Impact of ozonation on coagulation properties in drinking water treatment

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Abstract

The presence of Natural Organic Matter (NOM) cause many problems for the process of drinking water treatment. Major problems result from the reaction of NOMs in various ways in the treatment processes. At present there are set of methods for removal of NOM, namely a biofiltration and a nanofiltration, coagulation as well as advanced oxidizing processes. It was offered to use ozonation in combination with coagulation as an advance method for removal color and NOM. The studies were conducted at Norwegian University of Life Sciences, where the laboratory system of liquid-phase ozonation was developed. The purpose of scientific work was to prove positive influence of combination coagulation with ozonation on removal of color and NOM in surface water. Studies were conducted on model waters with the different content of humic compounds. Were observed positive results at small concentrations of ozone (0.2…0.8 ppm) and at small coagulation dose. Using only 20 µmol Al/l dosage PAX coagulant showed the color removal 80% and 70% with and without pre-ozonation, respectively. That is why ozonation can reduce the amount of PAX coagulant to achieve a satisfactory color removal as well as in generally low dose of ozone showed an improvement for coagulation.

Keywords: Optimization of coagulation; dissolved organic carbon; humic compounds, natural organic matter; ozonation.

Introduction

Natural organic matter consists of complex organic matter, which is synthesized or produced in the lithosphere. Until recently, humic substances were considered to include NOM. However, the evolution of research on humic substances has led to several confusing definitions used by various investigators and must be considered to be outdated. During the last decade, the environmental scientific community including ecologists, chemists, and biologists has gradually realized that the dissolved organic matter is involved in essentially all reactions in aquatic systems. NOM is an extremely complicated mixture of degradation products from plants and micro-organisms.

Organic matter has a great influence over the fate of inorganic colloids in water. The chemical nature and structure of NOM will be an important factor in determining whether colloids will be stabilized or destabilized by NOM. Fulvic acids are likely to be responsible for coating and imparting a negative charge to colloids. If the adsorbed organic coating produced and increase in absolute surface potential, it will act to stabilize colloids in the water column. On other hand, colloid organic carbon, especially chain-like structures can aggregate inorganic colloids through the formation of bridges. The importance of each process depends on nature and concentration of organic matter, as well as on other factors (e.g. origin of NOM, temperature, water treatment process).

The efficiency of ozonation as well as coagulation is reported to be higher when used in combination. The effects of ozonation combined with coagulants are not adequately documented. The impact of ozonation on coagulation properties is valuable to study as coagulation is the world's most widely used treatment process for drinking water.

It has become common practice for many water treatment plants to include pre-chlorination or pre-ozonation steps in water treatment plants. It was assumed that oxidation can enhance removal of NOM and turbidity during coagulation. During the 1980s, these coagulation effects were given the name microflocculation or ozone induced particle destabilization. However the mechanisms of ozone effect on coagulation are not fully understood. Some scientists and engineer still question whether there is any effect at all or it is an artifact.

Two possible mechanisms of ozone effect on coagulation were proposed (Rebhun and Lurie, 1993):

- Oxidation of adsorbed organics, their hydrophilization and eventual desorption leading to destabilization of the particles

- Catalyzed polymerization of DOC (dissolved organic carbon) and subsequent adsorption bridging.

Pre-ozonation effects are dependent on many factors including properties of organic matter, pH, type of coagulant, and concentration of calcium in water. It was found (Schneider and Tobiason, 2000) that when alum was used as a coagulant, pre-ozonation hindered turbidity and DOC removal. However, application of cationic polymers and pre-ozonation lead to small but statistically significant increases in the removal of both components. The authors hypothesize that pre-ozonation reduces the surface charge of particulates, leading to better coagulation by charge neutralization. Several years earlier (Chandrakantha et al, 1996) also related pre-ozonation effects to DOC, which is covering particles, beside they, found that ozone-induced particle destabilization occurred only in the presence of calcium. Ozone has been reported by some to improve coagulation and filtration efficiency (Reckhow et al, 1993; Stolarik and Christie, 1997). However, others have found no improvement in filter effluent turbidity due to ozonation (Tobiason et al, 1992; Hiltebrand et al,(1986).

Becker and O’Melia, (2001) provided an overview of the effects of ozone on coagulation and filtration processes. Although ozone has many benefits, its expense is significant and its placement in the treatment train should be chosen with a sound understanding of its effects on other unit processes. They stated that the effect of ozone on coagulation is shown to be dependent on the coagulant type and on the water quality characteristic, which is setting the optimum coagulant dose. For waters with moderate to high DOC levels, the coagulant dose is set by the DOC. Ozonation converts DOC into smaller, more oxygenated compounds that exert a greater metal coagulant demand than the parent compounds. In this case, ozonation can lead to an increase in the optimal coagulant doses, which was described (Edwards and Benjamin, 1992). For low DOC waters, the coagulant dose is set by the particle and the adsorbed organic matter. Ozone may react with the adsorbed DOC and alter the amount and conformation of the adsorbed organics, which can lead to a decrease in coagulant demand.

On the other hand, was stated (Wei and Yong-Mei, 2004) that NOM have a very strong influence on the stability of inorganic particles through adsorption, coating, etc., thus making surface water with high NOM concentrations difficult to treat efficiently by coagulation. Jar tests and pilot investigations were used to evaluate the effectiveness of ferrate pre-oxidation in enhancing the coagulation of NOM-rich lake water. A substantial reduction in residual turbidity after sedimentation and filtration was obtained by ferrate pre-oxidation at dose levels of 1-5 mg/L as K_2FeO_4. A similar improvement of color, DOC, iron, manganese, and total bacteria was observed. It was suggested that simple addition of ferrate prior to the coagulation step can reduce the coagulant dose demand in order to maintain acceptable residual turbidity. It was believed that additional coagulant (Fe (III)) was formed as a result of ferrate decomposition.

Edwards and Benjamin (1992) investigated the effects of ozone on several water quality parameters that affect particle behaviour in water treatment systems. They found that ozone did not decrease critical coagulant concentration for $AlCl_3$, $FeCl_3$, or alum coagulants; destabilize particles; or improve particle removal processes if pH was held constant. There was no evidence of disruption or desorption of organic coatings of particles that enhanced particle destabilization. In sum, all ozone-induced particle destabilization phenomena observed were primarily the result of a decrease in pH, an increase in pH, or precipitation of $CaCO_3$. Because these changes are produced more efficiently and at a lower cost with chemical addition, aeration, or both, they must be properly considered when evaluating the true benefits of ozonation with respect to particle removal.

Despite all the positive points, the impact of ozonation to coagulation further need to study in greater details, especially the impact of low dose of ozone on the destruction of natural organic matter as well as dissolved organic carbon (DOC). Also there is need to explore the effect of ozonation in different pH of process and in combination with different coagulants.

The objectives of this research were to prove the positive effect of ozonation on coagulation to the removal of natural organic matter, also determine the optimal dose and pH of ozonation as well as optimal dose and coagulants type for coagulation for the treatment of natural surface waters. Show ozonation efficiency for coagulation for color removal at wavelengths 410 nm and 254 nm and change of NOM after and before ozonation by laser diffraction particle size analyser.

Methods

For studies was developed laboratory setup of liquid-phase ozonation. The scheme of the laboratory setup is shown in Fig. 1.

Air with high oxygen content (70%) from the oxygen unit with internal air drying fed to ozone generator. Ozone-air mixture after the generator by using the regulator of supply enters reactor with magnetic stirrer and dissolved ozone monitor. Dissolved Ozone Monitor consists of measuring and controlling device DOSA Control DCW 120 MF and ozone sensor OZ7H. Sensor analyses concentration of ozone in the water, and transmits the signal to measuring and controlling device.

In these studies used indirect liquid-phase ozonation. At first the ozone-air mixture is passed through model water in different pH and ozone doses, and then jar test was performed with different coagulant and doses of coagulant.

Studies were conducted on model water, which consist of Humic acid sodium salt (for color – 50…60 Pt/Co scale), bentonite (for turbidity – 1...2 FNU) and $NaHCO_3$ – 0,5mmol/l (buffer capacity)

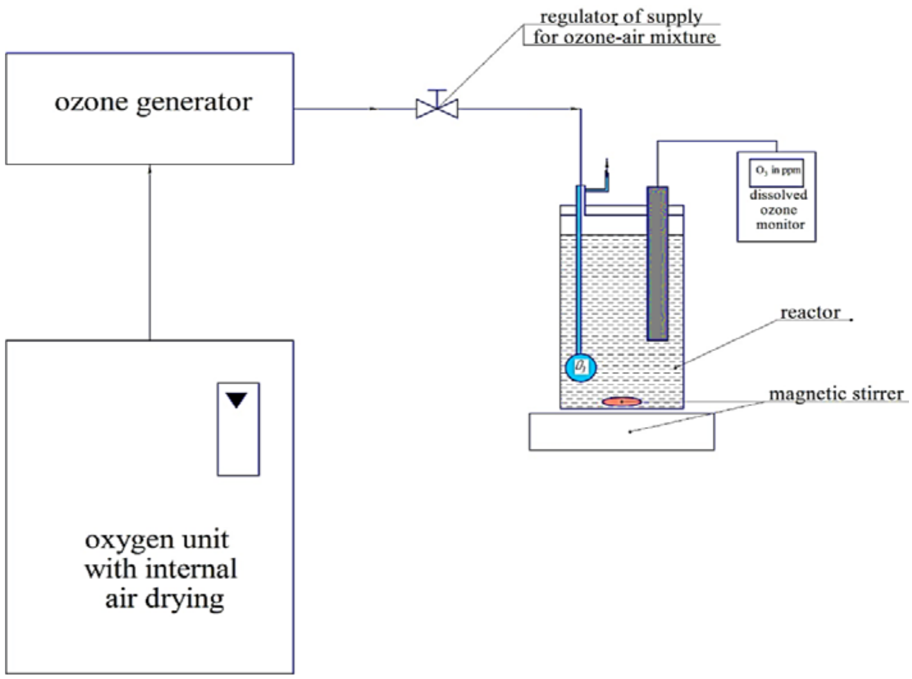

Figure 1 Basic scheme of the laboratory setup of ozonation.

For research, it was decided to use the ozone concentrations of 0.2 mg/L; 0.5 mg/L; 0.8 mg/L; and pH for ozonation 7 and 9. In jar test were analysed two type of coagulant: PIX 318 (produced by KEMIRA) and PAX 18 (produced by KEMIRA) and three different doses of each. The plan of whole experiment is shown in Fig. 2.

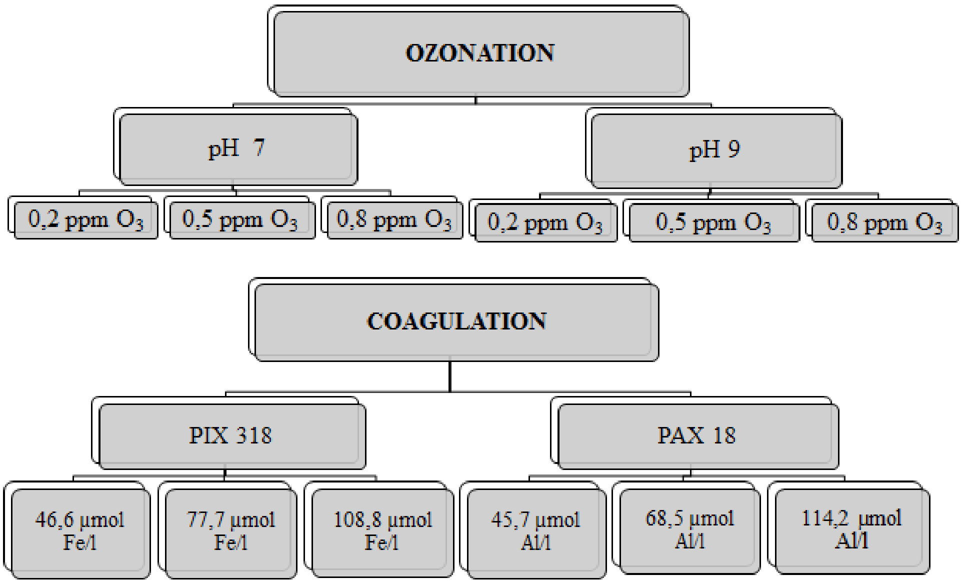

Figure 2 Basic plan of experiment.

In each series of experiment were analysed 50 samples of water: model water without any chemicals, model water after correcting pH (added HCl or NaOH), model water after ozonation as well as after coagulation only and after coagulation and ozonation alternatively.

All samples of waters were analysed for color Pt/Co scale at a wavelength of 410 nm with a spectrophotometer Hach Lange DR-3900, as well as at UV 254 and UV 410 with a UV-5800PC VIS Spectrophotometer.

Also turbidity analyses were conducted by using 2100Q Portable Turbidimeter for control settling process in coagulation.

Also for determination of changing the size of the particles in model water before and after ozonation was conducted MasterSizer analysis, where we applied laser diffraction particle size analyser MasterSizer 3000 – is a versatile tool for rapid and accurate particle size analysis (measurement of particle size distribution) suspensions, emulsions and dry powder. Method is based on measuring the angular dependence of the intensity of scattered light when passing through the laser beam is dispersed sample.

Results and discussion

For determination of varying the size of the particles in model water before and after ozonation were conducted. In this case, were analysed 9 samples of water in MasterSizer 3000, but because of high residual and low concentration of particles in water only few samples showed satisfactory result. The results are shown in Fig. 3:

There are two curves on each graphs – the curve with one extreme is for model water, and other – for ozonized water.

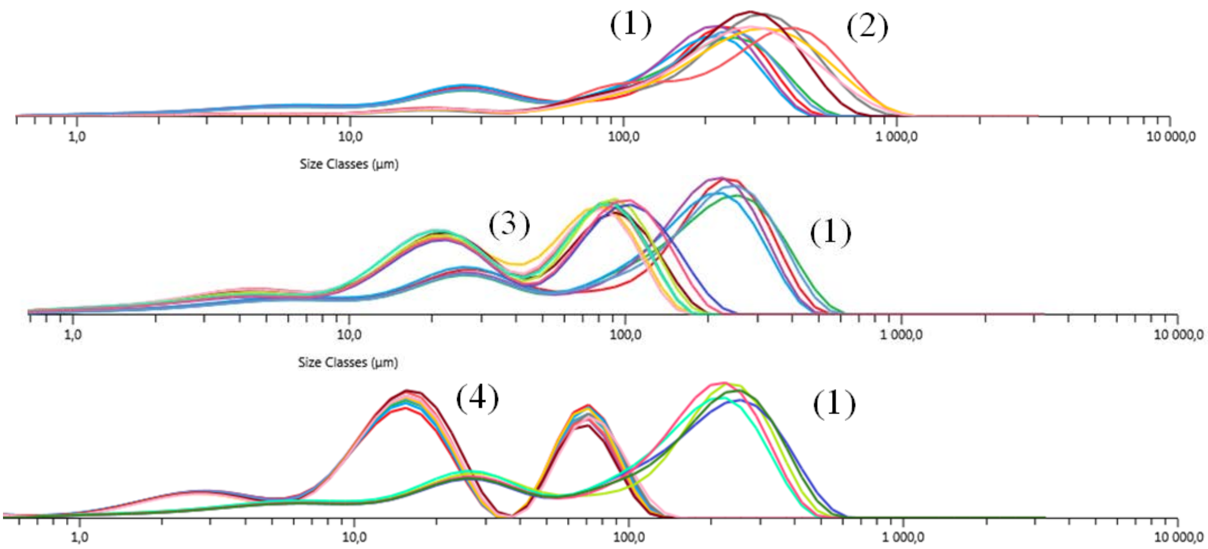

Figure 3 Changing the size of the particles in model water before and after ozonation. (1) Model Water, (2) Model Water after ozonation dosages 0.2 ppm (pH 9), (3) Model Water after ozonation dosages 0.5 ppm (pH 9), (4) Model Water after ozonation dosages 0.8 ppm (pH 9)

From the data graphs we can analyse the composition of the model water and changes of particle masses after ozonation for different ozone doses (pH 9).

Insignificant doses of ozone have a positive impact on the efficiency of further coagulation by changing particle size and division them for easier flocculation.

Analysing research data and background it can be concluded, that ozone can simultaneously aggregate fine particles and break down large ones, making them more mineralized and easier to remove.

The first ozonation-coagulation tests were performed for aluminium-based coagulant – PAX 18. Were conducted appropriate tests, the results of which are shown in Fig. 4, 5.

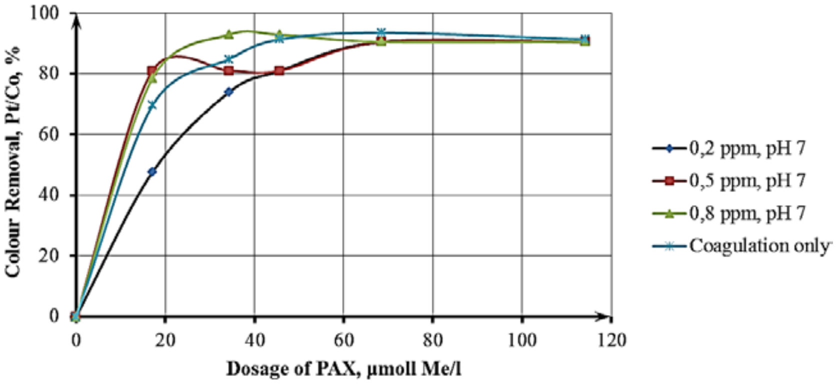

Figure 4 The dependence between removal of color (%) and dosage of coagulant PAX 18 for different ozone concentrations (ppm) at pH 7.

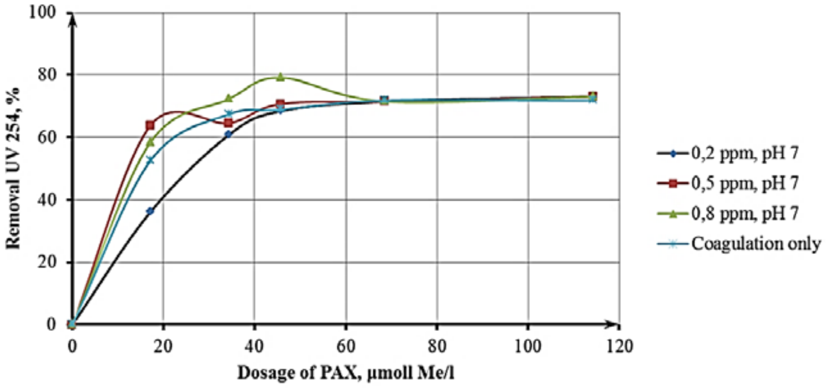

Figure 5 The dependence between removal of UV 254 and dosage of coagulant PAX 18 for different ozone concentrations (ppm) at pH 7.

From Graphs we can conclude that a low dose of ozone showed an improvement for coagulation. Using only 20 µmol Al/l dosage PAX coagulant showed the color removal ~80% and ~70% with and without pre-ozonation, respectively. Ozonation reduce the amount of PAX coagulant to achieve a satisfactory color removal (color removal after coagulation using pre-ozonation (0.8 ppm pH 7) even at 35 µmol Al/l is 93%, while to achieve similar results without ozonation required twice as much coagulant).

Next step was to research the same coagulant and dosage of coagulant, but different pH for ozonation– pH 9. Were conducted appropriate tests, the results of which are shown in Fig. 6, 7.

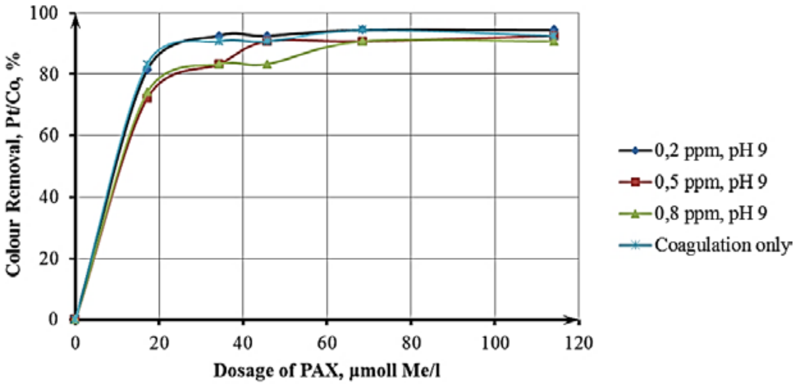

Figure 6 The dependence between removal of color (%) and dosage of coagulant PAX 18 for different ozone concentrations (ppm) at pH 9.

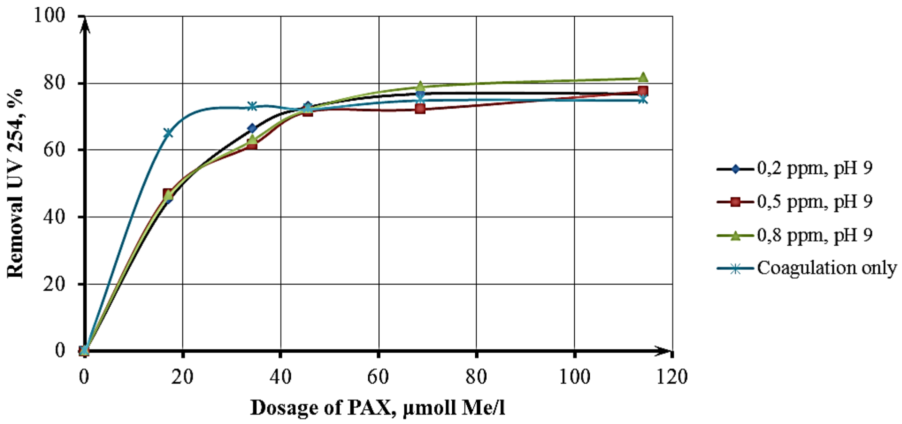

Figure 7 The dependence between removal of UV 254 (%) and dosage of coagulant PAX 18 for different ozone concentrations (ppm) at pH 9.

If we looking to Graphs from Fig. 6 – there is no so benign result that is why it can be concluded that pH 9 was not the appropriate pH for ozonation with coagulation for this type of water.

Next test were performed for iron-based coagulant – PIX 318.Were conducted appropriate tests, the results of which are shown in Fig. 8

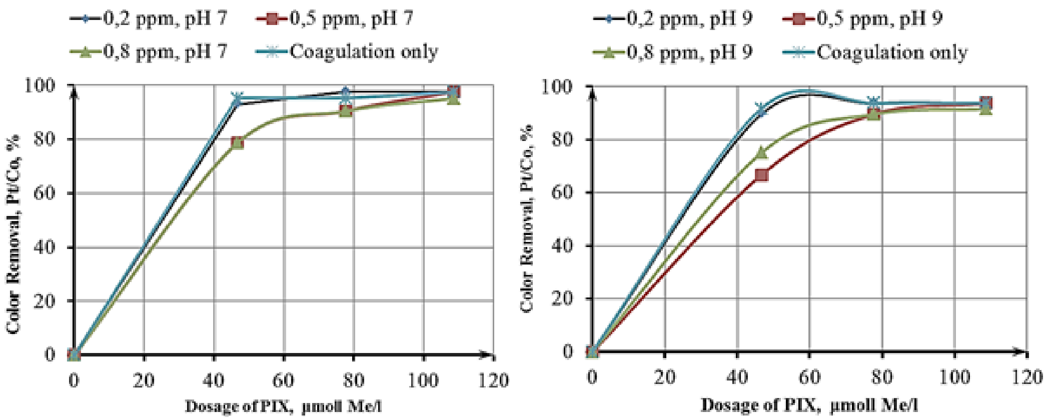

Figure 8 The dependence between removal of colour (%) and dosage of coagulant PIX 318for different ozone concentrations (ppm) at pH 7 and pH 9.

From the Graphs we can observe that ozonation combined with coagulation using Iron coagulant like PIX 318 did not give any improvement to coagulation process. In that way there is no point to use ozonation with coagulation with iron-based coagulant.

Conclusions

Results of studies show that pre-ozonation with coagulation positively influences on the removal of color, which is caused by presence of natural organic matter and DOC, ozonation improve NOM removal through coagulation as well as reduce the required coagulant dose in two times.

Low doses of ozone allows a controlled break humus molecules, that will allow to avoid reduction of molecular weight, which can lead to deterioration of flocculation in particular and worsening NOM removal in general. This is meant that low ozone doses showed an improvement for coagulation. Using only 20 µmol Al /l dosage PAX coagulant displayed the color removal ~80% and ~70% with and without pre-ozonation, respectively which is means that ozonation can reduce the amount of PAX coagulant to achieve a satisfactory color removal.

After analysing research data and background it can be concluded that: NOM with intermediate molecular weight increases at lower ozone dosage, favouring removal by coagulation because of possibilities of ozone to simultaneously aggregate fine particles and break down large ones, making them more favourable for coagulation and easier to remove.

But for Iron-based coagulant it is clear, that ozonation did not give any improvement to coagulation process. In further researches it is possible to get more defined results using lowest dose of ozone as well as lowest dose of coagulant.

Acknowledgments

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