Chapter 02

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Use of Dissolved Gases and Their Radicals in Technologies for Purifying Natural Water

Oleksandr Kvartenko[1], Ihor Prysiazhniuk[2], Gasim Mammadov[3], Oksana Pletuk[1], Vugar Abdullayev Hajimahmud[3]

[1]National University of Water and Environmental Engineering. Rivne, Ukraine.
[2]Rivne State University of Humanities. Rivne, Ukraine.
[3]Azerbaijan State Oil and Industry University. Baku, Azerbaijan.

ABSTRACT

The results of theoretical and experimental studies confirming the necessity and efficiency of using dissolved gases in biological and physicochemical technologies for purifying underground water from Fe^{2+}, Mn^{2+}, NH_4^+, humic acids, and phenols have been presented. Optimal pH-Eh parameters of the environment and activators of the biochemical oxidation process of Fe^{2+} and Mn^{2+} cations have been determined. The efficiency of the destruction of the compounds difficult to oxidize (phenols, humic complexes) using the hydrodynamic cavitation process has been proven.

Keywords: Water Purification; Ferrobacteria; Dissolved Gases; Cavitation Flow.

INTRODUCTION

Water is one of the fundamental elements for ensuring life on the planet and a key component in the development of any civilization, including modern techno genic society. However, despite the rapid growth of modern megacities, industry, energy, and agriculture, the amount of available water remains practically unchanged and constitutes 200 000 km^3. Meanwhile, over the past fifty years, humanity has invented more than 100 million new organic and inorganic substances that do not undergo natural degradation processes and affect human health. Despite natural protection, groundwater aquifers are also exposed to anthropogenic influence.(1,2)

As a result, the development of new and the improvement of existing technologies based on a scientifically grounded and rational combination of already known and advanced biological and physicochemical purification methods is a relevant issue today.

The main methods for removing contaminants from natural water include chemical, physicochemical, biological, and biochemical approaches, as well as technologies based on their combination.(2)

Many technologies use so-called dissolved gases: oxygen and its active forms, singlet oxygen, ozone, carbon dioxide, hydrogen peroxide, and nitrogen. The use of gases can be direct (introducing them into the system from an external source), indirect (producing gases within the system through biochemical reactions or via mechanical thermal decomposition of water molecules during hydrodynamic or acoustic cavitation), or combined.

High pressure and temperature inside the bubbles, formed during the cavitation process, lead to the disintegration of water molecules and the formation of radicals with high chemical activity:

H_2O -)))$\rightarrow H^{\bullet}, O^{\bullet}, HO^{\bullet}, H_2^{\bullet}, HO_2^{\bullet}, H_2O_2, O_2$. (1)

The most well-known application is the use of atmospheric oxygen for oxidizing Fe^{2+} cations in iron removal technologies based on simplified and deep aeration methods:

$4(Fe)^{2+}+O_2+10H_2O=4Fe(OH)_3\downarrow +8H\hat{}+$ (2)

$4(Fe)^{2+}+8HCO_3^-+O_2+2H_2O=4Fe(OH)_3\downarrow + 8CO_2\uparrow$ (3)

According to the given reactions, the oxidation of 1 mg of $FeCO_3$ produces 1,6 mg of free CO_2 while simultaneously reducing the total alkalinity of the water by 0,043 mmol/dm^3, which leads to a decrease in water pH and inhibits oxidation and hydrolysis processes.

To remove organic iron compounds, water ozonation method can be applied. The ozone dose is set equal to the Fe^{2+} concentration. As a result, oxidation of organic and mineral compounds (Fe^{2+}, Mn^{2+}) occurs, followed by a change in their phase-dispersed state, namely converting them into insoluble hydroxides, which can then be removed through filtration[3].

One of the significant advantages of ozone is its ability to oxidize hydrogen sulphide at pH 5,0 – 9,0:

$H_2S+O_3=S\downarrow + H_2O+O_2$ (4)

$3H_2S+O_3=3S\downarrow +3H_2O$ (5)

When removing iron from acidic and slightly acidic underground water containing complex compounds, the use of alkaline reagents may be applicable:

$4Fe(HCO_3)_2+8Ca(OH)_2+O_2=8CaCO_3\downarrow +4Fe(OH)_3\downarrow + 6H_2O$ (6)

$4Fe(HCO_3)_2+8\llbracket Na\rrbracket_2CO_3+10H_2O+O_2=16NaHCO_3+4Fe(OH)_3\downarrow$ (7)

The aim of this research is to analyse the effectiveness of dissolved gases in natural water purification technologies for removing Fe^{2+}, Mn^{2+}, NH_4^+, humic acids, and phenols based on modern theory as well as our own experimental research.

METHOD

Experiment 1

The concentrations of Fe^{2+} and Mn^{2+} ions were measured according to established methods,(3,4) using an experimental pilot installation (figure 1). Comparative researches were carried out concerning the determination of the efficiency of using iron bacteria in various conditions. The pilot experimental installation is composed from the capacity of rising water of 2000 ml volume, a reaction flask of 500 ml volume, a Kamovski pump, a flask with the changeable paper filter «blue line» and a ceramic filter, a magnetic mixer MM–5, a system of rubber hoses (figure 1). Into the outlet water capacity was added the calculated 0,1 n hydrochloric solution and iron (II) sulphate. A reaction flask was filled with 10 ml of sediment, with autotrophic bacteria

Gallionella (figure 2a), and depending on the experimental method, bacterial growth activators were added (table 1). All samples were taken in triplicate.

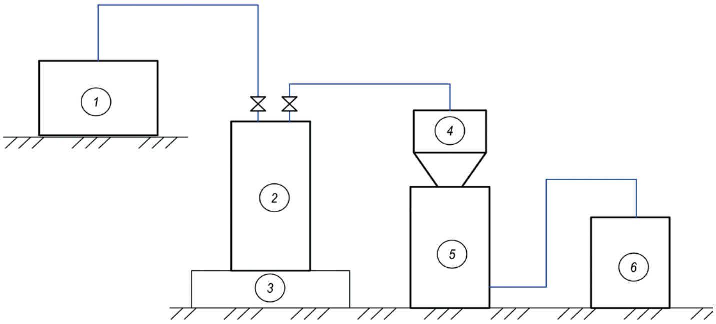
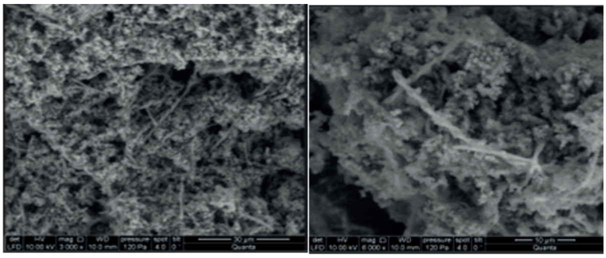


Figure 1. Scheme of experimental installation. 1 – outlet imitation solution capacity; 2 – reaction flask; 3 – magnetic mixer; 4 – hermetic ceramic filter; 5 – flask of filtrate collection; 6 – Kamovski pump

In a series of experiments on the oxidation of Mn^{2+}, a reaction flask was filled with 10 ml of sediment, with heterotrophic bacteria of the Leptothrix and Crenothrix genera (figure 2b).



a b

Figure 2. The electronic image of the matrix structures of Gallionella (a) and Leptothrix (b) from the sediment x 6000

Experiment 2

The pH values, concentrations of dissolved oxygen, phenols, and NH_4^+ were determined following the methods[(5,6,7,8)] using an experimental installation (figure 3).

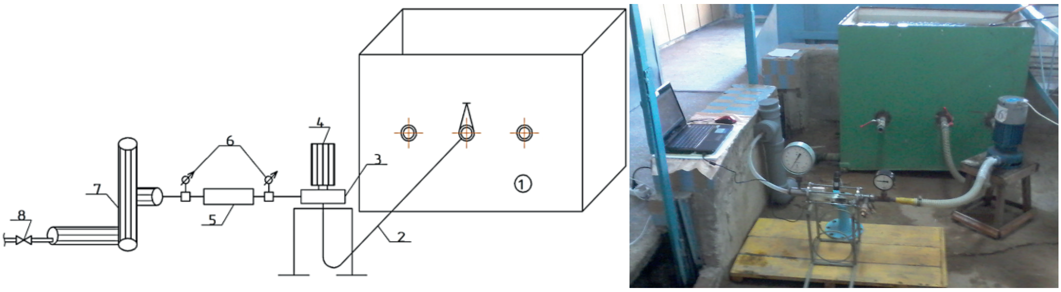


Figure 3. Experimental semi-production installation. a – the general scheme of the installation with the BC 1,1-18 pump; b – the installation with a multi-stage cavitator; 1 – a metal tank with a volume of 900 dm^3 with a model solution; 2 –a suction pipe of the pump; 3 – a pump unit; 4 – an electric motor; 5 – a hydrodynamic cavitator; 6 – manometers; 7 – a contact camera; 8 – shut-off valve

The installation (figure 3a) worked as follows: the pump 3 to the hydrodynamic cavitator 5 fed the model solution from container 1. The water treated in the cavitator entered the contact chamber 7, where the process of oxidation of destructured organic compounds with reactive radicals took place. Sampling from the contact chamber was carried out after certain time periods (5, 30, 60, 90, 120 min). All samples were taken in triplicate. The selected samples were treated sequentially with solutions of aluminum hydroxochloride (20 mg/dm^3) and nonionic flocculant. After the flake formation process took place, the treated model solution was filtered through a blue band paper filter.

RESULTS

Experiment 1

The water solution quality parameters (table 1) indicate that Fe^{2+} cations cannot be oxidized by chemical methods. Comparing the results of experiments № 1 and № 2 (table 1), it can be concluded that the kinetics of Fe^{2+} cation removal by iron bacteria, except for the initial period (0–5 minutes), were almost identical, differing by only 2-5 %.

The increased oxidative capacity of the system (experiment № 2) during the first five minutes is explained by the higher concentration of Fe^{2+} ions, which act as electron donors necessary for the respiration process of autotrophic Gallionella.(9) In the experiments № 3–4, the system received an additional external source of inorganic carbon in the form of Na_2CO_3 solution, which allowed iron bacteria to build new cellular mass and significantly accelerated the biological oxidation of Fe^{2+} cations.(9,10)

Table 1. The quality parameters of researched water with an increased content of cations Fe2+

№	Quality parameters of source water	Filtrate	Duration of contact, min				
			5	15	30	45	60
1	pH=6,0; Fe2+ =31,0 mg/dm3; O2= 2,0 mg/dm3; Hydro-carbonate alkalinity (HCA) 1,3 mmole/dm3	Fe2+ mg/dm3	25	15	7	3,8	2
		E, %	19	51,6	77,4	87,7	93,5
2	pH=6,5; Fe2+ =44,0 mg/dm3; O2= 1,0 mg/dm3; HCA =1,3 mmole/dm3	Fe2+ mg/dm3	27	19	12,5	6,3	2,3
		E, %	38,6	56,8	71,6	85,2	94,8
3	pH=6,0; Fe2+ =45,0 mg/dm3; O2= 1,0 mg/dm3; HCA =1,5 mmole/dm3; Na2CO3 = 40 mg/dm3	Fe2+ mg/dm3	24	14,5	6,0	2,3	1,5
		E, %	46,7	67,8	86,7	95	96,7
4	pH=6,3; Fe2+ =38,0 мг/дм3; O2= 1,7 мг/дм3; HCA =2,7 mmole/dm3; Na2CO3 = 80 mg/dm3	Fe2+ mg/dm3	13	7,8	3,8	0,8	0,1
		E, %	65,8	79,5	90	98	99,7

Note: *standard deviation values: Fe δ=±10 %; pH Δ=±0,05.

In a series of experiments on the oxidation of Mn^{2+} (table 2) cations by heterotrophic bacteria of the Leptothrix and Crenothrix genera, it was observed that without the addition of an external organic carbon source, the primary factors influencing the oxidation process were the pH and Eh values of the environment (experiments № 1, 3, 4, 5).

When 10 mg/dm^3 of $C_{12}H_{22}O_{11}$ was added (experiments № 2–6), the intensification of Mn^{2+} cations oxidation was observed in the bacterial environment of Leptothrix and Crenothrix.

Table 2. The quality parameters of researched water with an increased content of cations Mn^{2+}

№	Quality parameters of source water	Filtrate	Duration of contact, min							
			3	5	10	15	20	30	40	50
1	CMn2+ = 3 mg/dm3; pH 6,3 Eh = 120 mV	Mn2+ mg/dm3	2,8	2,65	2,0	1,3	0,7	0,4	0,3	0,28
		E, %	6,7	11,7	33,3	56,7	76,7	86,7	90,0	90,7
2	CMn2+ = 3 mg/dm3; pH= 6,3; Eh = 120 mV; 10mg/dm3 $C_{12}H_{22}O_{11}$	Mn2+ mg/dm3	1,5	1,0	0,9	0,7	0,6	0,3	0,15	0,15
		E, %	50,0	66,7	70,0	76,7	80,0	90,0	95,0	95,0
3	CMn2+ = 3 mg/dm3; pH 6,3 Eh = 150 мВ	Mn2+ mg/dm3	2,8	2,6	1,6	0,7	0,45	0,2	0,2	0,2
		E, %	6,7	13,3	46,7	76,7	85,0	93,3	93,3	93,3
4	CMn2+ = 3 mg/dm3; pH 8,3 Eh = 150 mV	Mn2+ mg/dm3	1,4	0,75	0,3	0,2	0,2	0,2	-	-
		E, %	53,3	75,0	90,0	93,3	93,3	93,3	-	-
5	CMn2+ = 3, mg/dm3; pH 7,4 Eh = 80 mV	Mn2+ mg/dm3	-	2,0	1,7	1,6	1,5	1,4	1,3	1,2
		E, %	-	33,3	46,9	50,0	53,1	56,3	59,4	62,5
6	CMn2+ = 3,2 mg/dm3; pH 7,4; Eh = 80 mV;10mg/dm3 $C_{12}H_{22}O_{11}$	Mn2+ mg/dm3	-	1,12	0,96	0,9	0,75	0,5	0,4	0,3
		E, %	-	65,0	70,0	71,8	76,5	84,4	87,5	90,6

Note: *standard deviation values: Mn2+ δ=±10 %; pH Δ=±0,05; Eh Δ=±0,05

Experiment 2

Table 3 presents the results of studies of the effectiveness of the destruction of phenols in an aqueous solution depending on the time of its stay in the pressure contact chamber (figure 3b).

The results showed that when a 3 % hydrogen peroxide solution was added to the cavitation range, an increase in the oxidation rate of phenols was observed. This effect is caused by the formation of an additional amount of hydroxyl radicals, which are formed during the decomposition of hydrogen peroxide in the void of cavitation: $H_2O_2 \leftrightarrow 2|OH^{\bullet}|$. A coagulant solution used to remove oxidized and colloidal compounds from the reaction zone in a timely manner.

Table 3. The results of the research of phenol destruction in cavitation flow

Tap water simulant quality parameters: C phenols 1,0 mg/dm^3; pH 6,5; t = 10,1^{0}C				
Time of water hold-up in the pressure contact chamber, min.	5	15	30	60
Output, mg/dm^3	0,31	0,21	0,15	0,06
E%	69	79	85	92
While introducing 3 % solution of H_2O_2 in the cavitation area				
Output, mg/dm^3	0,17	0,12	0,088	0,015
E%	83	88	91	98,5

DISCUSSION

Experiment 1

According to the data of $^{(10)}$, the bacteria of Gallionella genus use the energy of the iron carbonate oxidation to assimilate carbon dioxide, which acts as a carbon source as per the following equation:

$2FeCO_3 + 3H_2O + \frac{1}{2}O_2 = 2Fe(OH)_3 + 2CO_2 + 29$ calories (8)

This reaction is accompanied with the energy release in the amount of 125 g-cal per 1 g of the oxidized salt $FeCO_3$. This is the energy used in the cells of Gallionella for all the work, required for the breakage of carbon (IV) oxide (CO_2) and the synthesis of organic matter in the cell.$^{(10)}$

The process of enzymatic oxidation of Fe^{2+} ions occurs due to the transfer and integration of the electron into the breathing chain of the bacteria. The synthesis of 1g of the cellular biomass of the microorganism requires the enzymatic oxidation of 276 g of Fe^{2+} ions with the release of 500 g of ferric hydroxide, which, as a result of the biochemical transformation of $Fe^{3+} \rightarrow \gamma FeOOH$, creates the matrix structures of bio-minerals.

The mechanism of Mn^{2+} ion oxidation by the bacteria of Lepthothrix genera occurs by the peroxide pathway and appears in the capsules and on the surface of the cellular wall:

$Mn^{2+} + 2H_2O_2 \rightarrow MnO_2 + 2H_2O$ (9)

Hydrogen peroxide is a product of the bacterial metabolism of Leptothrix bacteria, formed during the oxidation of organic substances as electrons are transferred through the respiratory chain.

The oxidation of manganese by H_2O_2 occurs with the participation of catalase, which performs a peroxidase function. In this process, Mn^{2+} serves as an electron donor.

The physiological significance of Fe^{2+} and Mn^{2+} oxidation involving H_2O_2 is the detoxification of a harmful metabolic by-product.

It was found out that while using the biological purification method, there is a possibility of removing ferrichumic complexes, ammonium nitrogen (to 1,5 mg/cdm) from the underground waters. In the molecular form, the oxidation of the ferric-humic complexes (IGC) by the activity products of the ferrobacteria from Lepthothrix, Crenothrix genera can be shown by the following equation of the chemical reaction:

$Fe^{2+} - IGC + |O^{\bullet}| + 2H_2O \rightarrow Fe(OH)_3 - IGC + H^+$ (10)

Experiment 2

Phenols destruction mechanism

On the basis of the known free-radical mechanism of formation of $OH^{\bullet}$ radicals in the cavitation flow,$^{(11)}$ we have come up with a mechanism for the destruction of phenols followed by removal of the formed intermediates with the help of an electrolyte solution outside the reaction zone. According to $^{(11)}$, as a result of the reaction, H_2O_2 can be formed as its intermediate products:

$OH^{\bullet} + OH^{\bullet} = H_2O_2$ (11)

Under the effect of high cavitation pressure and temperatures, up to 5000 ^0C in the middle of the bubbles,$^{(12)}$ at the time of their destruction, hydrogen peroxide dissociates under a radical mechanism:

$H_2 O_2 \leftrightarrow 2OH^{\bullet}$ (12)

$H_2 O_2 \leftrightarrow H_2 O + O^{\bullet}$ (13)

$2O^{\bullet} \rightarrow O\_2$ (14)

Phenols in water dissociate as acids:

$C(6) H_5 OH \leftrightarrow C_6 H_5 O^{-} + H^{+}$ (15)

Radical reactions take place in the cavitator:

$C_6 H_5 O^{-} - 1e \leftrightarrow C_6 H_5 O^{\bullet}$ (16)

$H^{+} + 1e \leftrightarrow H^{\bullet}$ (17)

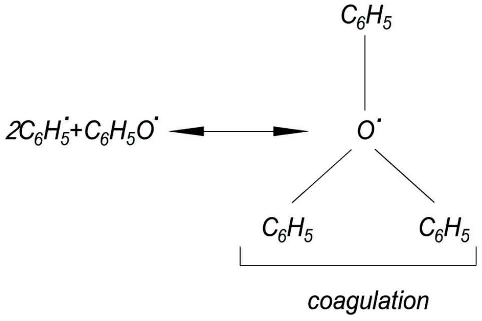
$C_6H_5OH \xrightarrow{10000^0K} \dot{C}_6H_5 + \dot{O}H$ (18)

The recombination of radicals leads to the formation of a number of compounds:

$2H^{\bullet} \rightarrow H(2)\uparrow$ (19)

$2C_6 H_5 O^{\bullet} + 2H^{\bullet} \rightarrow C_6 H_5\text{-}O\text{-} C_6 H_5 + H_2 O$ (20)

$2C_6 H_5^{\bullet} \rightarrow C_6 H_5\text{-} C_6 H_5$ (21)



(22)

The mechanism of removal of nitrogen and ammonium compounds

When cavitation bubbles are trapped under conditions of local high pressure (10 000 atm) and temperature (up to 10 000 K), the process of dissociation of hydrogen peroxide occurs by a radical mechanism (equations 12, 13) with subsequent oxidation of NH_3 and the formation of gaseous N_2:

$2NH_3 + 3|O^{\bullet}| \xrightarrow[10000K]{} N_2\uparrow + 3H_2O$ (23)

Thus, the application of HDC makes it possible to carry out the destruction of difficult-to-oxidize high-molecular organic and nitrogen-ammonium compounds with a change in their phase-dispersed state and makes it possible to significantly facilitate the functioning of the next stages of the technological schemes of natural water treatment.

CONCLUSIONS

As a result of the above theoretical and experimental studies, the importance of using dissolved gases in biological and physicochemical technologies for purifying underground water from Fe^{2+}, Mn^{2+}, NH_4^+, humic acids, and phenols has been proven. Optimal pH-Eh parameters of the environment and activators of the biochemical oxidation process of Fe^{2+} and Mn^{2+} cations have been obtained. The efficiency of the destruction and oxidation of the compounds difficult to oxidize (phenols, humic complexes) using the hydrodynamic cavitation process has been proven.

BIBLIOGRAPHIC REFERENCES

1. National report on drinking water quality and the state of drinking water supply in Ukraine. Ministry of Development of Communities and Territories of Ukraine Kyiv. 2022; Retrieved from https://mtu.gov.ua/content/nacionalna-dopovid-pro-yakist-pitnoi-vodi-ta-stan-pitnogo-vodopostachannya-v-ukraini.html (in Ukrainian)

2. Kvartenko O. The Use of Biotechnologies for Treating Underground Waters in North-Western Regions of Ukraine. Handbook Res Improv Nat Ecolog Condition Polesie Zone. IGI Global – May, 2023|Copyright: © 2023 |Pages: 479: 298–323. https://doi.org/10.4018/978-1-6684-8248-3.ch018

3. EPA Method 3500 Fe: Iron, Colorimetric Method. https://www.nemi.gov/methods/method_summary/7421 (in Ukrainian).

4. EPA Method 3500-Mn: MANGANESE, Persulfate Method. https://www.nemi.gov/methods/method_summary/4701/ (in Ukrainian).

5. EPA Method 150.1: Acidity (pH) of Water by Electrometric Method. https://www.nemi.gov/methods/method_summary/4685/ (in Ukrainian).

6. DSTU ISO 5813:2004. Water quality — Determination of dissolved oxygen — Iodometric method (ISO 5813:1983, IDT) https://www.iso.org/standard/11959.html

7. MVV № 081/12-0119-03 Surface, groundwater and return waters. Methodology for measuring the mass concentration of volatile phenols with vapor using 4-aminoantipyrine (0.001-50.0 mg/dm^3). (in Ukrainian).

8. Kvartenko O., Gryuk I., Sabliy L. Model of biomineralization of ferrum compounds by Gallionella cells immobilized on contact loading of bioreactor. Energy Engineering and Control Systems. 2017; Vol.3; 2:51–56. https://doi.org/10.23939/jeecs2017.02.051

9. Hallbeck L, Pedersen K Autotrophic and mixotrophic growth of Gallionella ferruginea. General Microbiol 137. 1991.11:2657–2661. https://doi.org/10.1099/00221287-137-11-2657

10. Emerson D, Field E, Chertkov O, Davenport KW, Goodwin L, Munk C, Nolan M, Woyke T. Comparative genomics of freshwater Fe-oxidizing bacteria: implications for physiology, ecology, and systematics. Frontiers in Microbiology / Evolutionary and Genomic Microbiology. 2013; Vol. 4; Article 254.

11. Vitenko T.M. Gidrodinamichna kavitaciya u masoobminnih, himichnih i biologichnih procesah: monografiya / T.M. Vitenko. Ternopil, v-vo TDTU im. I. Pulyuya. 2009; 224: (in Ukrainian).

12. Suslik KS, Mitlan MM, Reis JT. Chemistry induced by hydrodynamic cavitation. Journ. Amer. Chem. Soc. 1997; Vol. 119; 3: 9303–9306. https://doi.org/10.1021/ja972171i

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None.

CONFLICT OF INTEREST

None.

AUTHORSHIP CONTRIBUTION

Conceptualization: Oleksandr Kvartenko, Ihor Prysiazhniuk, Gasim Mammadov, Oksana Pletuk, Vugar Abdullayev Hajimahmud.

Data curation: Oleksandr Kvartenko, Ihor Prysiazhniuk, Gasim Mammadov, Oksana Pletuk, Vugar Abdullayev Hajimahmud.

Formal analysis: Oleksandr Kvartenko, Ihor Prysiazhniuk, Gasim Mammadov, Oksana Pletuk, Vugar Abdullayev Hajimahmud.

Drafting - original draft: Oleksandr Kvartenko, Ihor Prysiazhniuk, Gasim Mammadov, Oksana Pletuk, Vugar Abdullayev Hajimahmud.

Writing - proofreading and editing: Oleksandr Kvartenko, Ihor Prysiazhniuk, Gasim Mammadov, Oksana Pletuk, Vugar Abdullayev Hajimahmud.