WATER SUPPLY, SEWERAGE, BUILDING CONSTRUCTION OF WATER RESOURCES PROTECTION

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CHANGE IN THE QUALITY OF NATURAL WATERS DURING PHYSICAL AND CHEMICAL PROCESSING

Statement of the problem. During the processing of water for food and industrial use, the methods are employed to remove suspended matter coloured by organic compounds (humic and fulvic acids), to reduce the hardness and completely remove all the impurities from natural waters. It seems sensible to look into the impacts of common methods of water conditioning on its quality using distillation, coagulation, reagent and ion-exchange softening, chlorine and ozone decontamination.

Results. The study of natural waters prior and following the treatment using the above methods was performed. Permanganate oxidation, concentration of humic and fulvic acids, medium reaction (pH) were used for control. The impact of oxidizers on sorption of impurities during sorptional pre-treatment was assessed.

Conclusions. The quality was not found to be significantly dependent on the original impurity content. Aluminum sulphate coagulation is effective in removing not only humic and fulvic acids but also easily oxidized organic compounds. Reagent softening and Na-cation exchange lift pH into alkaline while N-cation exchange lift it into acid thus reducing the salt content of water. Ozone as well as chlorine treatment cause toxic compounds to occur in humic and fulvic acids.

Keywords: natural waters, humic acids, distillation, coagulation, decontamination, sorption.

Introduction

Any water treatment technology is a combination of a variety of methods, sequence and amount of which is defined both by the quality of raw water as well as the consumer needs. Open water reservoirs as well as artesian waters undergo treatment. According to the Health and Safety

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Guidelines for drinking water [1], the number of mineral compounds is restrained by the salt content of 1 g/l and organic compounds by permanganate oxidation of 5mg of O_2/л. The efficiency of water purification from humic and fulvic acids in drinking water supply is estimated based on coloration: it is not be to over 20 degrees on the Platinum-Cobalt Scale (Cr-Co) [1]. This test indirectly indicates there are high-molecular humic and fulvic acids.

If coloration of water is moderate, a lot of city's water purification stations would generally overlook the removal of coloured impurities. Consumers would generally get water with no changes made to the amount of organic compounds. The major argument for coagulation is turbidity which is contributed to by colloid and coarsely dispersed compounds.

For specific technological water needs, consumers have to design their own water treatment structures with the use of a variety of physical and chemical methods for impurities.

1. Experimental part. The major water processing procedures in drinking water provision on city's water purification stations are removal of weighed compounds until there is no turbidity at all; for high hardness it drops to 7 mg-eq/L. Besides, water safety concerns need to be addressed, i.e. making sure there are no pathogenic microorganisms, which is achieved by the chlorine sterilization, ozonation, ultraviolet radiation processing, ultrasounding, etc. [2—4].

Drinking water should be free of organic impurities, particularly high-molecular humic compounds that colour it in yellow. Humic and fulvic acids themselves, which are natural products of decomposition of organic residues in earth and water, pose no threat for people if a water reservoir is not affected by them. The issue is that there are hardly any left in industrially developed regions.

Water humus is an organic acid of a specific structure containing phenolic and carboxyl groups which are capable of addition reactions, substitutional reactions and complex formation with heavy metals [5]. These alloys were also found to contain ions of copper, aluminum, cadmium, chromium, nickel, lead, manganese, zinc, ferrum, etc. [6—11]. 90, 50, 75 and 90 % of lead, copper, zinc river water respectively contains were found to make up humic and fulvic acids [9]. Therefore it is daunting to ensure drinking water safety if it contains humic and fulvic acids. It is particularly worth noting that humic and fulvic acids are dominating organic components of impurities of any type of water [4].

Besides, humic and fulvic acids are not only capable of addition reactions, exchange reactions, neutralization and absorption reactions involving non-organic compounds but also a

variety of organics. As a result of these, there are alloys of humic and fulvic acids with groups of compounds that are dominated by halogen-containing products, proteins, plasticizers, herbicide, insecticide and others all being biologically active [12—14].

The above data indicate that humic and fulvic acids are sources of organic and minerla compounds that drinking and technological water is not supposed to contain. Therefore, during the removal of humic and fulvic acids, water also becomes free of the above compounds that are known to can health concerns.

For industrial applications it becomes necessary to remove not only natural humic and fulvic acids but also artificial ones occuring in e.g., the biosynthesis of amino acids and antibiotics. Waste waters of food industries contain a lot of organics that are removed using biochemical oxidation in aerotanks. However, while penetrating waste waters, humic and fulvic acids colour them and hinder biological decomposition of toxic impurities [4].

2. Distillation. This type of water treatment has long been in use till the ion exchange was discovered and ion-exchange materials were synthesized. Distillation is still used in chemical laboratories, pharmaceuticals, small productions, etc. In State Standard (ГОСТ) for distilled water, the electrolyte content is described using electric conductivity χ or specific resistance ρ [15], and the organic substance content by permanganate oxidation which indicates the amount of easily oxidized compounds with no specific information regarding their quantity and quality. However, the research revealed that even in distilled water there are still enough organic impurities left (Table 1).

Table 1

Organic compounds in water prior and following distillation

City, source	PO, (±0.2) mg O_2 /l	Humic acids, (±10) mkg/l	Fulvic acids, (±50) mkg/l	Amino acids, (±0.5) mkg N/l	Carboxylic acids, (±0.5) mkg-equiv/l	Sugars, (±0.02) mg/l
Moscow, water pipe	9.0	40	13450	6	17.0	–
Moscow, distillate	0.3	10	100	1	4.0	–
St. Petersburg, water pipe	7.4	540	13250	6	22.5	0.27

End of Table

City, source	PO, (±0.2) mg O_2 /l	Humic acids, (±10) mkg/l	Fulvic acids, (±50) mkg/l	Amino acids, (±0.5) mkg N/l	Carboxylic acids, (±0.5) mkg-equiv/l	Sugars, (±0.02) mg/l
St. Petersburg, distillate	0.4	40	200	1	7.0	0.06
Voronezh, water pipe	1.2	100	1100	20	9.5	0.65
Voronezh, distillate	0.4	10	100	8	3.0	0.08

As Table 1 suggests, oxidation of the distillate does not depend much on the quality of the original water. Humic and fulvic acids are effectively removed, which cannot be said about carboxylic acids. They are 25—30 % of the original. This is due to the volatility of carboxylic acids which penetrate the distillate as steam condensation takes place.

3. Coagulation. In large-scale productions, the major method for removing weighed and coloured compounds is reagent coagulation [2, 4]. The most common is the use of ferrum salt (II), ferrum (III), aluminium: $FeSO_4$, $FeCI_3$, $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, etc. Their efficiencies are compared in [16].

Coagulation of natural impurities is performed at different water temperatures and varying coagulant doses. It was proved to be effective to treat river waters with aluminum suphate with the optimal dose being ~ 1 mg-equiv/l at the temperature of ~ 20—30 ^oC. This type of the process ensures the residual colouring of water of 5—10 degrees Cr-Co scale; drop in the permanganate oxidation from 12—14 to 2—3 mg O_2/l: a 70—80 % reduction in the concentration of humic and fulvic acids [16].

The impact of $Al_2(SO_4)_3$ on the organic component of water in different regions was studied: the Bystritsa Nadvornyanskaya River (Ivano-Frankovsk, Ukraine), the Nevėžis River (Nevėžis, Lithuania), the Neva River (St. Petersburg, Russia). As well as in [16], the experiment was performed by treating 0.5 l of river water with 4-percent solution of $Al_2(SO_4)_3$.

The results of identifying the permanganate oxidation, the content of humic and fulvic acids are shown in Table 2.

Table 2

Change in the content of organic compounds in river water as a result of aluminium sulphate coagulation

Source	Original water			Coagulated water		
	PO, mg O_2/l	Humic acids, mg/l	Fulvic acids, mg/l	PO, mg O_2/l	Humic acids, mg/l	Fulvic acids, mg/l
The Bystritsa	2.8	0.1	2.5	1.4	0.03	0.9
The Nevėžis	14.4	0.5	13.4	6.3	0.1	3.5
The Neva	9.4	1.0	10.8	6.4	0.3	8.8

Above the components identified in Table 2, the colouring of the original water and the filtrate was measured using photometry. One more feature was identified, i.e. no correlation of the colouring and oxidation of clarified water. Compared to a significant drop of the colouring (80—90 %), the oxidation reduced by no more than 50 %. It is obviously due to the fact that it is humic and fulvic acids that give water colouring, which are effectively removed using coagulation thus there is no significant drop in its colouring. However, this does not affect the oxidation so much as humic and fulvic acids are hard to oxidate with potassium permanganate, therefore “permanganate oxidation” do not seem to contribute much to the gross carryover. It had been previously noted that ferrum salts are 20 % more effective in removing humic acids than aluminium suphates but are less influential on the oxidation, i.e. aluminum salts precipitate non-coloured organic compounds more completely which are easily oxidated by $KMnO_4$ [16].

In the process of reagent coagulation, there is change in the mineral composition of water impurities. Strong acids are the result of hydrolysis of heavy metal salts:

$$Al_2(SO_4)_3 + 3H_2O = 2AI\ (OH)_3\downarrow + 3H_2SO_4.$$

Therefore reagent coagulation involves an increase in the amount of anions of strong acids by the dose of a coagulant, mg-equiv/l. The resulting acid is neutralized in reactions of the interaction of oxygen with hydrocarbonate alkaline or alkaline-earth metals, e.g. according to the reaction:

$$2NaHCO_3 + H_2SO_4 = Na_2SO_4 + 2CO_2 + 2H_2O.$$

This means that the concentration of sulphate ions is on the increase. For 60 mg/l of aluminium it is ~ 1 mg-equiv/l. There is an equal increase in hydrocarbonate alkalinity of water.

This change of the anion composition does not affect the quality of drinking water at all. However, desalination of water causes an increase in the amount of anions to be removed. If the original water contains 1 mg-equiv/l, the load on anion filters is to increase by 100 %, i.e. there is a double increase; if 2 mg-equiv/l, it is to increase by 50 %, etc.

This causes a shorter service life of the filter, an increase in its regenerations and thus larger amounts of alkali to regenerate the filter and alkaline waste water. This is not to be said about electrocoagulation which does not involve reagents but presents a few challenges. Therefore it is less common than reagent water treatment particularly in large-scale water treatment.

4. Water softening. Softening water is reducing the concentration of calcium and magnesium salts in hard water. This is an extremely complicated technological process. An enormous amount of softened water is used as heat sources in heat systems of residential buildings and industrial premises as well as to cool them.

There can be no hard salts in steam boilers in service. At high temperatures they cause sludge on the boiler. Scale does not conduct heat too well, therefore some parts of the metal are overheated thus causing an explosion. These same compounds precipitate onto the tube walls in water cooling systems, impact water exchange and cause the system to fail [2, 4].

Salts of ferrum, manganese, aluminium, weighed compounds, colloid impurities contribute to sludge. Layers of sludge can be so large that it almost fills up the entire tube section [4]. The sludge is to be removed from the boiler. It would be more reasonable to allow for it, i.e. to remove the hardness salt ions before water is supplied to the customer.

Water softening is essential for dissalination using electrodialysis and reverse osmosis [17, 18]. The reason is that in pre-membrane water the concentration of calcium ions increases achieving the sum of the solubility of $CaSO_4$, which causes the membranes to plaster thus making them more vulnerable and as a result causes them to fail.

There are a few methods for reducing the hardness of water. The choice of a method depends on how much residual hardness of water is deemed acceptable in a specific industry. Harder water can on large scale be softened using, e.g., the lime-soda method [4]:

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3\downarrow + 2H_2O,$$

$$Mg(HCO_3)_2 + Ca(OH)_2 = Mg(OH)_2\downarrow + 2CaCO_3\downarrow + 2H_2O.$$

As there are sludges of calcium carbonate and magnesium hydroxide, free carbon dioxide is released:

$$H_2CO_3 + Ca(OH)_2 = CaCO_3\downarrow + 2H_2O.$$

Sodium, the combination of lime and soda ash, warm lime etc. are also known to be used for softening (NaOH is dosed). They all cause the pH of the clarified water to increase to 8—9. This is accompanied by decreasing carbonate alkalinity (HCO^-_3-ion content) and increasing hydrate alkalinity (OH^- ion content) [4].

Modern technologies of water softening involve the use of ion-exchange materials. Ions can be removed using N-cation exchange and Na-cation exchange of water [4, 17, 19].

In the former case, ions of cation hydrogen (R-H) are swapped for magnesium and calcium cations, e.g., according to the following reactions:

$$\begin{aligned} &CaCI_2\ Ca\ HCI, \\ &R\text{-}H + MgSO_4 \rightarrow R\ Mg + H_2SO_4, \\ &Ca(HCO_3)_2\ Ca\ H_2O + CO_2. \end{aligned}$$

It is obvious that as a result of N-cation exchange, natural water is converted to the dilute solution of strong and weak mineral acids with pH dropping to 3—5 depending on the salt content and the amount of anions of strong acids with a decrease in the total salt content of water due to the decomposition of hydrocarbonates of calcium and magnesium as

In the process of Na-cation exchange ions of cation natrium are swapped with ions of calcium and and water magnesium, e.g., according to the following reactions:

$$\begin{aligned} &Ca(HCO_3)_2\ Ca\ NaHCO_3, \\ &R\text{-}Na + CaCI_2 \rightarrow R\ Ca + NaCI, \\ &MgSO_4\ Mg\ Na_2SO_4. \end{aligned}$$

The residual content of hardness ions in water is not over 0.1 mg-equiv/l. For deeper softening the second stage of Na-cation exchange is used. It involves a two-step process where water is passed through another filter. The regeneration of the filters of the first and second steps require different specific consumption of NaCI. The first layer of water (the first step) is re-

generated by a bit excessive salt therefore the regeneration is not very high. The second layer of the cation (the second step) is regenerated with a large specific consumption of salt. Due to a high regeneration of this layer of the cation, the residual hardness of Na-cation exchange water after the second filter is on the threshold of sensitivity of complexometric titration, i.e. < 2 mcmole-equiv/l [4, 19].

As a result, Na-cation exchange water according to the above reactions is converted into a solution of natrium salts of strong and weak mineral and organic acids. The total salt content does not change. However, there is an increase in the alkalinity of water: pH goes up to 9—10.

The reason is that calcium and magnesium salts are hydrolyzed resulting in hydroxides $Ca(OH)_2$ and $Mg(OH)_2$. They are strong electrolytes and their disassociation α in the first step ($Ca(OH)_2 \leftrightarrow Ca(OH)^+ + OH^-$) might be high but there are no table data regarding this. Even in the second step it is fairly significant and is $4.3 \cdot 10^{-2}$ and $2.5 \cdot 10^{-3}$ respectively [20].

However, there cannot be a lot of OH^-ions, since these hydroxides are not easy to dissolve (1.6 and 0.006 g/kg of water) [20]. Hydrolysis of natrium salts of weak acids (carbonic, flint, nitrogen, etc.) results in weakly dissociated acids and natrium hydroxide ($NaHCO_3 + H_2O \leftrightarrow H_2CO_3 + NaOH$) with a dissociation degree $\alpha = 5.9$ [20], which indicates its almost complete dissociation followed by the decomposition of OH^-ions. Therefore as the concentration of natrium hydrocarbonate increases as a result of ion-exchange reactions, the softened water will be more alkaline than the original water with the salts $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$.

If the original water has a lot of humic and fulvic acids and a high colouring, it is more preferable to employ reagent softening in large-scale water supply where humic compounds are partially removed with $CaCO_3$ co precipitation. Subsequent desalination of softened water using electrodyalysis results in ion-exchange membranes of the tools in being less likely to be poisoned with the rest of humic and fulvic acids due to the water being alkaline (Fig. 1) [21].

According to Fig. 1, as the pH increases from 6 to 10, the sorption of the fulvic acid decreases by ~ 2 times, which ensures a longer service life of the membrane in the alkaline environment.

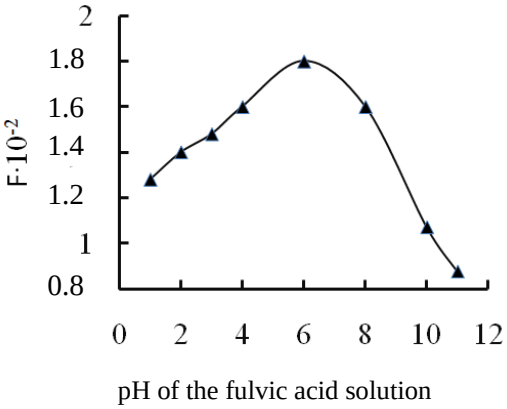


Fig. 1. Dependence of the saturation of the anion-exchange membrane MA-40 with the fulvic acids on the pH of the solution

5. Water chlorination. Disinfection is an essential part of drinking water treatment [2, 4]. Up till now, chlorination has been in common use. Its disadvantage is the resulting chlorine derivatives that from as a result of the interaction between chlorine-containing reagents and organic compounds of water which are mainly humic and fulvic acids [22] which are said above to be present in natural waters. Besides, chlorine reacts with other nitrogen-containing organic compounds — amino acids, pesticides, pigments, chlorophyll, etc. From 10 to 90 % of the organicc compounds react with chlorine [22].

As a result of water chlorination containing humic acids, there are mono-, di-, trichloroacetic acids, chloroform, organobromine compounds, chloral hydrate, tetrachlorated carbon, chlorophenols and other aliphatic as well as aromatic compounds [23, 24]. The above suggests that chlorination of natural waters for their disinfection causes more variety of chlorine-containing impurities. Halogen-containing organic compounds are known to have mutagenic and carcinogen properties, which poses a threat to humans.

These negative aspects of chlorination come with a few positive ones including an easy access and effective performance of it and its compounds when used with organic compounds of a bacterial cell as well as water conservation over a long period of time. It should be nevertheless mentioned that resulting chlorine organic compounds compromise the health and safety, quality of water [4].

Chlorine and its compounds are aggressive to reverse osmotic and electrodyalysis membranes. If there is a large amount of chlorination products of organic compounds and bacteria, tubercular corrosion of the membrane takes place [25]. Besides, in [26] it was found that chlorine is absorbed by polyvinylchloride and polyethylene pipes and then for a long time (2—50 days) is released into water increasing the amount of chlorine in it.

As a result of chlorination, there is a significant reduction in the colouring of water, which is due to the break of the double bonds in the molecules of humic and fulvic acids. This causes a reduction in the molecular mass of the compounds.

We assumed that the fragmentation of large molecules results in the increase in the sorption of fulvic acids as the diffusion of parts of the sorbent pores becomes easier. However, it was found that the efficiency of sorption treatment in deep desalination setups of the Neva water is lower than that of non-chlorinated one.

6. Ozone treatment of water. It has long been considered that ozone used for water treatment is not as adverse as chlorination in terms of toxic compounds, a decline in organoleptic properties, etc.

The efficiency of disinfection degrades as the contamination is on the rise as some of the ozone is used for the oxidation of organic compounds [27]. The amount of ozone should be always be under control: in [28, 29] it was shown that < 1 mg/l of ozone causes an increase in the amount of bacteria but > 2 mg/l causes all of them to die.

It was experimentally shown that in order to discolor water more water is needed than to disinfect it [28]. It depends on the amount of weighed compounds. In [28] it was found during treatment of lake water that organic impurities (phytoplankton) make ozone impact colouring less. Even if the concentration of weighed compounds increases, mineral salts do not cause ozone to impact the coloured water components less.

PH of the environment is essential in water solution treatment as it contributes to the intensification of water discolouring. This becomes a central issue while developing technological water treatment. In a study of the impact of pH on a discoloring reaction of humic acid solutions it was found that for pH ~ 3 colouring is down by 0.5 degrees and for pH ~ 9 — by 1.8 degrees, for 1 mg of O_3/colouring degress, ozonation efficiency increases by almost 4 times in an alkaline environment [30].

The advantages of preliminary ozonation using 0.7—2.0 mg/l are lower amounts of a coagulant [31]; it was also found in [32] that biochemical water treatment promotes biodecomposition of organic water contaminants. These are due to the break of the double bonds and thus a burst of long molecules of humic acids followed by the formation on compounds with a smaller molecular mass.

In addition, ozone is capable of curbing negative impacts of chlorination. Ozonation is therefore known to be used to remove harmful compounds including chlorine-containing ones. Primary mutagenic compounds occurring in chlorination actually fail during the ozonation with small amounts of ozone (about 2 mg/l) [33]. Mutagenic activity correlates well with the optical density of water in ultraviolet.

7. Negative aspects of ozonation. It was also found that at the ozonation as well as oxidation stage mutagenic compounds occur. It was thus concluded that ozone cannot be considered to be a chlorine substitute. Due to its high reaction capacity, ozone is not only a water disinfectant but by interacting with impurities it forms compounds that undermine the quality of water [34].

Over the last decade destruction of organic compounds has been a major concern as it was acknowledged that there should be sufficient information regarding ozonolysis products in order to evaluate their toxicity and possible removal employing a variety of methods as well as sorption and membrane ones. Therefore there have been a few accounts in literature dealing with the ozone oxidation of humic and fulvic acids as well natural waters.

Ozone reaction products with organic compounds included in water are presumably [35] aldehydes, ketones, carboxylic acids and other hydroxylated aliphatic and aromatic compounds.

Aliphatic mon- and dicarboxylic acids and some ketomes, cyclic compounds were identified in humic and fulvic acid ozonolysis products [36]. It is deemed essential to identify how toxic these compounds are. The humic acid ozonolysis products actually revealed both mono-, di- and tricarboxylic and benzenetricarboxylic acids with little succinic and maleic acids [37].

Ozonation of drinking water also reveals side products such as formaldehyde and acetaldehyde [38], with [39] indicating that formaldehyde release is higher in the alkaline environment. The content of the total organic carbon in surface waters was 0.5 mg/l and the ozone concentration of 19—26 mg/l formed 13 carbonyl compounds which were identified using the gas chromatography method [39].

Presently, there are increasingly more compounds identified employed the latest methods in the products of the interaction between ozone and soil humic acids. Not only the above benzenepolycarboxylic acids and kinones but also phenols, aromatic aldehydes, nitrogen-containing heterocycles, polyaromatic hydrocarbons, terephthalic acid, monopolysaccharide,

normal alkanes, fatty acid, etc. were identified [39]. Up to 60—70 % of compounds were found in fumic acids and 65—90 % in humic acids.

It was noted [40] that following the ozonation, water takes on a non-typical smell. N-heptanal was found as well as n-decanal, phenylacetaldehyde, vanillin, etc. Fulvic acids were shown to be capable of being followed by smelly impurities occurring in ozonated water. Subsequent ozonation of fulvic acids results in an increase and followed by a decrease in the amount of some compounds.

8. Ozonation of fulvic acids. In a number of papers a point is made that ozonolysis of natural water impurities does not result in complete mineralization of organic compounds, there is by contrast failure and oxidation, i.e. transformation of the original compound with some of carbon lost [41]. [42] indicates that ozone merely transforms organic compounds without oxidizing them till complete mineralization, which was assumed based on the the optical density at the wavelength of 254 nm. No quantitative assessment of the humic and fulvic acids was performed.

To possibly compare the properties of the humic and fulvic acids prior and following the ozonation, a completely demineralized set of water fulvic acids extracted from the Neva River was oxidized. Ozonation took place with pH ~12. Table 3 presents the results of determining the composition of fulvic acids prior and following ozonation over varying periods of time as well as the mass of the dry remains of the set prior and following the ozonation of the fulvic acid solution (drying under the *Infratherm* lamp at 34—38 °C).

Table 3

Composition of fulvic acids

O_3, mg/mg of fulvic acid	Content, %				Fulvic acid, g/kg (±0.002)	Reduction in fulvic acid g/kg	PO, mg O_2/l (±10)
	C (±0.2)	H (±0.05)	N (±0.04)	O (±0.03)			
0	46.7	5.0	1.2	47.1	2.168	–	500
0.23	40.4	6.4	1.5	51.7	1.984	0.184	310
0.36	38.1	9.3	2.5	50.1	2.010	0.158	–

As the Table suggests, there is an insignificant reduction in the mass of fulvic acids in a sample. However, it does not suggest the compostion of the set remains unchanged. With the content of carbon noticeably decreasing, there is a dramatic increase in the amount of carbon, nitrogen and oxygen. A significant reduction in the amount of easily oxidizing fractions of the fulvic acids – PO is seen to be down by 40 % (fulvic acids are hard to oxidize with $KMnO_4$).

It should be noted that the masses of an organic compound has grown smaller; there has been a change in the nature of the impurities, i.e. they have become less sensitive to the oxidation with potassium permanganate as this (oxidation of easily oxidized parts of the fulvic acids) was performed as they came in contact with O_3. This is in agreement with the assumption that strongly oxidized compounds hardly fail to simplest compounds CO_2 and H_2O.

An increase in the amount of nitrogen in the sample is accounted for with nitrogen oxide emerging in the ozonator from the air nitrogen joining together. Some of the carbon might have oxidized to CO_2. A decrease in the amount of the fulvic acids is made up for oxygen-containing groups which do not have to be carboxylic. These can be ketone, aldehyde, ether groups or alcohol hydroxyles.

The sets of the fulvic acids were studied in different ways including potentiometric titration to allow one to determine the amount of functional groups, their ionization constants as well as the equivalent molar mass, specific electrical conductivity (Table 4), etc.

Table 4

Change in the physical and chemical characteristics of fulvic acids under the effect of ozone

τ, min	O_3, mg/mg of fulvic acid	Concentration of fulvic acid, g/kg of the solution	Concentration of $_{COOH}$, $\frac{mg-equiv}{gfulvicacid}$	pH ±0.04	Equivalent mass of the fulvic acid, g/mole-equiv	pK_a	$\chi \cdot 10^{-4}$, $Ohm^{-1} \cdot cm^{-1}$
0	0	1.016	4.15	237	242	4.2	3.87
20	0.13	0.930	6.46	2.17	148	3.7	7.17
60	0.23	0.883	6.62	2.18	138	3.5	7.82
90	0.29	0.831	6.68	2.22	153	3.6	9.90

Table 4 suggests that the ozonolysis products have 50 % more COOH-groups than the original fulvic acids do. In addition, they are more ionized and mobile: pH dropped; the ionization constant pK_a increased from 4.2 to 3.6 (remember that $pK_a = -lgK_{dist.}$) and so did the electric conductivity. A decrease in the equivalent mass confirms the failure of the fulvic acids takes place.

A study of the products of the interaction of the fulvic acids and ozone using ultraviolet and infrared spectroscopy, gel chromatography, high-performance liquid chromatography, potentiometric titration, measurement of the composition make us assume that the major change in the physical and chemical properties and structure of the fulvic acids occurs over the first 20 minutes of the ozonation when some of the ozone id absorbed, i.e. 0.13 mg/mg of the fulvic acid overall. A loss of the mass is not significant and is 7—8 % in the neutral environment, 17—19 % in the alkaline environment. Not only high- but low-molecular fractions of the fulvic acids undergo a failure. The ozonolysis products are less aromatic than the original fulvic acids and have a smaller molecular mass. These changes appear to positively affect the sorption capacity of the fulvic acids with porous anionites.

9. Sorption of ozonated fulvic acids. The literature analysis and our own observations [43—45] conclude the underperformance of the coagulation method for prior treatment for high requirements for the quality of desalinated water. Therefore it should be substituted or supplemented by other physical and chemical methods. These are ultrafiltration, reverse osmosis, sorption on activted carbons and synthetic ionites, failure of organic molecules using different radiation and oxidizers, etc.

For high requirements for treated water, sorbents to remove organic impurities are applied. Special macroporous anionites are effective at absorbing them from natural waters [43, 44]. However, there are still humic and fulvic acids remaining in conditioned water. One of the reasons for low selective criteria for humic and fulvic acids is no agreement between the size of the sorbent pores and sorptive molecules. If an increase in the porosity of ionites causes the sorption to be on the rise, a decrease in the size of the sorptive molecule might yield a similar result.

This is based on the fact that the speed of sorption of PAV, humic and fulvic acids with anionites is constrained by mass transfer in the solid phase [45]. It is obvious that the influence of the steric factor can be reduced with the failure of high-molecular compounds to

low-molecular parts. In order to do this, oxidation failure of the Neva fulvic acids was performed using ozone.

In order to identify the way prior ozonation of the fulvic acid solutions influences the anionite soprtion, the method of output curves was used (Fig. 2).

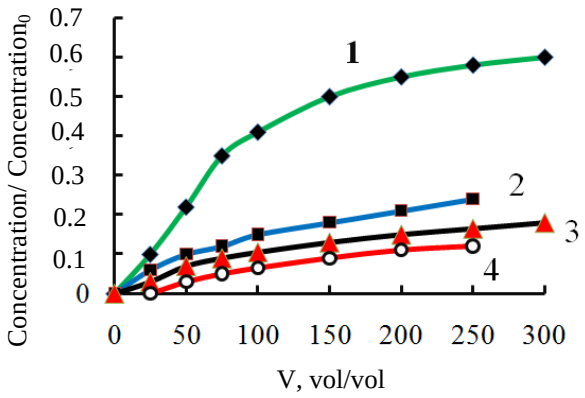


Fig. 2. Output curves of the sorption of the fulvic acids using AB-17-2П anonite prior (1) and following the absortion of 0,13 (2), 0,23 (3) ad 0,29 (4) mg of ozone for O_3/mg of the fulvic acid.
$C_{ФК}$ = 19,6 mg/l; V = 10 ml; u = 10 m/h

The experiment was conducted under the same conditions: a column with the diameter of 10 mm, the volume of the chloride ionite is 10 ml; the volume of the filtrate fraction is 250 ml, the amount of the fulvic acid solution passed through is 3000 ml (i.e. 300 volumes through a loading volume, vol/vol). There was spectrophotometric (СФ-46) control of the fulvic acids in the filtrate, the optical length of the cell was 100 mm, λ = 300 nm. Apart from the fulvic acids, some of the samples were selected for permanganate oxidation of the middle samples of the filtrate.

The fulvic acid solutions with pH 2.3 and the concentration of 16.0—19.0 mg/l were passed through low-base anionites ИА-2 and АНТ-511, middle-base anionite *Wofatit* AD-41, high-base porous anionite АВ-17-2П. The efficiency of water treatment using ozonated fulvic acids appeared to increase significantly on all of the anionites. Compared to non-ozonated fulvic acids, a filtrate skip dropped even for the smallest amount of ozone. The output sorption curves for the fulvic acids using anionite АВ-17-2П are in Fig. 2. Here C/C_0 is the concentration ratio of the fulvic acids to their original content.

It should be noted that an increase in the *amount* of the absorbed ozone causes the sorption capacity of anionites to grow for fulvic acids: e.g., after anionite ИА-2 was used, their content at the end of the cycle was 3 % overall of the original concentration of the fulvic acids. A sim-

ilar thing is observed in high- and middle-base anionites with the improvement of sorption using АВ-17-2П for ozonated fulvic acids being more pronounced compared to non-ozonated ones (see Fig. 2).

Conclusions

1. Common methods of water treatment were shown to significantly impact the composition of organic impurities among others and determine the efficiency of the treatments stages that follow. There is a change in pH, water salt content; sorption treatment becomes more or less effective.

2. Water desalination using not only chlorine but also ozone was shown to have negative impacts.

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