} (chloroform) or mg dm^{-3} (iron and aluminum) according to the corresponding officially approved methods. Chloroform was extracted from a water sample by the purified isooctane, and then its content was found using a gas chromatograph equipped with an electron capture detector and a 0.32 mm capillary column with the polyethyleneglycol-containing stationary phase [16].

Iron content was found by the following generalized procedure. All Fe^{3+} ions were reduced to Fe^{2+} by ascorbic acid. Then, the acetate buffer was added to a sample of water, followed by adding some particular amount of phenantroline. Sample absorbance was measured at 490 nm and then recalculated into Fe content by a preliminary built calibrating chart [17].

The content of aluminum was measured in water samples after reduction of interfering Fe^{3+} as described above, followed by adding a 1:2:22 reaction mixture of ammonium sulfate, aluminon, and acetate buffer. The measuring was performed photometrically at 540 nm using a preliminary built calibrating chart [18].

All further requirements to the sampling, samples preparation and treatment are given in details in the corresponding documents cited above.

When testing the coagulant's activity, it was added at the required technological stage to ensure the concentration of 20 mg dm^{-3}. This concentration was chosen in our investigation to compare the coagulation effectiveness of Polvak 15/72 with that of some other coagulants, for which 20 mg dm^{-3} was the highest applied concentration [13]. Further, the water was treated in the due way. During the experiments, the equipment involved in this investigation was temporarily disconnected from the municipal water supply network.

RESULTS AND DISCUSSION

A comparison between some water quality parameters of the raw and treated water samples, the coagulation of which was carried out by Polvak 15/72, is given in Fig. 1 - 5. The vertical bars in the Figs show the experimental error ranges of the corresponding data.

As seen from Fig. 1, this coagulant is effective and brings controlled water quality parameters within the corresponding sanitary limits. The water chromaticity increased in May and June because of the more intense proliferation of water protozoa and algae blooming, however, this parameter remained within

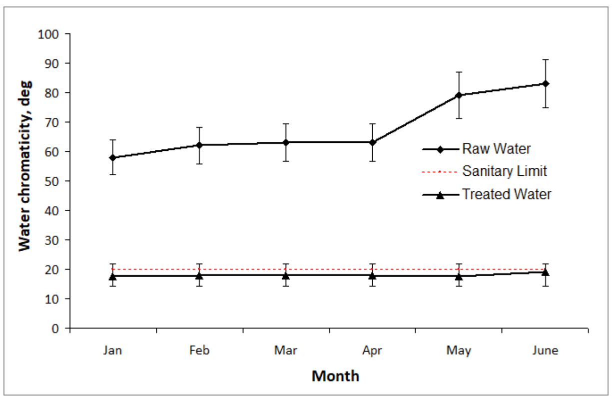

Fig. 1. Chromaticity of the raw and treated water samples after coagulation with Polvak 15/72.

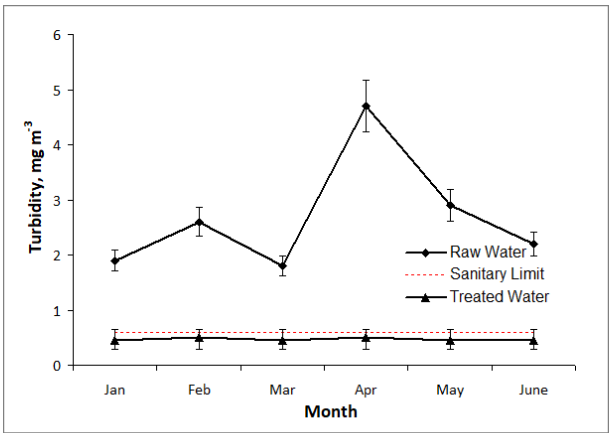

Fig. 2. Turbidity of the raw and treated water samples after coagulation with Polvak 15/72.

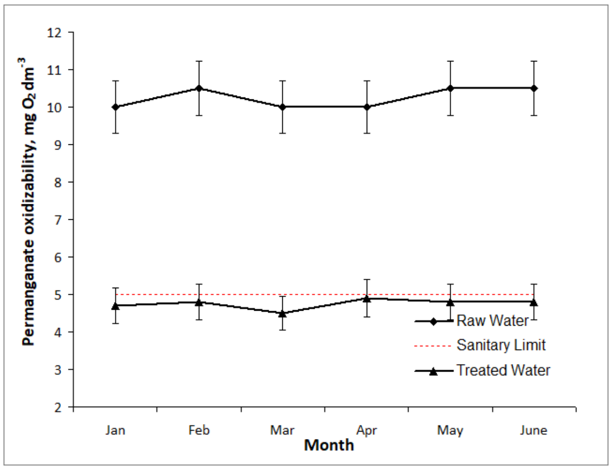

Fig. 3. Permanganate oxidizability of the raw and treated water samples after coagulation with Polvak 15/72.

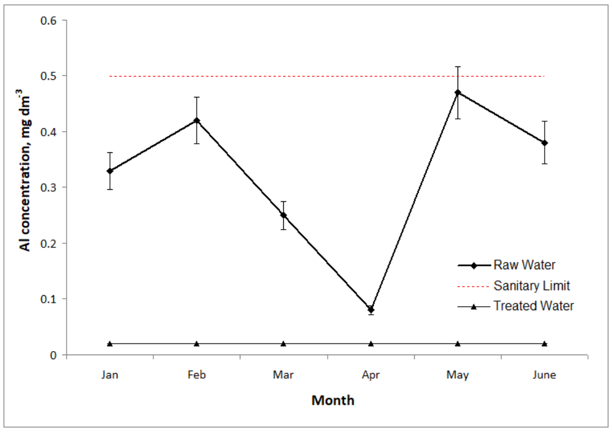

Fig. 4. Concentration of Al^{3+} in the raw and treated water samples after coagulation with Polvak 15/72.

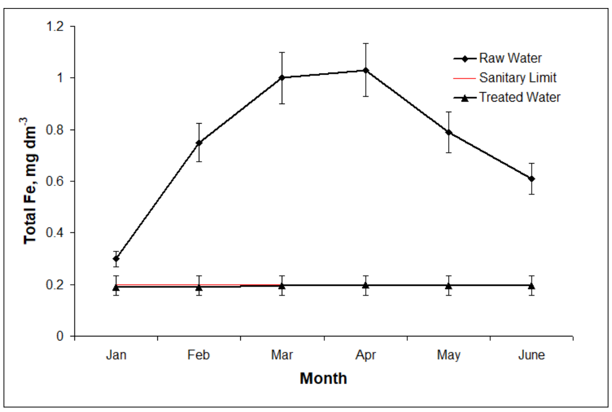

Fig. 5. Concentration of total iron in the raw and treated water samples after coagulation with Polvak 15/72.

the requirements, almost reaching the limit in June. Even though water turbidity increased significantly because of high water in April (Fig. 2), the turbidity of the treated water remained under the maximal value without the need to add an extra coagulant. Regarding the permanganate oxidizability, it did not change much over the period of investigation (Fig. 3), and a coagulant's concentration of 20 mg dm^{-3} was sufficient to keep this parameter within the required range.

An initial concentration of aluminum in fresh water is low because it comes from comparatively poorly soluble alumosilicates, and even if its soluble forms are present in water, they undergo intense hydrolysis [11]. The Al-based coagulant increases this concentration, but after the treatment, it never reached the maximal permissible value (Fig. 4). Some spread of Al^{3+} concentration in the treated water depends on the change in the pH of raw water, which significantly affects the depth of hydrolysis that determines the concentration of soluble aluminum.

The concentration of Fe^{3+}/Fe^{2+} in the treated water should also be controlled. This agent is not present in the coagulating agents used in our investigation. However, it is already present in raw water and must be extracted together with other pollutants. As seen in Fig. 5, the initial concentration of iron was always above the limits, but the flocks formed because of the coagulant, effectively captured this component and removed it. As a result, the concentration of iron dropped below the maximal permissible level.

Therefore, it can be concluded that this coagulant effectively decontaminates drinking water and removes excessive colorization, turbidity, organic pollutants, and iron, while extra aluminum added for coagulation does not result in exceeding its permissible concentration.

It is interesting to compare the performance of Polvak 15/72 with other coagulants that can be involved in water cleaning. I. Trus et al. reported the results of comparative study of the water cleaning effectiveness of various coagulants [13]. According to them, a 20 mg dm^{-3} of Polvak-68 ensured the water chromaticity of 19.3 - 20.5 degrees, which is quite close to the performance of the same concentration of Polvak 15/72 (Fig. 1). Since total Al content (as Al_2O_3) in Polvak-68 is higher than that in Polvak 15/72 (18.0 % and 15.3 % respectively) [13], Polvak 15/72 ensures almost the same water cleaning effectiveness

Table 1. Concentration of THM recalculated to pure chloroform in the drinking water after chlorination, coagulation, and filtration (maximal permissible concentration is 60 μg dm^{-3}).

Month	Jan	Feb	March	Apr	May	June
Content, μg dm^{-3}	48	52	64	58	60	58

at a lower amount of aluminum added to water. The effectiveness of other mixed Al/Fe coagulants reported by Trus et al. is even better, but since they bring extra Fe, for which the toxicity is higher than that of Al, the content of total Fe in the drinking water should be thoroughly controlled. Residual contents of Fe were not reported by Trus et al., so we cannot compare the effectiveness of total Fe removal by Polvak 15/72 with other agents [13].

Since the outdated indirect chlorination technology is still used to disinfect water (no chlorine gas is used, but some chemicals that release it when added to water), a content of highly-toxic THM in water should also be controlled. Table 1 represents the results of chloroform content determination.

As seen from Table 1, the concentration of THM remained below or slightly exceeded (in March) the sanitary limit. Such a low concentration of chloroform (60 μg dm^{-3}) is significantly below its solubility limit (8.09 g dm^{-3} at 20^{o}C). Therefore, it forms a genuine solution and should be removed by adsorption rather than by coagulation that affects the colloidal pollutants, but is ineffective against the dissolved ones. Since chloroform is a low-polar compound, while aluminum hydroxychloride is a highly polar one, the adsorption of chloroform on that adsorbent cannot be high, and either specific non-polar adsorbent or another chlorination-free disinfection technology should be employed to decrease the content of THM in drinking water.

CONCLUSIONS

Polvak 15/72 provides sufficient water cleaning effectiveness and brings water chromaticity, turbidity, permanganate oxidizability, and the contents of iron and aluminum within the sanitary limits. This result can be achieved by a 20 mg dm^{-3} concentration of the coagulant. Since the content of Al in Polvak 15/72 is lower than that in other traditional Al-based coagulants, and it does not contain Fe, the use of Polvak 15/72 in the production of drinking water seems safer and more effective than Polvak-68 or the mixed Al/Fe agents.

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