# Efficiency of ozonation for disinfection and removal of color and humic substances from surface water

**V. Fedorenko[1]*, H. Stolyarenko[1], H. Ratnaweera[2]**

[1] Cherkasy State Technological University, 460 Shevchenko boulevard, 18006, Cherkasy, Ukraine.
[2] Norwegian University of Life Sciences, PO Box 5003-IMT, 1432 Aas, Norway
* Corresponding author. E-mail: vita_fedorenko92@mail.ru; tel.: +38 063 17 17 726

## Abstract

In Norway, as in the other Nordic countries, the surface water is used as a common source for the production of drinking water. Surface waters are often characterized by a high content of Natural Organic Matter (NOM), which leads to high color and low hardness due to natural conditions. Processing of such treatment involves the removal of color, as well as control of corrosion and disinfection. Results of studies show that ozonation positively influences on the removal of chromaticity, which is caused by presence of natural organic matter and DOC, and as on removal of the heterotrophic bacteria and coliforms.

**Keywords:** surface water, ozonation, humic compounds, color removal, coliforms, heterotrophic bacteria.

## Introduction

In Norway, as well as in other Scandinavian countries, surface water is used as the general source for production of drinking water. Surface waters are often characterized by the high content of natural organic matter (NOM), which conducts to high chromaticity (color rate) and low hardness due to natural conditions. Processing of such waters consists of removal of chromaticity and control over corrosion and disinfection. At present exist the set of methods for removal of natural organic matter, namely a biofiltration and a nanofiltration, coagulation, also combined and advanced oxidizing processes. In Norway at all water treatment and purification plants usually used coagulation, that rather well removes color and NOM. But coagulation doesn't influence in any way on the maintenance of microorganisms and bacteria in surface water. It was offered to use ozonation as an alternative method for removal of chromaticity and water disinfection. The studies were conducted at the 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 ozonation on removal of chromaticity and bacteria in surface water. Studies were conducted both on natural surface water, and on model waters with the different content of humic connections and bacteria. Were observed positive results at small concentrations of ozone (0,25 – 1 mg/l) after 10 minutes of contact with test water. Were observed extent of color removal for a natural surface water up to 21-43%, and up to 10-40% for model waters on the basis of humic compounds. Also the quantity of the heterotrophic bacteria considerably decreases on 91-94% and coliforms – on 88-90% in natural and model waters.

In Norway, surface water is the main source of drinking water. The microbial quality and high content of humic substances and color are the main problems in water treatment (Ødegaard, 1996; Melin and Ødegaard, 1999). Natural water from lakes, rivers, reservoirs, etc. is the source for the preparation of drinking water. Although it has much lower pollution than wastewater, natural water also contains numerous and different compounds, most of them of the organic type, defined as natural organic matter, NOM.

This matter may contain a large variety of substances from vegetable plant degradation and animal wastes, and pollutants from agricultural, industrial, and urban activities, which are often grouped into macromolecules that constitute humic substances. Humic substances can also contain metal linked to them as complexes or as simple molecules such as pesticides, etc. Because NOM constitutes the major fraction of the matter present in surface waters, the parameter usually employed to characterize the water is dissolved organic carbon, DOC (Fernando J. Beltrán, 2005).

Since the discovery of ozone in 1840, this oxidant has been much used for water purification, due to its strong bactericide activity. However, a widespread application of ozone was only seen in a few countries in Europe, namely France, Germany and Switzerland. During the last decades however ozonation is introduced in more and more water treatment plants as a replacement of primary chlorination in order to control the formation of chlorination by-products (T. Juhna, E. Melin. 2006). Ozone is a very effective disinfectant and also reacts with humic molecules reducing color (Ødegaard, 1996; Melin and Ødegaard, 1999).

Today ozone is considered an alternative oxidant-disinfectant agent with multiple possible applications in water, air pollution, medicine, etc. In water treatment, in particular, ozone has the ability to disinfect, oxidize, or to be used in combination with other technologies and reagents. Much of the information about these general aspects of ozone has been reported in excellent works, such as Langlais et al. (1991) (Beltrán Fernando J., 2005).

Because ozone is a strong oxidant, it can be used not only for disinfection but also for removal (oxidation) of organic substances. Ozone is used for the treatment of water polluted with pesticides or other anthropogenic substances. Ozonation can be combined with UV and $H_2O_2$ treatment in order to increase the oxidation power. Such advanced oxidation processes (AOP) appear to be potentially effective methods for the removal of emerging substances like endocrine disruptors, pharmaceuticals, resin softeners, new disinfections by-products, etc. Ozone can also be added prior to coagulation to improve particle removal efficiency by inducing so-called microflocculation. This potential beneficial effect of preliminary ozonation is however dependent upon several factors: including water hardness and DOC concentration. Thus, preliminary ozonation effective at a low level of dissolved organic carbon, while it may have an adverse effect of high level of DOC. By using ozonation it is possible to combine disinfection and removal of organic substances, which are transformed into the biologically degradable organic compounds (BDOC), which can be removed in the biofilter (T. Juhna, E. Melin. 2006).

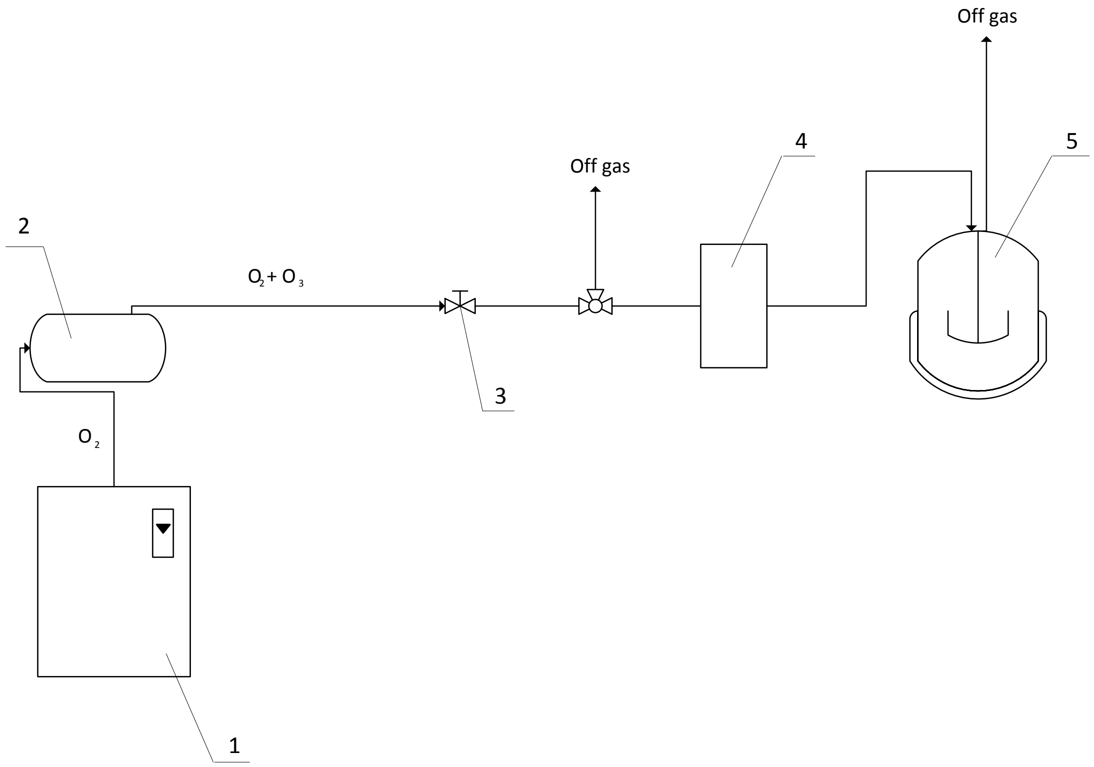
Despite all the positive points, the impact of ozonation further need to study in greater details, especially the impact of ozonation on the removal of total organic carbon (TOC) and dissolved organic carbon (DOC). Also there is need to explore the effect of ozonation on the level of biodegradable organic carbon (BDOC), microbially available phosphorus (MAP) and bromate formation and bromorganic compounds.

Therefore, the objectives of this research were to prove the positive effect of ozonation on the removal of natural organic matter, also determine the optimal dose of ozone for the treatment of natural surface waters. Show ozonation efficiency for color removal at wavelengths 410 nm and UV 254 nm for removing of coliforms and E.coli and heterotrophic bacteria, and also total organic carbon. Show the effective impact of pre-ozonation process on removing natural organic matter in combination with coagulation.

## Methods

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

Air with high oxygen content (70%) from the oxygen unit with internal air drying 1 fed to ozone generator 2. Ozone-air mixture after the generator by using the regulator of supply 3 is fed to the absorber 4. After absorber ozone-air mixture enters reactor 5 with magnetic stirrer and dissolved ozone monitor. Dissolved Ozone Monitor consists of measuring and controlling device DOSAControl DCW 120 MF and ozone sensor OZ7H. By using sensor concentration of ozone is determined in the water, and data enters the measuring and controlling device.




1 - oxygen unit with internal air drying; 2 - ozone generator; 3 - regulator of supply for ozone-air mixture; 4 - absorber; 5 - reactor with magnetic stirrer and dissolved ozone monitor.

**Figure 1** Basic scheme of the laboratory ozonation setup.

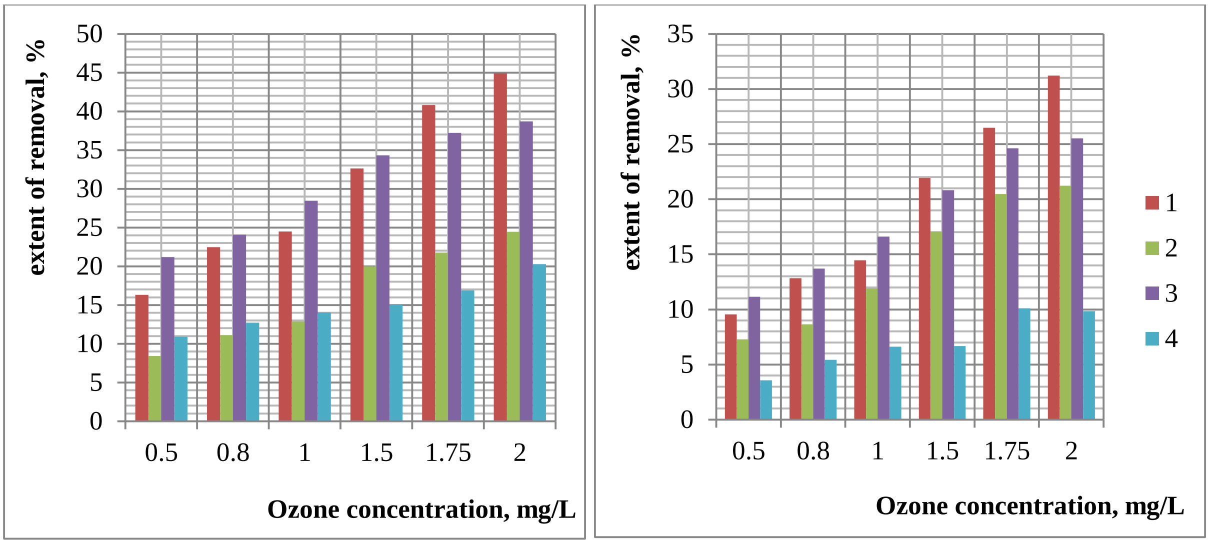
In these studies used indirect liquid-phase ozonation. At first the ozone-air mixture is passed through ionized water, and then in the water, saturated with ozone, added the same volume of test water. This method allows to more accurately determining the concentration of ozone in water directly. Studies were conducted on several types of waters. The tests were conducted on the natural surface waters from the lake Årungen and from the drinking water treatment plant Vannsjå (MOVAR). Also been used water model: model water from the powder of humic salts, model water from the liquid concentrate of humic acids, the model from gray water with a high concentration of coliforms. For research, it was decided to use the ozone concentrations of 0.5 mg/L; 0.8 mg/L; 1 mg/L; 1.5 mg/L; 1.75 mg/L; 2 mg/L in ionized water. The contact time of test water with water, saturated with ozone - 10 minutes.

Test waters after ozonation were analyzed for chromaticity at a wavelength of 410 nm with a spectrophotometer Hach Lange DR-3900 and at wavelength 254 nm with a spectrophotometer Shimadzu UV Mini-1240.

Also microbiological analyzes were conducted by using standard techniques and methods (Eugene W. Rice et al., Standard Methods 22nd ed., 2012). To determine the quantity of colonies of heterotrophic bacteria was used method - Heterotrophic spread plate counting, which needs universal KPG agar and sample volume of 0.1 ml of water. To determine the number of colonies of coliforms and E.coli bacteria was used - Membrane filtration method, which needs TTS-Lactose agar and sample volume of 100 ml of water.

## Results and discussion

Effect of ozonation on waters with various compositions shows quite different results on the color removal (Figure 2) and on the removal of heterotrophic bacteria and coliforms (Figures 4,5).




a b

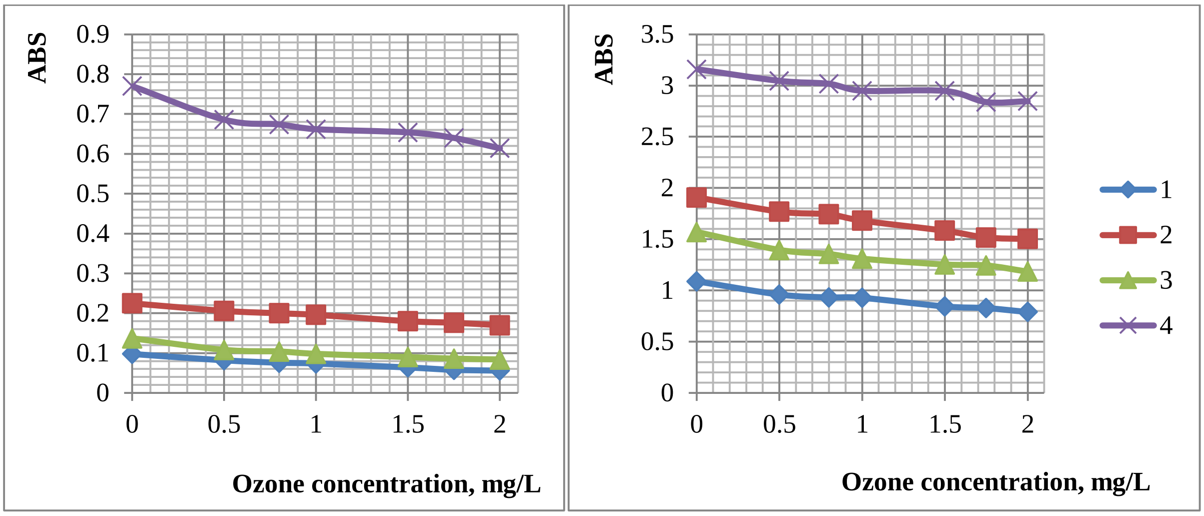
1 - lake Årungen; 2 – drinking water treatment plant Vannsjå (MOVAR); 3 - model water from the liquid concentrate of humic acid; 4 – model water from powder of humic salts.

**Figure 2** The dependence of extent removal of color (%) from ozone concentrations (mg/L): a - at wavelength 410 nm; b - at wavelength 254 nm.

For natural surface waters and model water from liquid concentrate of humic acids extent of removal of color of is higher than for the model water from the powder of humic salts. Water from Årungen lake at wavelength 410 nm has extent of removal up to 16-45%, and at wavelength 254 nm – up to 9-31%. Water from drinking water treatment plant Vannsjå (MOVAR) at a wavelength of 410 nm has extent of color removal 8-24% and at wavelength 254 nm – up to 7-21%. Also, model water from liquid concentrate of humic acids has high removal extent: 21-39% at wavelength 410 nm, 11-26% at wavelength 254 nm. The extent of removal of chromaticity for model water from the powder of humic salts is much less than for other test waters. The reason for this may be the chemical nature of the powder of humic salts, which is not natural and not consist of natural humic acids and salts. The degree of color removal for model water from the powder of humic salts is 11-20% at a wavelength of 410 nm, and up to 3.5-10% at a wavelength of 254 nm. Graphic dependence of absorbance from the concentration of ozone is shown in Figure 3.

Also microbiological tests were conducted for determination number of colonies of heterotrophic bacteria in natural surface waters and tests to determine the amount of coliforms and E.coli bacteria in natural surface water from the Årungen lake and in the model water based on gray water. The results of the removal efficiency of heterotrophic bacteria are presented in Figure 4. At the highest ozone concentration of 2 mg / L extent of removal of heterotrophic bacteria in the water of the Årungen lake up to 91-97.3%, and for water treatment plant Vannsjå (MOVAR) - 93.9-97.5%. To achieve 99-100% extent of removal of heterotrophic bacteria can be used higher ozone concentration up to 3-5 mg/L.

During the research it was noticed that in all Petri dishes over time the number of colonies of bacteria growing. So, it was decided to conduct counting three times - after 3 days, after 7 days and after 10 days. Increasing of the number of bacteria can be explained by the fact that all the different types of bacteria have different levels of survival after exposure of ozone. Some species of bacteria need time to grow under normal conditions (7-14 days).




a b

1 – Årungen lake; 2 – drinking water treatment plant Vannsjå (MOVAR); 3 - model water from the liquid concentrate of humic acids; 4 – model water from powder of humic salts.

**Figure 3** The dependence of absorbance from the ozone concentrations (mg/L): a - at wavelength 410 nm; b - at wavelength 254 nm.

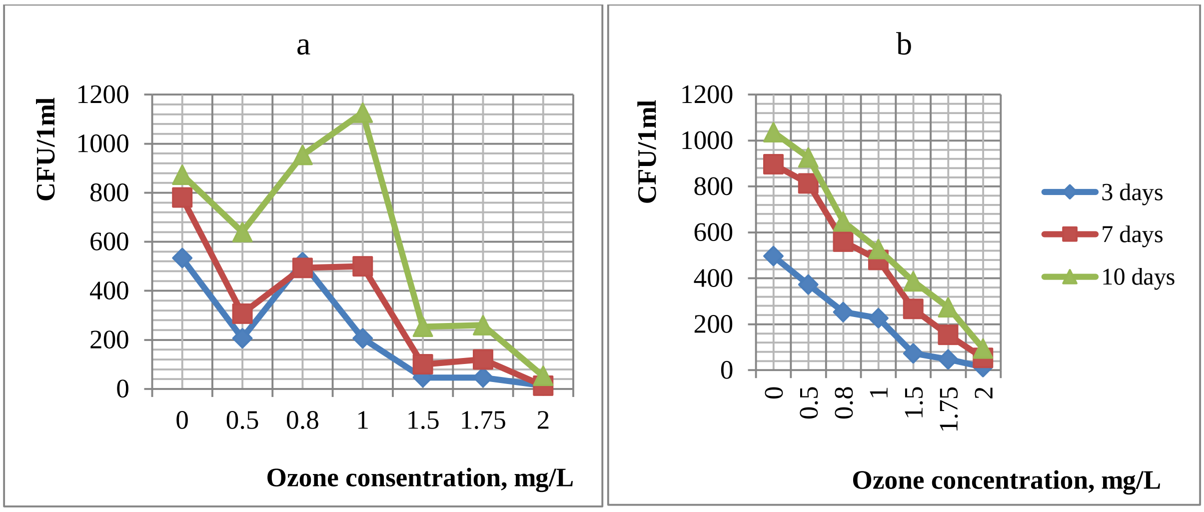



**Figure 4** Dynamics of change the number of colonies of heterotrophic bacteria from ozone concentration (mg/L) for 3, 7 and 10 days: a - drinking water treatment plant Vannsjå (MOVAR); b - lake Årungen.

Figure 5 shows how the numbers of coliforms in the natural and model waters are dependent on the concentration of ozone. For the model water based on gray water the extent of removal is 89.2% and for the surface water from lake Årungen – up to 90.7% for ozone concentration of 2 mg/L.

The method that was used to determine coliforms – membrane filtration – not quite suitable for the analysis of water, which contains a large amount E.coli bacteria or coliforms. Therefore, this method may be inaccurate, since because of large amount of coliforms it is hard to count the number of colonies. This method is suitable for water, which contain small amounts of coliforms.

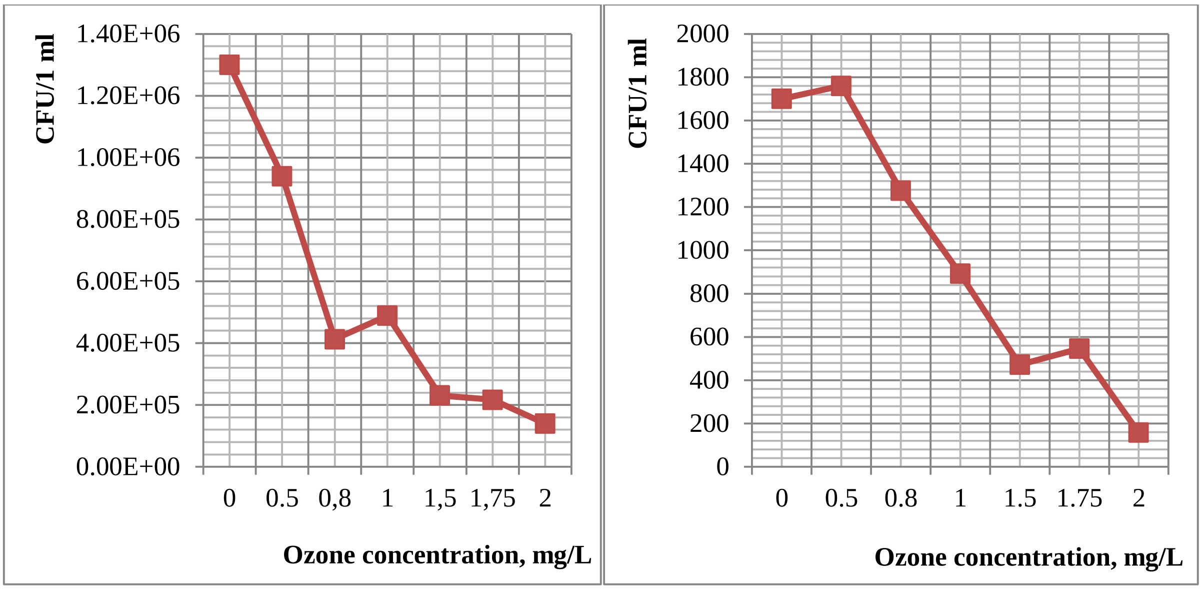
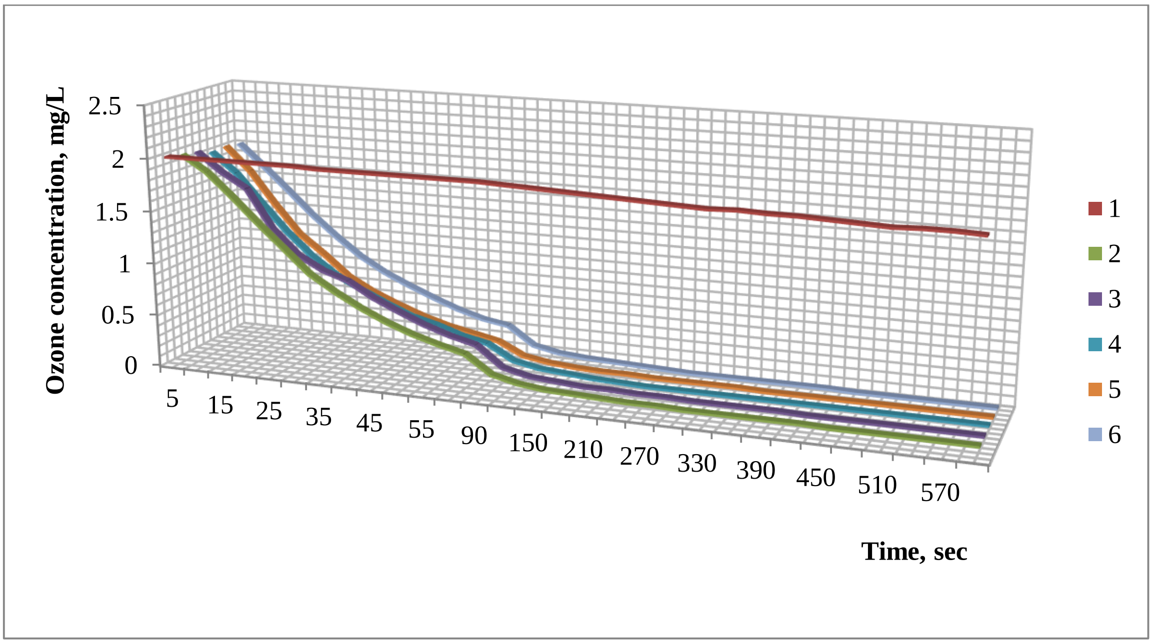



**Figure 5** Dynamics of change the number of colonies of coliforms from ozone concentration (mg/L): a – model water based on gray water; b – lake Årungen.

During the experiments, it was also observed that during ozonation – test water contacts with ionized water, which saturated with ozone - ozone concentration after 3-4 minutes of contact quickly drops to 0.02-0.03 mg/L of ozone (Figure 6). Drop in the concentration for all types of waters can be explained by the fact that ozone is consumed very quickly by reaction with natural organic matter, humic acids, bacteria etc.




1 - ionized water; 2 - lake Årungen; 3 – drinking water treatment plant Vannsjå (MOVAR); 4 – model water from liquid concentrate of humic acids; 5 – model water from powder of humic salts; 6 - model water based on gray water.

**Figure 6** Dynamics of change of ozone concentration over time (for the initial ozone concentration of 2 mg/L).

Ozone concentrations, which were used in the studies are quite low due to the dilution. Therefore, further research is necessary to use higher doses of ozone to confirm the results of this study.

## Conclusions

These studies confirm that ozonation has a positive effect on removal of color (natural organic matter) and humic compounds and also removal of different types of bacteria, such as heterotrophic bacteria and coliforms. Removal rate of color, generally, for different types of water for a wavelength of 410 nm reaches 8-45%, for a wavelength of 254 nm – 3.5-31%. Extent of removal of the heterotrophic bacteria for a natural surface water is 9-24% at concentration of ozone 0.5 mg/L, and up to 91-97,5% at concentration of ozone 2 mg/L. Removal rate of coliforms in natural and model water at concentration of ozone 0.5 mg/L reaches 24.9-27.7%, and at concentration of 2 mg/L – 89-91%. Ozone not only decomposes difficult organic substances, but also works as the strong oxidizing and disinfecting agent.

In further researches it is possible to get higher extents of removal of chromaticity and bacteria by using higher concentration of ozone.

## References


Beltran Fernando J. (2004) *Ozone reaction kinetics for water and wastewater systems / Fernando J. Beltran. p. cm. Includes bibliographical references and index. ISBN 1-56670-629-7 (alk. paper).*

Hulsey B., Budd G. *Ozonation and biofiltrarion.*

Eikebrokk B., Juhna T., Røstum J. (2010) *Optimization of water treatment: Enhanced coagulation and ozonation-biofiltration. Summary report on performance assessment tools and optimization, Techneau.*

Juhna T., Melin E., Eikebrokk B. (2006) *Ozonation and biofiltration in water treatment operational status and optimization issues. Operation of water treatment facilities –Optimization efforts and modelling of unit processes, TECHNEAU*

Melin E., Eikebrokk B., Brugger M., Ødegaard H. *Treatment of humic surface water at cold temperatures by ozonation and biofiltration.*

Melin, E. and Ødegaard, H. (1999) *Biofiltration of ozonated humic water in expanded clay aggregate filters. Wat.Sci.Tech.* Vol 40, No. 9, pp. 165-172.

Meyn T. (2011) *NOM removal in drinking water treatment using dead-end ceramic microfiltration. Assessment of cagulation/flocculation pretreatment.*

Rice E.W., Baird R.B., Eaton A.D., Clescen L.S. (2012) *Standard Methods for the Examination of Water and Wastewater, 22nd edition.*

Ødegaard, H. (1996) *The development of an ozonation/biofiltration process for the removal of humic substances*. In: *Advances in Slow Sand and Alternative Biological Filtration*, N. Graham and R. Collins (eds), John Wiley and Sons, pp. 39-49.

Świderska-Broz M., Wolska M. (2012) *Efficiency of ozonation followed by filtration through a biologically active adsorption bed at removing biogenic organic substances from surface water.* Environment Protection Engineering, Vol. 38, No. 2.