

The effect of ozone technology in the process of surface water decontamination on coagulants and filters

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Abstract. The presence of natural organic matter (NOM) poses many challenges in the process of purifying water intended for drinking. The presence of NOM leads to high coloration due to natural conditions. During the coagulation and flocculation processes, NOM stabilizes dispersed and colloidal particles. Currently, there are many methods for removing natural organic matter. In Kazakhstan, coagulation is commonly used for treating most waters, which effectively reduces color and NOM. It is known that the efficiency of ozonation and coagulation is high when they are used together. The impact of ozonation on the properties of coagulation is significant because coagulation is the most widespread process for treating drinking water. The combination of ozonation with coagulation has been proposed as an improved method for reducing coloration and removing surfactants. The studies were conducted at the K.I. Satpayev Kazakh National Technical University, where a liquid phase ozonation laboratory system was developed. The aim of the research was to demonstrate the positive effect of combining ozonation with coagulation on the removal of color and surfactants in surface waters. Studies were conducted on model waters with different contents of humic substances. Positive results were obtained at low concentrations of ozone (0.1...0.8 mg/l) and low doses of coagulant. A low dose of ozone showed improvement for coagulation. The results of the study indicate that ozonation, combined with coagulation, has a positive effect on color removal, enhances the removal of NOM, and reduces the necessary dose of coagulant.

1. Introduction

Over the past decade, the issue of providing the population with quality drinking water has become increasingly urgent. On one hand, this is due to the deterioration in the quality of natural water bodies as a result of anthropogenic impact, and on the other hand, it is due to the increasing requirements for drinking water quality [1]. Accordingly, the development and improvement of technologies for purifying and disinfecting surface waters have become priority directions in the field of water treatment. Ozone technology has started to be widely used in the processes of disinfecting surface waters due to its high efficiency in destroying bacteria, viruses, and other microorganisms, as well as its ability to oxidize organic and inorganic substances [2, 3, 4]. However, the introduction of ozone technology not only offers opportunities but also presents challenges, especially in the context of its interaction with filter systems used in water treatment plants.

Natural organic matter consists of complex organic substances synthesized or produced in the lithosphere. Until recently, it was believed that humic substances comprise NOM. However, the development of research on humic substances has led to several confused definitions used by different researchers, which should be considered outdated. In the last decade, the scientific community, including ecologists, chemists, and biologists, has gradually accepted that dissolved organic substances participate in all reactions in water systems. NOM is a very complex mixture of decomposition products of plants and microorganisms [5].

Organic substances significantly affect the fate of inorganic colloids in water. The chemical nature and structure of surfactants are important factors determining the stability or instability of colloids to NOM. Fulvic acids can provide colloids with a negative charge and potentially act as coatings. Organic carbon colloids, especially those with chain structures, can aggregate inorganic colloids through bridging. The significance of each process depends on the nature

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and concentration of organic substances, as well as other factors (for example, the origin of NOM, temperature, water purification process) [6, 7]. For many water treatment works, it is common practice to introduce pre-chlorination or pre-ozonation operations in water hydraulic structures [8, 9].

Two possible mechanisms of ozone's effect on coagulation were proposed 30 years ago, in 1993 [10]:

- Oxidation of adsorbed organic substances, their hydrophilization, and eventually desorption lead to destabilization of particles;
- Catalytic polymerization of DOC and subsequent bridge adsorption. The effect of pre-ozonation depends on many factors, including the properties of the organic substance, pH, type of coagulant, and concentration of calcium in the water.

Twenty years ago, in the early 2000s, Schneider O. D., Tobiason J. E. discovered that when pre-ozonation was used as a coagulant, it made the removal of turbidity and DOC more difficult. However, the use of cationic polymers and pre-ozonation both led to a small, but statistically significant improvement in removal [11]. The authors suggested that pre-ozonation reduces the surface charge of particles, which improves coagulation through charge neutralization. Similarly, in 1996, Chandrakantha, M., and others also studied the effects of pre-ozonation on DOC, finding that destabilization of ozone-generated particles only occurred in the presence of calcium [12].

It has long been known that ozone can improve the efficiency of coagulation and filtration. Bose P., Reckhow D. A. collected data from a large water treatment plant and showed that pre-ozonation is more effective than pre-chlorination filters in reducing turbidity [13]. In 2001, Becker W. C., O'Melia C. R. reviewed the effects of ozone on coagulation and filtration processes [14]. Despite its many advantages, the cost of ozone is significant, and its deployment in a treatment facility should be chosen with an understanding of its impact on other processes. They reported the effect of ozone on coagulation, which can be adjusted based on water quality and the type of coagulant. The optimal dose of coagulant in water with medium and high levels of DOC is determined by the amount of DOC. Ozonation converts DOC into smaller, oxygen-saturated compounds, which have a greater effect on the metal coagulant than the original compounds. In this case, ozonation might lead to an increase in the optimal doses of coagulant [15]. Ozonation can react with adsorbed DOC, changing the number and conformation of adsorbed organic particles, potentially leading to a reduction in the coagulant dose. In 2004, Wei L., Yong-Mei L. reported that NOM has a strong effect on the stability of inorganic particles through adsorption, coating, etc., making effective water surface treatment through coagulation difficult when NOM concentration is high [16].

There is no evidence for the disruption or desorption of organic coatings on particles leading to the destabilization of expanded particles. Generally, all phenomena of destabilization of ozone-generated particles are primarily caused by a decrease in pH, an increase in pH, or the oxidation and settling of CaCO_3 , as well as heavy metals such as iron and manganese ions [17, 18]. Despite all its positive aspects, the effect of ozonation on coagulation needs further detailed research, especially the effect of low doses of ozone on the destruction of natural organic substances and dissolved organic carbon (DOC), as well as the effect of ozonation in different pH processes and with different coagulants. Therefore, the objectives of this study are to demonstrate the positive effect of ozonation on coagulation for the removal of natural organic substances, as well as to determine the optimal dose of ozone and pH, and the optimal dose of coagulant to be introduced for the treatment of natural surface waters. However, it is important to note that analyzing the effect of ozone technology on the disinfection process of surface waters on sedimentation and filters is a primary goal. The study will consider the potential positive aspects of using ozone, such as improving filtration quality and reducing the concentration of harmful substances in treated water, including the wear of filter elements and the emergence of secondary pollutants, as well as the effectiveness of coagulation in color removal during ozonation, ultraviolet (UV) range from 210 to 410 nm [22], and changes in NOM before and after ozonation using a laser particle size analyzer.

This research is based on the analysis of modern scientific literature, as well as the results of experimental works conducted in laboratories and real situations. It highlights the need for a comprehensive approach to assessing the effectiveness of ozone technology, which considers not only its high disinfection potential but also its impact on the elements of the water purification system, specifically sedimentation and filters.

Introducing ozone technology into the process of disinfecting surface waters opens up new possibilities for improving the quality of drinking water. However, to achieve positive results, it is necessary to thoroughly understand all processes occurring in the system and develop optimal solutions to minimize potential adverse effects. This article offers a comprehensive perspective on the issue, contributing to the further development and efficiency enhancement of water purification technologies.

2. Materials and Methods

The methodology of the scientific research. The scientific research work was conducted at the K.I. Satpayev Kazakh National Technical Research University. Experimental trials were carried out using the ETRO-02 ozonator device,

which is based on a special electrical discharge method [19, 20]. The laboratory device's generator is shown in Figure 1 below.



Fig. 1. Laboratory ozonator generator

For the studies, a laboratory system for liquid-phase ozonation was created. The schematic of the laboratory system is shown in Figure 2. The digital spectral correlation method was used to control the operation of the ozonator and to increase its efficiency. The digital spectral correlation method improves the reconstruction of the analytical signal for processing the incomplete spectrum of a signal [23, 24].

High-oxygen content air (80%) is passed from the oxygen block to the ozone generator by dehumidifying the internal air. After the generator, the ozone-air mixture is delivered to the reactor, which has a magnetic stirrer and a sensor for monitoring ozone in the solution, through a delivery regulator. The monitoring of ozone in the solution consists of the measurement block and the control device DOSA Control DCW 120 MF, and the ozone sensor OZ7H. The sensor analyzes the ozone concentration in the water and sends a signal to the measurement and monitoring device. This research uses liquid-phase ozonation. Initially, ozone-air mixtures are passed through water models at various pH levels and ozone doses, followed by coagulation with different coagulants and coagulant doses. The studies were conducted on water models consisting of sodium salts of humic acids (for color – 55...60), bentonite (for turbidity – 1...2), and NaHCO_3 – 0.5 mmol/L (for buffer capacity).

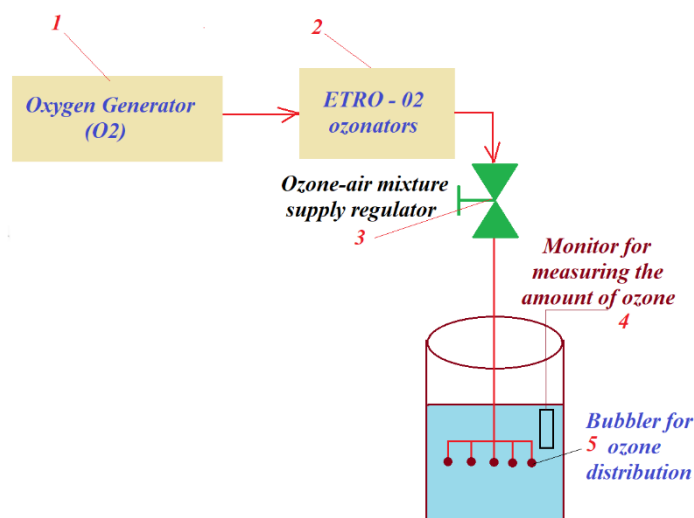


Fig. 2. Structural Schematic of the Laboratory Device for Ozonation

The diagram includes: 1) Oxygen generator (O₂) - where oxygen (O₂) is produced; 2) ETRO-02 ozonator - ozone generators where oxygen is converted into ozone (O₃); 3) Ozone-air mixture delivery regulator - this device regulates the pressure and flow of the ozone and air mixture; 4) Monitor for measuring the amount of ozone; 5) Diffuser for dispersing ozone into the liquid. In the diagram, the diffuser is placed inside a cylinder filled with water, where ozone is dispersed into the liquid in the form of fine bubbles. Overall, this structural schematic represents the layout of a laboratory device designed for various applications of ozone in water purification or disinfection.

During the scientific research work, ozone concentrations of 0.1 - 0.8 mg/L and a hydrogen index of 7 - 9 pH were used for ozonating the water. Two types of coagulants were used in the research work: PIX 318 and PAX 18, and three different doses of each were analyzed (Table 1). The plan for the experimental works is shown in Figure 3.

Several types of sample works were conducted in the experimental works: 1) Sample water without chemicals; 2) Sample water after pH adjustment (with HCl or NaOH added); 3) Sample water after ozonation; 4) Water after coagulation; 5) Water before coagulation and after ozonation.

Table 1. Types of Coagulants and Their Dosage Range

Coagulation	PIX 318	46,6 $\mu\text{mol Fe/l}$	77,7 $\mu\text{mol Fe/l}$	108,8 $\mu\text{mol Fe/l}$
	PAX 18	45,7 $\mu\text{mol Al/l}$	68,5 $\mu\text{mol Al/l}$	114,2 $\mu\text{mol Al/l}$

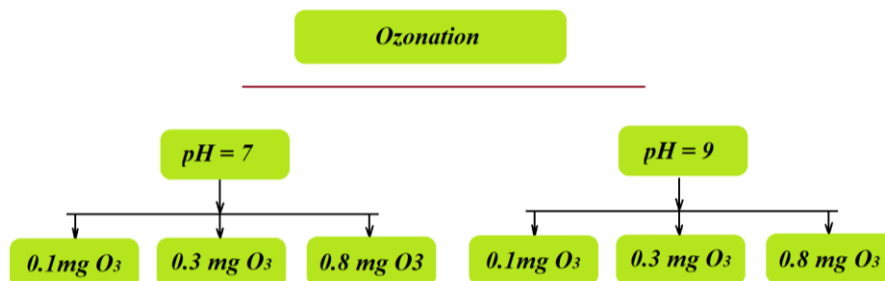


Fig. 3. Experimental Scheme for Ozone Concentration According to pH Levels

During the experimental work, the color was measured on the Pt/Co scale using a Hach Lange DR-3900 spectrophotometer at a wavelength of 410 nm, as well as with a UV-5800PC VIS spectrophotometer at wavelengths of 210 and 410 nm. Additionally, during coagulation, the settling of sediments was monitored using a 2100Q portable turbidity meter. Furthermore, to determine the change in particle size in the model water before and after ozonation, analysis was conducted with a Mastersizer analyzer, using the Mastersizer 3000 laser particle size analyzer – a general tool for the rapid and accurate analysis of the particle size distribution (by size) of suspensions, emulsions, and dry powders. The method is based on measuring the angular dependence of the intensity of scattered light as a laser beam passes through the sample.

3. Results and Discussion

For the qualitative assessment of the ozonation process, a total of 9 water samples were analyzed on the MasterSizer. However, due to the high sensitivity of the method and the low concentration of particles in the water, only a few samples showed positive results. The results of the research work are shown in Figure 4.

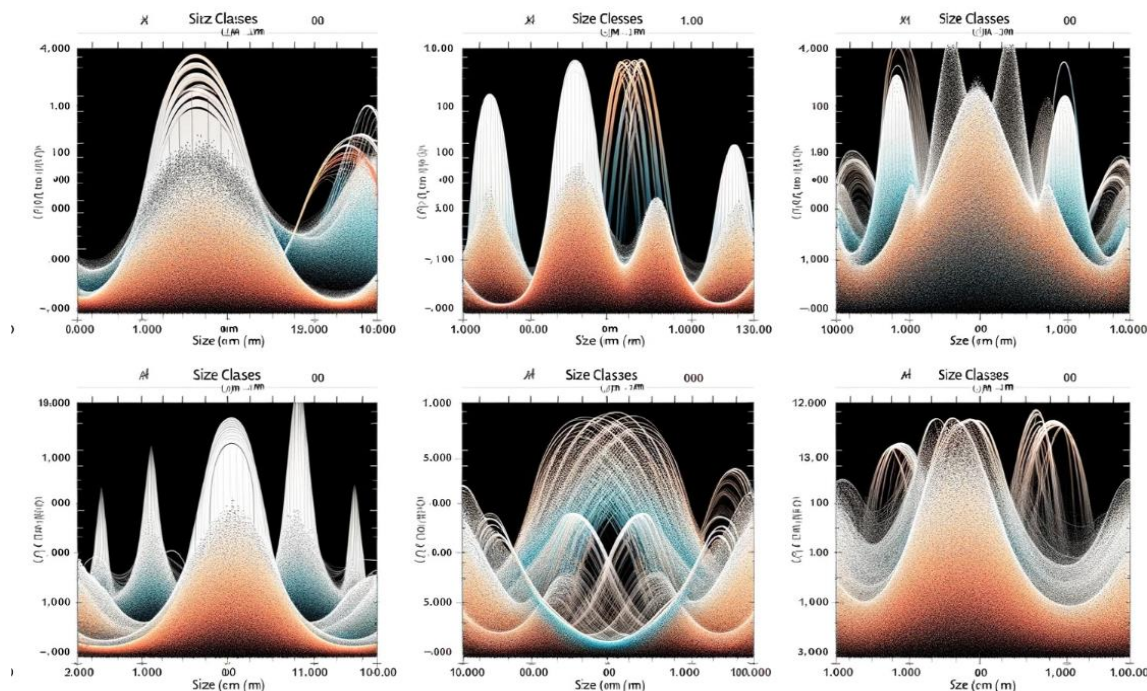


Fig. 4. Change in the Size of Model Water Particles Before and After Ozonation

Figure 4 presents a series of graphs that illustrate the change in the size of model water particles before and after the effect of ozonation. The scale units are given in micrometers (μm). The upper three graphs and the lower three graphs on the left side display various effects on the sizes and numerical distribution of the particles. It shows the initial sizes of the particles before ozonation and the changes they undergo during ozonation: a decrease in particle size or the breaking down of larger particles into smaller ones can be observed. The numbers and text above and below each graph indicate their series, the dose of ozone, and the pH level. Each corresponds to specific parameters of the ozonation process. Similar research work was conducted by Vereshchuk, N., and his colleagues (Figure 5) [21].

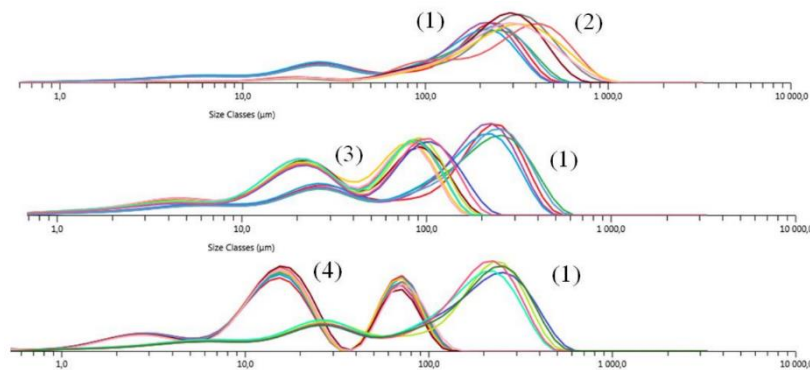


Fig. 5. Change in the Size of Model Water Particles Before and After Ozonation: Model Water (1), Model Water After Ozonation with a Dose of 0.2 ppm (pH 9) (2), Model Water After Ozonation with a Dose of 0.5 ppm (pH 9) (3), Model Water After Ozonation with a Dose of 0.8 ppm (pH 9) (4) [21]

This figure displays four linear graphs. Each graph represents the change in the size of model water sample particles after the effect of ozonation. The variously colored lines on the graph show how the ozonation effect has impacted the particle size over different time intervals. The X-axis shows the size of the particles in micrometers, while the Y-axis indicates the frequency distribution of the sizes. Each individual line on the graph corresponds to a water sample treated with a specific dose of ozone (ppm) and pH level. From the graph, it is observable that as the ozone dose increases (from 0.2 to 0.8 ppm), the particle size uniformly and comparatively shifts towards becoming smaller. To understand the data from these graphs, it is necessary to know the properties of the water sample particles when interacted with ozone and how they changed. The data graphs allow for the analysis of the composition of model water and the changes in particle mass after ozone treatment, where changes are determined according to different ozone doses (pH 9). Low doses of ozone positively affect the efficiency of further improving coagulation, by altering the size of the particles and dividing them for easier flocculation. Through analyzing the research data and literature, it can be concluded that ozone can simultaneously aggregate small particles and break down large particles, making them mineralized and easier to remove. This information is crucial for water purification processes as it helps in evaluating the efficiency of ozone treatment. Ozonation - the initial test for coagulation was conducted for an aluminum-based coagulant - PAX 18. Relevant tests were carried out, and their results are shown in Figures 6 and 7. From the graphs, it can be inferred that low dose ozone coagulation showed improvements. Using only 20 μmol Al/L PAX coagulant demonstrated a removal of approximately 70 - 80% of color when ozonation was not applied. Therefore, ozonation allows for a reduction in the amount of PAX coagulant needed, which is sufficient to achieve satisfactory levels of color removal.

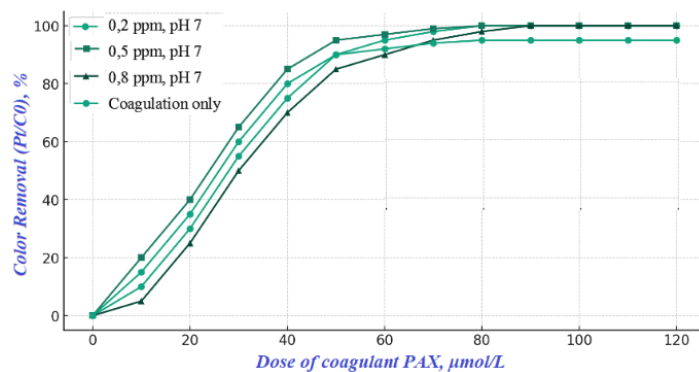


Fig. 6. Relationship between the removal of color (%) at pH 7 for various ozone concentrations (ppm) and the dosage of PAX 18 coagulant

This graph shows the efficiency of color removal (%) at pH 7 with different ozone concentrations (ppm) using PAX 18 coagulant. The X-axis represents the dosage of the coagulant in micromoles per milliliter, while the Y-axis indicates the percentage of color removal. There are four lines on the graph:

- 0.2 ppm ozone and pH 7;
- 0.5 ppm ozone and pH 7;
- 0.8 ppm ozone and pH 7;
- Coagulation only (without ozonation).

From this graph, it can be observed that the efficiency of color removal improves with an increase in the ozone dose. Higher doses of ozone are more effective compared to coagulation with a 0.2 ppm dose of ozone. The graph also shows that there is a maximum efficiency of color removal at a certain dose of coagulant, and further increasing the dose has a diminished effect on efficiency. Without ozonation, the efficiency of color removal is the lowest, indicating that ozonation enhances the coagulation process.

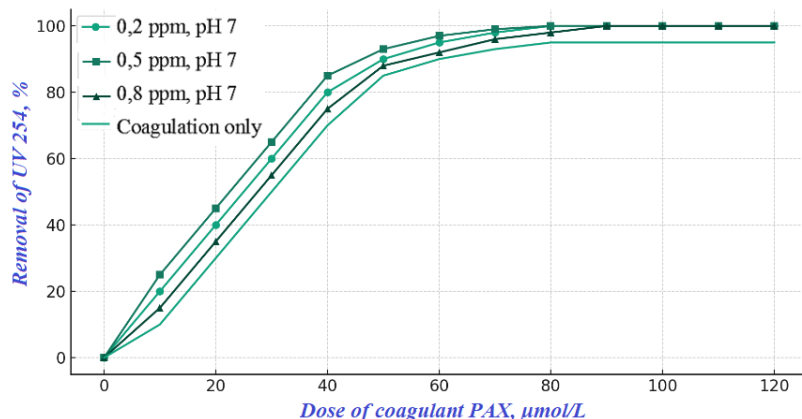


Fig. 7. Relationship between UV 254 removal and the dosage of PAX 18 coagulant at pH 7 for various ozone concentrations (ppm)

This graph in Figure 7 illustrates the relationship between the efficiency of UV 254 removal and the dosage of the PAX coagulant at pH 7 for different ozone concentrations (0.2 ppm, 0.5 ppm, 0.8 ppm). The graph, composed of four lines, presents the following information:

- The lowest efficiency of removal (blue line) is shown using the coagulation method alone, which demonstrates how effective the process is without the application of ozone but only with the coagulant;
- The three other lines (green, black, and brown) display the efficiency of various doses of the coagulant at pH 7 under different ozone concentrations.

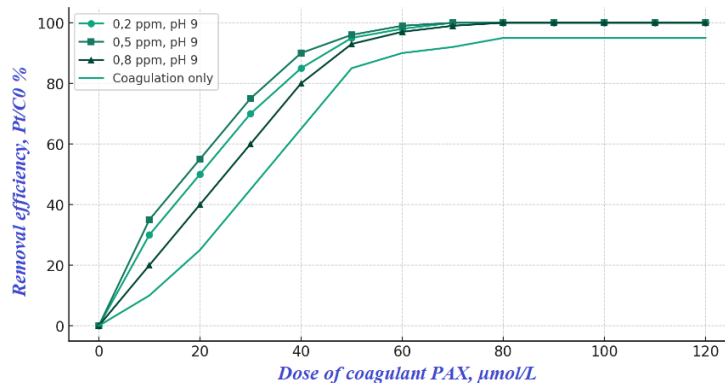


Fig. 8. Relationship between color removal (%) at pH 9 for various ozone concentrations (ppm) and the dosage of PAX 18 coagulant

As indicated by the graph, generally, an increase in the coagulant dose leads to higher UV removal efficiency, but after a certain dose, this increase stabilizes, reaching a limit of efficiency. The rise in ozone concentration leads to higher efficiency, which suggests that ozone amplifies the coagulation process. This graph could be useful for optimizing coagulant dosage and ozone application in water purification or chemical processing procedures. The

increase in ozone concentration leads to higher efficiency, indicating that ozone strengthens the coagulation process. This data could be beneficial for optimizing coagulant dosage and the use of ozone in water treatment or chemical processing.

The following step involved studying the same coagulant and coagulant dosages but with a different ozonation process around pH 9. Corresponding experiments were conducted, the results of which are presented in the subsequent Figure 8.

This Figure 8 demonstrates the dependency of color removal efficiency on the dosage of the PAX coagulant in the water purification process. The green lines in the graph show the efficiency of color removal at different ozone concentrations (0.2 ppm, 0.5 ppm, and 0.8 ppm) and when only the coagulation process is used, all measured at a pH value of 9. All lines exhibit an upward trend, indicating that as the coagulant dosage increases, the efficiency of color removal also increases. This increase stabilizes after reaching a certain dosage, indicating the saturation of the color removal process (reaching full efficiency). The gaps between the lines demonstrate the impact of ozone concentration on the color removal process. Additionally, the line for the coagulation process alone shows a slight difference from the others, indicating that ozone enhances the coagulation process. This research could be significant in the field of water treatment, as it provides necessary data for optimizing the dosage and quality of the coagulant. This can improve economic efficiency and environmental sustainability.

In addition, another promising and environmentally friendly way to solve these problems is pre-sowing treatment of seeds and plants with ozone. An analysis of a number of studies [25-30] has shown that ozone has a positive effect on seed germination, plant growth and development when using moisture measurement systems, helps to increase yields and can be used to combat mildew.

4. Conclusions

The results of this scientific research conclude that pre-coagulation ozonation positively affects color removal, which is associated with the presence of natural organic matter (NOM) and dissolved organic carbon (DOC), enhancing the removal of NOM through coagulation and also allowing for a reduction in coagulant dosage by up to two-fold. Low doses of ozone can control the fragmentation of humic substances, avoiding a decrease in molecular mass which could impair flocculation, particularly deteriorating the complete removal of NOM. This indicates that low doses of ozone improve coagulation. By utilizing a dosage of approximately 20 $\mu\text{mol Al/L}$ PAX coagulant, it is possible to reduce color by about 70 - 80% with and without ozonation, respectively, suggesting that ozonation can reduce the amount of PAX coagulant needed for satisfactory color removal. Analysis of data and literature sources indicates that the quantity of NOM with average molecular masses increases during low-dose ozonation, which facilitates ozonation in simultaneously aggregating small particles and breaking down larger ones, making them more susceptible and easier to remove through coagulation. The use of ozone in various industries ensures environmental safety, especially in agriculture.

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