
PHYSICAL CHEMISTRY OF WATER
TREATMENT PROCESSES

Peculiarities of Preparation of Drinking Water from Surface Sources with High Contents of Natural Organic Compounds, Iron, and Manganese

O. Yu. Kulishenko^{a, *}, N. A. Klymenko^a, L. A. Savchyna^a, S. V. Grechanyk^a, L. V. Nevylna^a,
L. K. Patyuk^a, V. A. Kostiuk^b, and L. P. Avramenko^b

^a Dumansky Institute of Colloid Chemistry and Water Chemistry, National Academy of Sciences of Ukraine,
Kyiv, 03680 Ukraine

^b Private Joint Stock Company Kyivvodokanal, Kyiv, 02660 Ukraine

*e-mail: kullish@gmail.com

Received September 6, 2021; revised September 14, 2021; accepted September 16, 2021

Abstract—The peculiarities of the Dnieper river water that contains natural organic compounds of allochthonous origin, in the composition of which fulvic acids with a molecular mass of about 1.0 kDa predominate, are investigated. It is established that the use of iron-containing coagulants in the process of purification of such water leads to its enrichment with iron compounds and a corresponding increase in its color intensity. Comparison of the effectiveness of aluminum and iron coagulants showed that both reagents lead to a stable decrease in Dnieper water coloration caused by humic acids. However, the use of iron(II) sulfate does not reduce water coloration caused by fulvic acids because of the formation of stable soluble hydroxofulvate complexes. It is shown that the redox system of Dnieper water is at the transition boundaries between Fe^{2+} and hydroxide $\text{Fe}(\text{OH})_3$ and between Mn^{2+} and oxides MnO_2 and Mn_2O_3 . The replacement of the standard chlorine agent with chlorine dioxide results in moving this boundary with the formation of finely dispersed flakes of iron hydroxide and particles of manganese oxides. As a result, the use of chlorine dioxide (ClO_2) in doses of 0.2–1.25 mg/dm³ in the final stage of water purification leads to an increase in water coloration intensity, which can be successfully reduced by filtration. With an increase in the dose of ClO_2 , an inverse relationship is established between the dynamics of water coloration intensity growth and the decrease in the Mn content during filtration. The correlation coefficient between these factors is $r = -1$, which indicates that the presence of manganese is the main factor for increasing the color intensity upon the treatment of water with chlorine dioxide in the summer season. On the basis of the obtained results, a flexible scheme is proposed for chlorine dioxide supply with the following stages: primary treatment at the entrance to water treatment facilities, secondary treatment after coagulation and settling of water before fast filtration, and final disinfection before supplying drinking water to the city.

Keywords: chlorine dioxide, iron, turbidity, chromaticity, manganese, natural organic compounds, fulvic acids

DOI: 10.3103/S1063455X21060059

INTRODUCTION

Preparation of high quality drinking water from surface sources with high content of natural organic compounds (NOCs) is among the most problematic issues of contemporary water treatment technologies. The presence of NOCs in water from surface sources and their conversion after oxidation lead to increase in the content of bioavailable carbon, which causes biological instability of drinking water. As a result of its disinfection, organic chlorinated compounds are formed in quantities that exceed the regulatory requirements. Natural organic compounds determine the bioavailability of traces of heavy metals for microorganisms (phytoplankton, zooplankton, algae, etc.). Acid/base properties of NOCs favor complex formation with metals, which substantially limits the possibility of extracting the latter in water treatment processes. This primarily applies to iron and manganese, which are most often present in natural waters [1, 2]. Deep removal of NOCs in water treatment processes allows one not only to prevent the formation of toxic products of disinfection and secondary microbial contamination of water, but also to prevent the ingress of heavy metal ions into drinking water.

Iron can be present in natural water in the form of a finely dispersed suspension, in a soluble form, in complexes, and in an adsorbed form on living organisms and on the surface of bottom sediments. Humic and fulvic acids (HAs and FAs, respectively) have the highest ability to form complexes with iron [3]. In natural waters, the typical oxidation states of iron are +2 and +3. More often, iron is in the form of Fe(III) because of the fact that this form is a thermodynamically more stable state [3–5]. The ratio between Fe(III) and Fe(II) in natural waters depends on the values of redox potential E_h and pH of water, on the concentration and elemental composition of NOCs, and on the biological activity of the environment [6–8]. Most of the amounts of Fe(III) dissolved in surface waters are in the form of stable complexes with organic ligands, in particular, with humic substances (HSes) or organic compounds produced by phytoplankton and bacteria. Divalent iron predominates in waters with low E_h values [7]. A special role is played by FAs, which reduce Fe(III) to Fe(II) with subsequent binding of the latter into complexes. Owing to the formation of complexes, a substantial part of iron migrates in the dissolved state into the anionic and neutral fractions of NOCs [7]. Organometallic complexes play an important role in water treatment processes, in particular, in the oxidation process. Upon the destruction of organic substances involved in complexes, Fe(III) is released from the composition of complexes and hydrolyzed.

The waters of the Dnieper basin are characterized by increased contents of NOCs (up to 20 mg C/dm³) and iron and manganese in some periods of the year. The composition of Dnieper water is formed under the influence of swamps and algal blooms. The basic indicators of its quality are those associated with natural organic compounds. These include the chromaticity (Chr), the permanganate and dichromate oxidizability (PO and DO, respectively), and the total organic carbon (TOC). The NOCs of Dnieper water is dominated by FAs with a molecular weight of around 1.0 kDa (up to 80–85 wt %). Fulvic acids are colored less than humic acids, but they determine the Chr value of water owing to larger amounts. The NOCs of the Kiev water reservoir containing HAs and FAs are of an acidic nature and present in the water in the form of stable highly dispersed sols with a negative charge, which causes the formation of mainly anionic metal complexes with iron (up to 80 wt %) and then cationic (about 4–5 wt %) and neutral (about 17–18 wt %) complexes [9]. Neutral complexes with carbohydrates with a molecular weight of less than 5 kDa contain from 39.0 to 46.9 wt % of iron on the average. In water treatment processes, it should be borne in mind that carbohydrates are compounds that are easily oxidized and are capable of transforming into substances with low molecular weight and release potentially bioavailable iron [7].

An analysis of long term water quality indices of the Dnieper River allows one to assert [10] that the main problems arisen during the operation of water treatment facilities of the Dnieper Water Supply Station of Kyiv (DnWSS) are caused by the hydrophilic fraction of FAs with low molecular weight, as well as by high biological and chemical resistance of organomineral complexes with iron, which are not removed by traditional reagents and get into the clean water tanks (CWTs).

The aim of this study was to establish conditions for the preparation of high quality drinking water from surface water sources that contain high concentrations of natural organic compounds, iron, and manganese using Dnieper water as an example and chlorine dioxide as an oxidant and a disinfectant.

EXPERIMENTAL

The results of analyses of Dnieper water samples for 2012–2021 are used in this study, which were provided by the DnWSS of Kyiv. The changes in water quality indices associated with NOCs during this period are shown in Fig. 1a. The changes in the iron and manganese contents during the same period are shown in Fig. 1b.

Figure 1 shows the unstable behavior of seasonal changes in the quality of the Dnieper water, but there is a certain pattern in their long term fluctuations and visual correlation between them. In this study, the last research was conducted in 2021 with increased values of Chr, PO, DO, and TOC, and the increased contents of iron and manganese.

Optimal doses of reagents and other water purification indices and parameters were determined using jar tests, silt density index (SDI) tests, and other laboratory methods. The parameters of dosing and mixing of reagents with water were agreed with real operation modes of the DnWSS. To compare the results, the concentrations and doses of reagents were calculated with reference to oxides (Fe₂O₃ and Al₂O₃).

The results of studying indices (factors) were statistically analyzed using Microsoft Excel. The correlations of the factors were evaluated by Pearson's linear correlation coefficients r ; the correspondence of the trend curves to the experimental results was evaluated using determination coefficients R^2 .

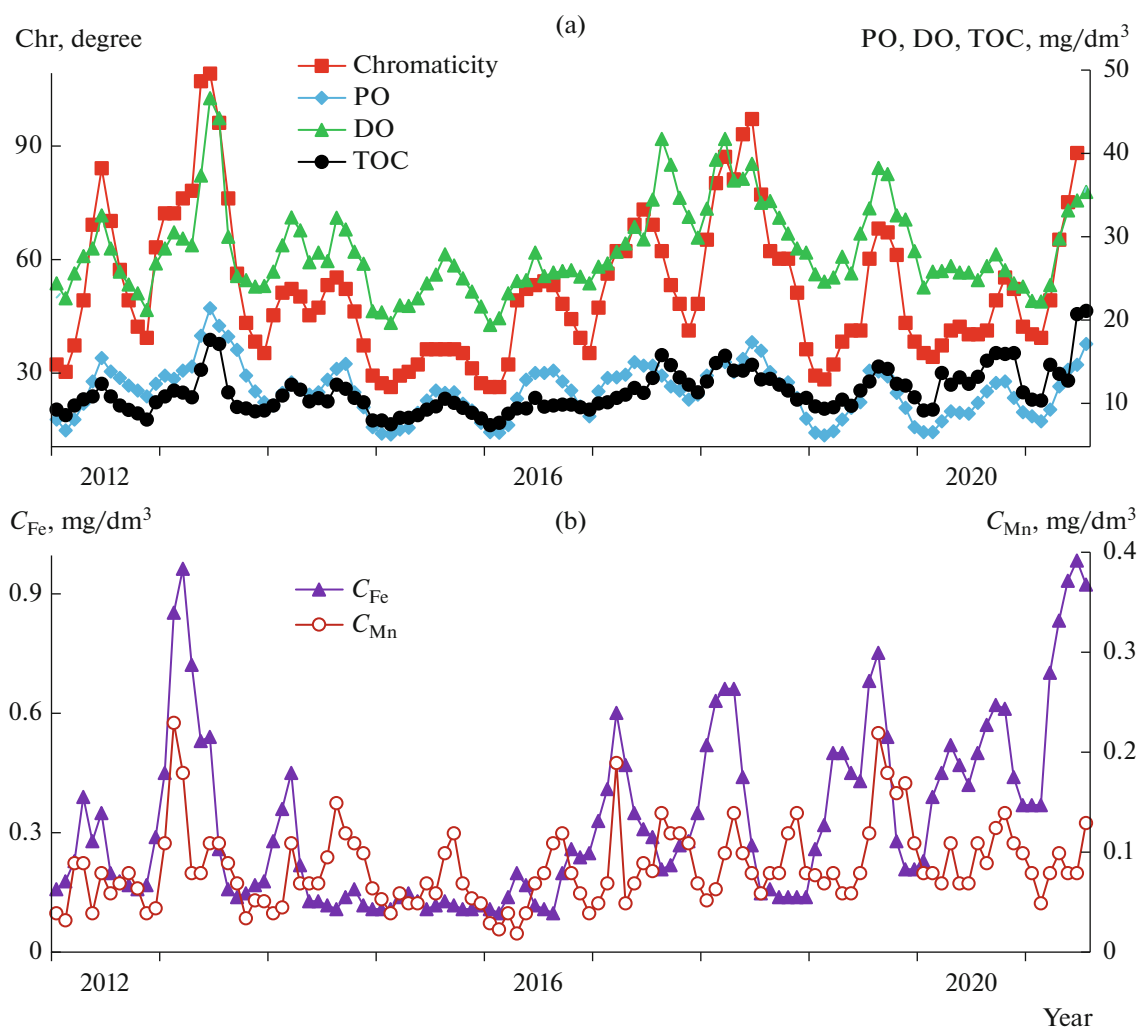


Fig. 1. Dynamics of changes in the monthly average indices of Dnieper water.

RESULTS AND DISCUSSION

Coagulation of Dnieper Water

Coagulants for water purification are divided into aluminum and iron coagulants. As a rule, aluminum sulfate (AS) is used in the DnWSS despite the fact that iron-containing coagulants are believed to be more effective in eliminating NOCs. However, testing of iron-containing coagulants on Dnieper water samples gave negative results. Ferrous sulfate (FS) proved to be good in the muddy low colored waters from mountain rivers of western Ukraine, but it contributed to a radical increase in the iron content and an increase in coloration intensity in the process of purification of Dnieper water. As shown in our previous studies published in this journal in 2018, the use of composite coagulants (CCs)—which are mixtures of iron- and aluminum-containing components—leads, under certain redox conditions (pH and E_h), to the situation when iron introduced into the water with the reagent cannot be removed by filtration at all. Secondary addition of iron into water from natural humic compounds (HCs) is not excluded. This requires a further study of the possible ways, by which iron may enter purified water, taking into account its complexation with FAs.

The numerous study results, an example of which is given in Fig. 2a, show a negative effect of coagulation of Dnieper water with iron-containing coagulants (curve 2) even at pH values favorable for these reagents. Instead, coagulation of Dnieper water with aluminum sulfate allows one to obtain a stable decolorization effect (curve 1). Coagulation with a composite coagulant in the form of FS and AS mixed in the Fe_2O_3/Al_2O_3 ratio of 3/1 gives an intermediate result (curve 3).

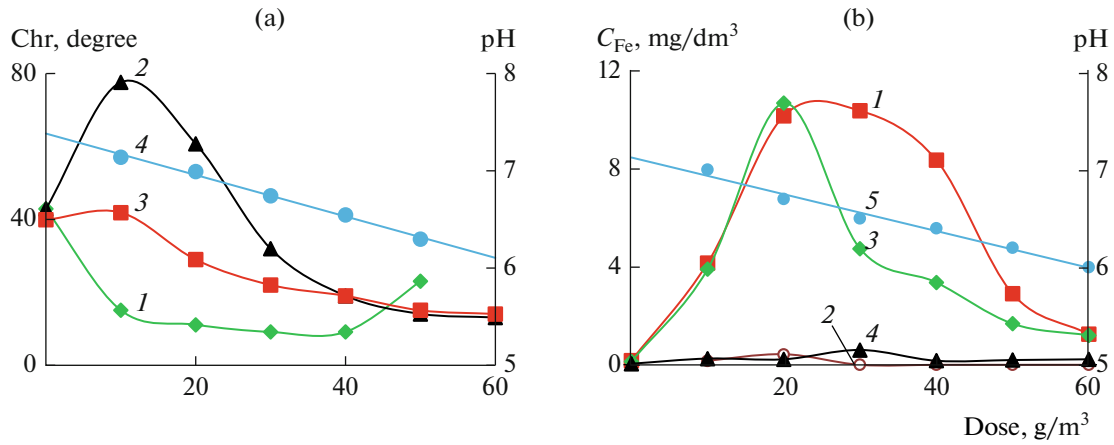


Fig. 2. Changes (a) in the chromaticity upon coagulation (AS (1), FS (2), and CC (3)) and (b) in the concentrations of iron in settled and filtered water after coagulation (FS (1, 2) and CC (3, 4)) against pH changes (4) in part (a), (5) in part (b).

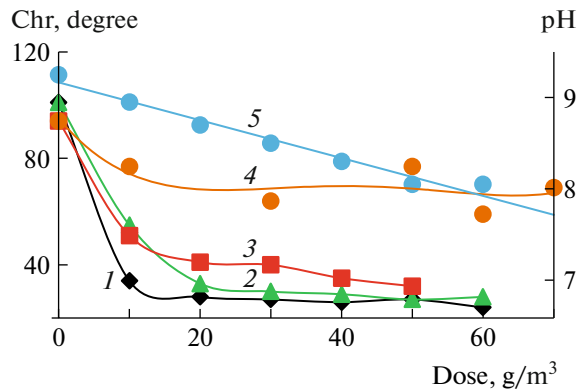


Fig. 3. Coagulation of model solutions of HAs (1, 2) and FAs (3, 4) when using AS (1, 3) and FS (2, 4) against pH changes (5).

The dynamics of changes in the iron concentration in the settled and filtered water obtained in the same experiment are shown in Fig. 2b. It is shown that the water sample is simultaneously enriched with iron compounds in the process of coagulation (curves 1 and 3) and most of these compounds are removed during settling and filtration (curves 2 and 4). It is easy to find out what is the additional iron load potentially precipitating in the settling tanks and remaining on the filters. Nevertheless, it is seen from Fig. 2a that even small residual concentrations of iron are sufficient to noticeably deteriorate the Chr parameter of water.

The study performed on model solutions of HAs and FAs allows one to demonstrate (Fig. 3) which one of these NOC components plays a major negative role in coagulation. Traditional reagents AS and FS provided a stable decrease in the Chr associated with humic acids (curves 1 and 2). Aluminum sulfate performed slightly worse in the purification of water from fulvic acids (curve 3). And there was almost no purification of water from fulvic acids when using FS (curve 4).

As can be seen from Figs. 2 and 3, the studies were performed with reagent doses of up to 60–70 g/m³ with reference to metal oxides (Me₂O₃). Doses calculated for commercial products are several times higher and never used in real conditions. The base dose is used in practice, which is determined by the Chr and turbidity (Trb) indices of water. However, the optimum decrease in the PO and DO does not always correspond to this dose and exceeds it by a factor of 1.5–2. Therefore, it was proposed to use the so-called “enhanced coagulation” for deep removal of NOCs [11]. The optimal dose for enhanced coagulation is

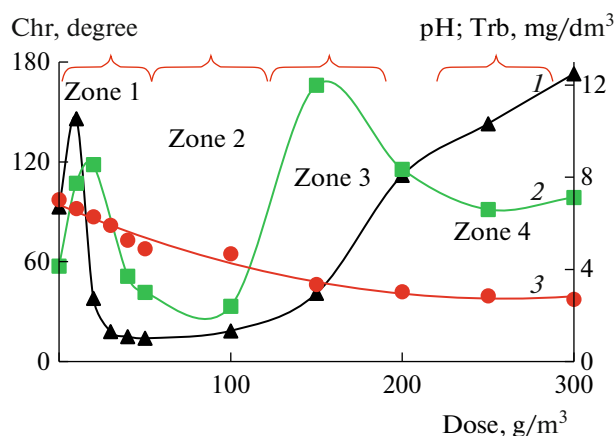


Fig. 4. Coagulation of Dnieper water in a wide range of CC doses: (1) chromaticity curve; (2) turbidity curve; (3) pH curve.

the dose with which an increase in the reagent supply by 10 g/m^3 leads to a decrease in the concentration of NOCs by less than 0.3 mg/dm^3 .

With an increase in the reagent doses, the pH of the system decreases and the hydrolysis balance shifts. In [12], the processes that take place were divided into the following four zones:

Zone 1 with very small doses of coagulants, in which the particles are negatively charged and stable.

Zone 2 with low doses of coagulants, in which the charge of the particles is neutralized, and their adhesion and primary (basic) coagulation occur.

Zone 3 with high doses of coagulants, in which the charge of the particles changes from “–” to “+” and, as a result, suspended particles are stabilized again in the absence of coagulation.

Zone 4 with very large coagulant doses that lead to the so-called “sweep flocculation”, in which secondary extensive precipitation of hydroxides and efficient water purification occur.

Figure 4 shows an example of coagulation curves obtained in the excessive range of doses of CCs, i.e., mixtures of ferrous and aluminum sulfates. Curve 2 related to the turbidity index shows the same principle of zoning. But the chromaticity index (Curve 1) continues to grow monotonously with a substantial increase in the doses.

Sweep flocculation leads to the extensive formation and precipitation of flakes with contact coagulation of contaminants on them. However, it also creates a large mass of loose flakes that increase the load on fast filters, which potentially causes leakage of contaminants and residual aluminum and iron into the filtrate. In the case of using iron-containing coagulants, obviously iron recovery with a corresponding increase in the chromaticity is observed.

This emphasizes the importance of redox conditions on the coagulation of Dnieper water and confirms the published data [13] on the potential impact of FAs on iron recovery in surface waters. However, problems obviously arise not only at the level of colloidal or true solutions of NOCs, but also at the border between homogeneous and heterogeneous systems. The vagueness of the transition in this region causes an imaginary correlation between the color and turbidity of Dnieper water [10]. The Chr index in the above figures also includes iron hydroxide microflakes that are not retained on the blue ribbon filter paper with a pore size of 3 to $5 \mu\text{m}$, which was used to filter the samples before analyses.

A Study of Water Microfiltration

Other studies also indirectly point to the influence of different fractions of NOCs on water purification. Thus, the silt density index was used to assess the risk of contamination of nanofiltration membranes [14]. The principle of determining the SDI is based on estimating the reduction of water flow during filtration through test laboratory membranes with a pore size of $0.45 \mu\text{m}$ at a constant inlet pressure of 207 kPa. The standard SDI value [15] cannot exceed 3–5 units with a test filtration period of 15 min according to the requirements of different membrane manufacturers.

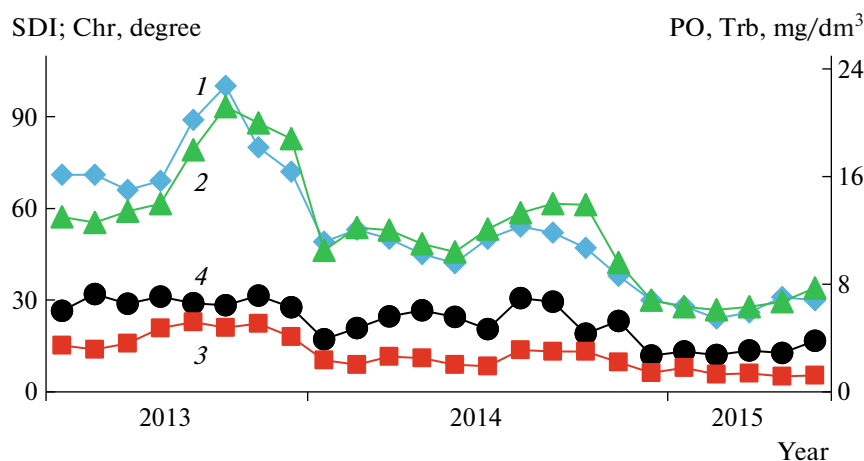


Fig. 5. Graphical correlations between the Chr (1), PO (2), Trb (3), and SDI₃ (4) indices.

However, standard Millipore membranes could not be used in many cases to test water samples taken from the Dnieper River or from CWTs of the DnWSS. The filters do not allow water to pass after 3–5 min from the start of test filtration, i.e., much earlier than 15 min. Thus, the existing water treatment facilities of the DnWSS were insufficient to ensure water quality that would meet the requirements of manufacturers of membrane treatment systems.

Figure 5 shows the series of dynamics of the average monthly changes in the SDI and parameters that characterize the content of NOCs (Chr and PO) and turbidity of Dnieper water. Instead of the standard SDI₁₅ parameter, the one corresponding to the filtering time of 3 min (SDI₃) is used.

The graphs and correlation coefficients indicate strong relationships between all factors. The SDI₃ parameter determining the content of suspended particles correlates with both the Trb index (which is understandable) and the Chr and PO indices (which should be impossible by definition).

Consider that the pore size of Millipore filters (0.45 μm) corresponds to the microfiltration mode (0.02–10 μm) and is commensurate with the minimum size of algae (starting from 0.25 μm) or macromolecules of organic substances. As is known [16], the latter can create clusters from 30–200 to 450 nm (0.45 μm) in size or even larger filamentous structures. According to the classification given in [17], these contamination ranges belong to group I of heterogeneous systems in accordance with the phase dispersion state (suspensions, emulsions, microorganisms, and phytoplankton). With such test results, it is not reasonable to expect that the existing water treatment facilities of the DnWSS will remove colloids and macromolecular compounds (group II) and, all the more, molecular solutions of organic substances (group III).

In natural water reservoirs, natural organic compounds include biopolymers (polysaccharides, polypeptides, and proteins), humic compounds, building blocks (products of weathering and oxidation of HCs), and low molecular weight compounds and organic acids [14]. The organic content of Dnieper water consists of allochthonous natural NOCs dominated by HCs that come from Polesia bogs and algal NOCs (autochthonous) that are formed during blooming from extracellular macromolecular compounds and cellular debris. Water supply issues are created in the region of residual NOCs with a molecular weight from 0.5 (0.35) to 2 kDa [14]. The fractional composition of wetlands water that contain natural organic matter with molecular weights of 1 to 10 kDa agrees well with this range. Experiments with NOCs resistant to coagulants [18] showed that coagulation with aluminum-containing reagents mainly removes high molecular weight compounds, while low molecular weight (around 500–700 Da) compounds remain in the treated water. The latter parameter correlates with the scope of nanotechnology, including nanofiltration.

Criteria and Ratios of Quality Indices

To characterize changes in water quality over time and in water treatment processes, it is important to use not only the absolute levels of Chr, PO, BO, and TOC, but also the relationships between them, which

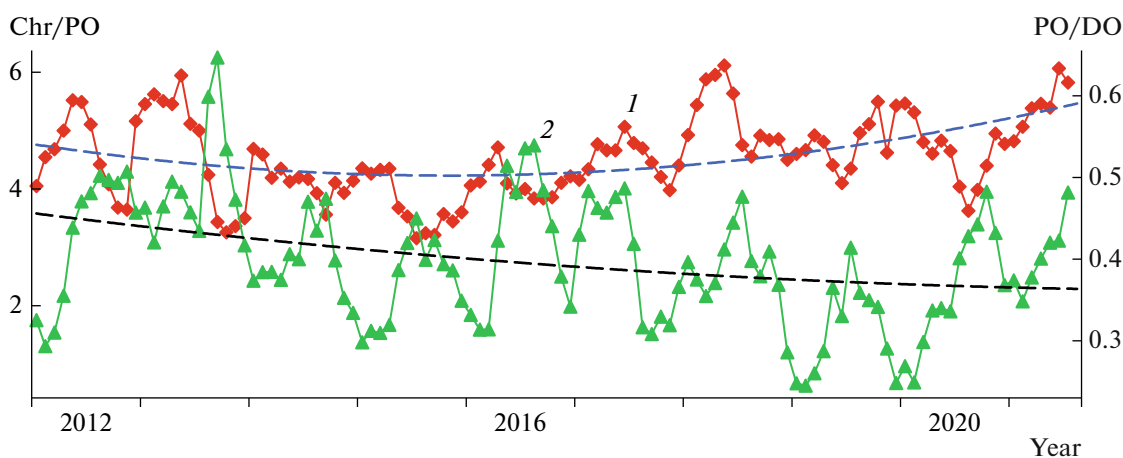


Fig. 6. Dynamics of average monthly changes in the Chr/PO (1) and PO/DO (2) ratios for the past 10 years.

were proposed to characterize by coloration coefficients $K_{\text{col}} = \text{Chr}/\text{PO}$ and the PO/DO ratio [19, 20]. Their changes over the past ten years are shown in Fig. 6. One can see the gradual increase in the content of organic substances of nonhumic origin in Dnieper water, which are difficult to oxidize.

In [21, 22], it was proposed to evaluate the degree of hydrophobicity/hydrophilicity of NOCs and the possibility of their removal by coagulation on the basis of the aromaticity parameter based on specific ultraviolet absorption (SUVA), which is the amount of absorption at $\lambda = 254 \text{ nm}$ (UV_{254}) per unit concentration. As was shown in [23], the SUVA value for Dnieper water in the water intake area of the DnWSS is in the range of $3.0\text{--}3.5 \text{ dm}^3/\text{m mg}$ during the year, i.e., the water contains a mixture of humic and non-humic substances. This conclusion actually complies with the conclusion drawn above on the basis of the K_{col} and PO/DO values.

Joint consideration of traditional indices of Dnieper water quality (Chr, PO, DO, TOC, and the contents of iron and manganese) and nontraditional ratios (Chr/PO, PO/DO, and SUVA) expands the understanding of what is going on. We will show this using the recent problems with the Dnieper water quality, which arose in the summer of 2021, as an example.

Analysis of Situation with Deterioration of Dnieper Water Quality

Water treatment facilities of the DnWSS include bucket water intake, bulk mixers, horizontal settling tanks, fast filters, and CWTs. As a result of the recent reconstruction of the station, liquid chlorine was replaced by chlorine dioxide (ClO_2). In connection with deterioration of the color of purified water in the summer of 2021, an inspection of water treatment facilities of the DnWSS and related studies were carried out. In the studies at the station, chlorine dioxide with a dose of $2.5 \text{ g}/\text{m}^3$ (primary chlorination) was introduced into the avancamera before the mixers. A dose of $0.5 \text{ g}/\text{m}^3$ of ClO_2 was also first fed into the contact chambers before the CWT, which was then replaced by a conventional chlorine agent (secondary chlorination). Table 1 shows an example of Dnieper water quality indices at the inlet and outlet of the water treatment facilities. Figure 7a shows the changes in these and other indices over the network of main facilities. As can be seen from Table 1 and Fig. 7a, there is some deterioration of organoleptic characteristics of water quality and its oxidizability at the final stage of water treatment. The SUVA index becomes equal to $1.2\text{--}1.7 \text{ dm}^3/(\text{m mg})$. The latter indicates that the composition of NOCs is dominated by substances of hydrophilic nature with low molecular weight and low charge density.

As can be seen from Fig. 7b, the major part of changes in the pH and E_h occurs before the filters after reagent treatment and settling. It should be noted that the pH after the main water treatment facilities decreased to $6.2\text{--}6.4$ and the E_h value increased to $165\text{--}170 \text{ mV}$.

To simulate the treatment of water with chlorine dioxide, water samples were taken from the Dnieper River, at the entrance to the mixers, after settling tanks, after filters, and from the CWT. Using a laboratory flocculator with a stirring frequency of 100 rpm, they were treated with ClO_2 doses of $0.5\text{--}2.5$ and $0.2\text{--}1.25 \text{ g}/\text{m}^3$ for the Dnieper water samples and the samples from other water purification steps, respectively. The duration of contact was 20 min. The obtained samples were filtered through blue ribbon filters. The

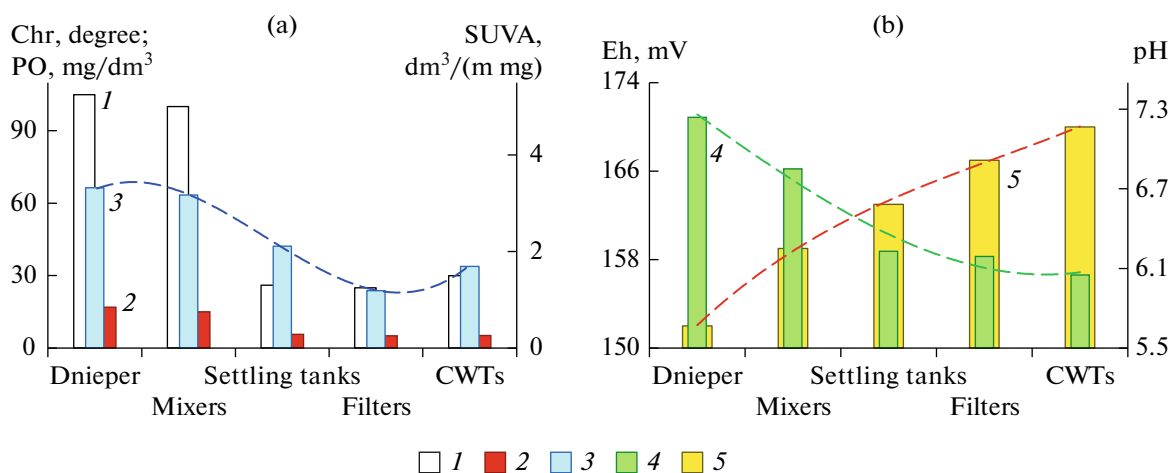


Fig. 7. Dynamics of (a) changes in the Chr (1), PO (2), and SUVA (3) indices and (b) changes in the pH (4) and E_h (5) over the network of facilities.

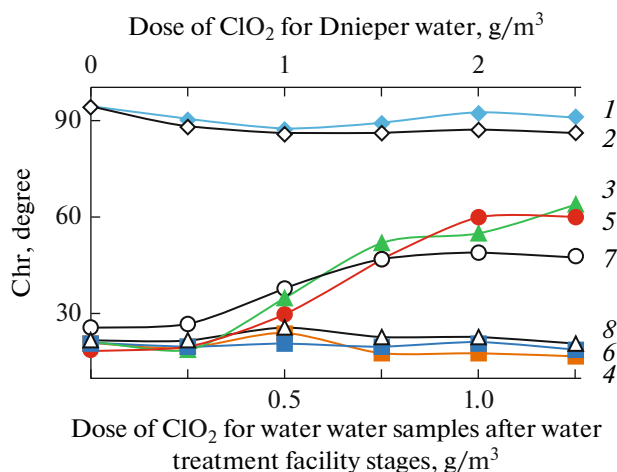


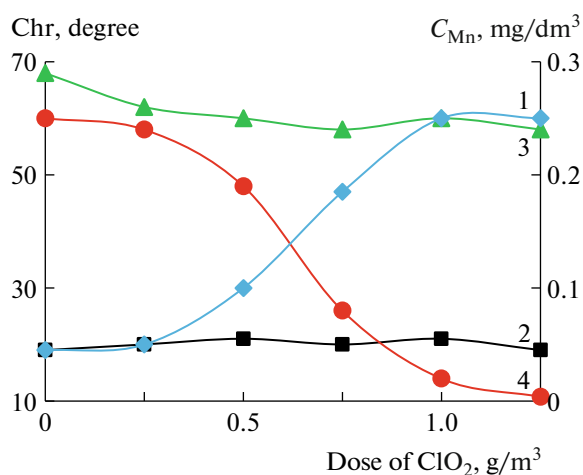
Fig. 8. Results of treatment of Dnieper water with chlorine dioxide for the following water samples after settling and filtration through a blue ribbon filter: (1, 2) incoming water, (3, 4) water after the settling tanks; (5, 6) water after fast filters; (7, 8) water from a clean water tank.

results for Chr are shown in Fig. 8. As can be seen from Fig. 8, the additional introduction of chlorine dioxide only slightly changes the Chr of Dnieper water (curves 1 and 2) and triples the Chr of water in other samples. The chromaticity is successfully reduced after the filtration through blue ribbon filters. However, this residual Chr level is not much lower than the initial value (for this step) and ranges from 17 to 21 degree.

The reason for this increase in coloration intensity may be the presence of iron and manganese compounds. However, we note a small content of iron in the studied water sample when returning to the data given in table. Instead, the concentration of manganese in it is 7.6 times higher than the value required by regulatory standards, i.e., 0.05 mg/dm³. According to the Pourbaix diagrams for iron, the system is at the transition boundary between Fe^{2+} and $Fe(OH)_3$. For manganese, the system is close to the transition from Mn^{2+} to oxides Mn_2O_3 and MnO_2 . Iron did not manifest itself through the Chr parameter during secondary treatment with ordinary chlorine at the steps of settling tanks, filters, and CWTs. But the replacement of chlorine with stronger oxidant ClO_2 was enough for the iron to oxidize and to produce a precipitate of hydroxide $Fe(OH)_3$, and for manganese to form oxides Mn_2O_3 and MnO_2 from Mn^{2+} ions.

Table 1. Resulting indices of water purification in the DnWSS

Water	Chr, degree	Trb	PO	Fe	Mn	SUVA, dm ³ /(m mg)	pH	ROP, mV
		mg/dm ³						
Entrance to water treatment facilities of DnWSS (Dnieper)	105	4	16.9	0.15	0.38	3.32	7.2	152
Output from filters of DnWSS	25	0.87	5.06	0.06	0.28	1.69	6.2	167

**Fig. 9.** Synchronicity of changes in the Chr of settled (1) and filtered (2) water and changes in the Mn content in settled (3) and filtered (4) water sampled after fast filters of the DnWSS during chlorine dioxide treatment.

Suspended $\text{Fe}(\text{OH})_3$ microflakes and manganese oxide microparticles give yellow color to water, which does not reproduce chromaticity (as a regulatory index), but reproduce turbidity at the level of colloids. Therefore, the level of correlation between the Chr and Trb indices reaches $r = 0.92\text{--}0.98$. These particles are effectively removed on blue ribbon filters, as illustrated in Figs. 8 and 9.

Upon an increase in the dose of ClO_2 (see Fig. 9), an inverse relationship between the dynamics of Chr growth (curve 1) and a decrease in the Mn content during filtration (curve 4) are observed. The correlation coefficient between these indices is $r = -1.0$; therefore, the presence of manganese compounds is the main factor leading to an increase in the coloration intensity of water in the period under consideration. Those manganese compounds that are not removed in the case of conventional chlorination are oxidized and filtered off in the case of using ClO_2 . In the absence of a filtration stage, this kind of colored water enters the CWT and causes complaints from consumers.

CONCLUSIONS

The peculiarities of Dnieper water that contains natural organic compounds of allochthonous origin, in the composition of which fulvic acids with a molecular mass of about 1.0 kDa predominate, are investigated. It is established that the use of iron-containing coagulants in the process of purification of such water leads to its enrichment with iron compounds and a corresponding increase in its coloration intensity.

The comparison of the effectiveness of aluminum and iron coagulants shows that both reagents provide a stable decrease in the intensity of Dnieper water coloration caused humic acids. However, the use of fer-

rous sulfate does not reduce water coloration caused by fulvic acids because of the formation of stable soluble hydroxulfate complexes.

It is shown that the redox system of the Dnieper water is at the transition boundaries between Fe^{2+} and hydroxide $\text{Fe}(\text{OH})_3$, and Mn^{2+} and oxides MnO_2 and Mn_2O_3 . Replacement of the conventional chlorine agent with chlorine dioxide promotes the shift of this boundary with the formation of fine iron hydroxide microflakes and manganese oxide particles. As a result, the use of chlorine dioxide doses of 0.2–1.25 mg/dm³ at the final stage of water purification leads to an increase in the water coloration intensity, which can be successfully reduced by filtration.

With an increase in the dose of ClO_2 , an inverse relationship between the dynamics of water coloration growth and a decrease in the Mn content during filtration are observed. The correlation coefficient between these factors is $r = -1$, which indicates that manganese is the main factor responsible for an increase in the chromaticity upon the treatment of water with chlorine dioxide in the summer season.

On the basis of the obtained results, a flexible scheme is proposed for chlorine dioxide supply with the following stages: primary treatment at the entrance to water treatment facilities, secondary treatment after coagulation and settling of water before fast filtration, and final disinfection before supplying drinking water to the city.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Ma, X. and Green, S.A., Fractionation and spectroscopic properties of fulvic acid and its extract, *Chemosphere*, 2008, vol. 72, no. 10, pp. 1425–1434.
2. Swietlik, J., Dabrowska, A., and Raczyk-Stanislawiak, U., Reactivity of natural organic matter fractions with chlorine dioxide and ozone, *Water Res.*, 2004, vol. 38, no. 3, pp. 547–558.
3. Rabajczyk, A. and Namiesnik, J., Speciation of iron in the aquatic environment, *Water Environ. Res.*, 2016, vol. 86, no. 8, pp. 741–758.
4. Rabajczyk, A., Influence of land development on heavy metal forms in the Bobrza River ecosystem (Świętokrzyskie Province, Poland), *Centr. Eur. J. Chem.*, 2011, vol. 9, no. 2, pp. 326–336.
5. Arpadjan, S., Tsekova, K., Petrova, P., and Knutsson, J., Field sampling, speciation and determination of dissolved iron(II) and iron(III) in waters, *Bulg. Chem. Commun.*, 2012, vol. 44, no. 4, pp. 299–306.
6. Dinu, M.I. and Shkinev, V.M., Complexation of metal ions with organic substances of humus nature: Methods of study and structural features of ligands, and distribution of elements between species, *Geochem. Int.*, 2020, vol. 58, no. 2, pp. 200–211.
7. Linnik, P.N., Zhezherya, V.A., and Linnik, R.P., Iron in natural surface waters of Ukraine: Content, peculiarities of migration and biological role, *Hydrobiol. J.*, 2018, vol. 54, no. 5, pp. 63–80.
8. Kovzun, I.G., Prokopenko, V.A., Panko, A.V., Tsyganovich, O.A., Oliinyk, V.O., Nikipelova, O.M., and Ulberg, Z.R., *Nanochemical, Nanostructural and Biocolloidal Aspects of the Transformation in Dispersion of Iron-Aluminosilicate Minerals*, Kyiv, 2020, ch. 1.7, pp. 28–31.
9. Adusei-Gyamfi, J., Ouddane, B., Rietveld, L., Cornard, J.-P., and Criquet, J., Natural organic matter cations complexation and its impact on water treatment—A critical review, *Water Res.*, 2019, vol. 160, pp. 130–11.
10. Kulishenko, A.E., Ostapenko, V.T., Kravchenko, T.B., Kvasnitsa, E.A., and Ostapenko, R.V., The statistical analysis of quality indicators of the Dnieper river water and directions for reconstruction of water treatment facilities of the Dnieper waterworks in Kiev, *J. Water Chem. Technol.*, 2011, vol. 33, no. 2, pp. 117–129.
11. Lin, J.-L. and Ika, A.R., Enhanced coagulation of low turbid water for drinking water treatment: Dosing approach of floc formation and residuals minimization, *Environ. Eng. Sci. Mar.*, 2019, vol. 36, no. 6, pp. 732–738.
12. Gregory, J. and Duan, J.M., Hydrolyzing metal salts as coagulants, *Pure Appl. Chem.*, 2001, vol. 73, pp. 2017–2026.
13. Lee, S., Roh, Y., and Koh, D.-C., Oxidation and reduction of redox-sensitive elements in the presence of humic substances in subsurface environments—A review, *Chemosphere*, 2019, vol. 220, pp. 86–97.
14. Gaid, K., A large review of the pre treatment, in *Expanding Issues in Desalination*, London: InTech Open, 2011, pp. 3–56.
15. *ASTM D4189-95: Standard Test Method for Silt Density Index (SDI) of Water*, West Conshohocken, PA: ASTM Int., 1995.
16. Manning, T.J., Bennett, T., and Milton, D., Aggregation studies of humic acid using multiangle laser light scattering, *Sci. Total Environ.*, 2000, vol. 257, nos. 2–3, pp. 171–176.
17. Kul'skiy, L.A., *Teoreticheskie osnovy i tekhnologiya konditsionirovaniya vody* (Theory and Technology of Water Conditioning), Kiev, 1980.

18. Chow, C.W.K., van Leeuwen, J.A., Fabris, R., and Drikas, M., Optimized coagulation using aluminium sulfate for the removal of dissolved organic carbon, *Desalination*, 2009, vol. 245, nos. 1–3, pp. 120–134.
19. Shevchenko, M.A., *Organicheskie veshchestva v prirodnoi vode i metody ikh udaleniya* (Organic Substances in Natural Water and Methods of Their Removal), Kiev, 1966.
20. Goronovskii, I.T., *Fiziko-khimicheskoe obosnovanie avtomatizatsii tekhnologicheskikh protsessov obrabotki vody* (Physical and Chemical Substantiation of Automation of Water Treatment), Kiev, 1975.
21. Matilainen, A., Removal of the natural organic matter in the different stages of the drinking water treatment process, *PhD Thesis*, Tampere, 2007.
22. Archer, A.D. and Singer, P.C., SUVA and NOM coagulation using the ICR database, *J. Am. Water Works Assoc.*, 2006, vol. 98, no. 2, pp. 110–115.
23. Klimenko, N.A., Samsoni-Todorova, E.A., Savchina, L.A., Lavrenchuk, I.N., and Zasyad'ko, T.N., Seasonal variations of characteristics of organic matter in the Dnieper River water, *J. Water Chem. Technol.*, 2012, vol. 34, no. 3, pp. 154–161.

Translated by O. Kadkin