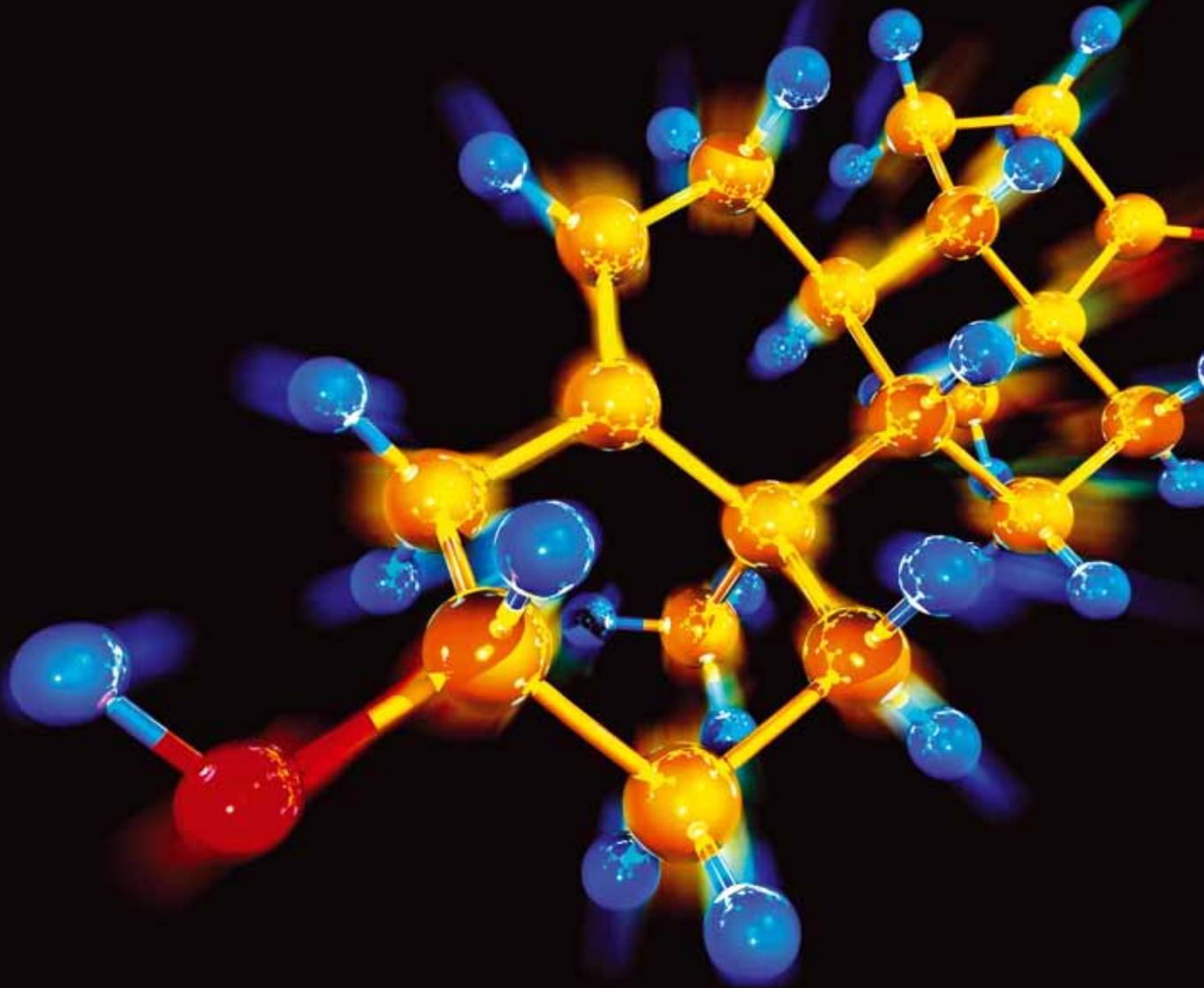


Journal of Chemistry

Chemistry, Physics, and Biology of Water

Guest Editors: Oleksandr A. Loboda and Vladyslav V. Goncharuk





Chemistry, Physics, and Biology of Water

Journal of Chemistry

Chemistry, Physics, and Biology of Water

Guest Editors: Oleksandr A. Loboda and
Vladyslav V. Goncharuk



Copyright © 2013 Hindawi Publishing Corporation. All rights reserved.

This is a special issue published in "Journal of Chemistry." All articles are open access articles distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Contents

Chemistry, Physics, and Biology of Water, Oleksandr A. Loboda and Vladyslav V. Goncharuk
Volume 2013, Article ID 715626, 2 pages

Layered Double Hydroxides as Effective Adsorbents for U(VI) and Toxic Heavy Metals Removal from Aqueous Media, G. N. Pshinko
Volume 2013, Article ID 347178, 9 pages

The New Standard for Drinking Water, V. Goncharuk
Volume 2013, Article ID 321609, 7 pages

Water as the Earth's Buffer and Immune System, Vladyslav V. Goncharuk
Volume 2013, Article ID 472323, 14 pages

Evaluation of Efficacy of Anionic Surfactant Degradation in the Presence of Concomitant Impurities of Natural Waters, Yuliya Shvadchina, Vera Vakulenko, Elena Alekseenko, and Anatoliy Sova
Volume 2013, Article ID 978764, 8 pages

Photocatalysis: Oxidative Processes in Water Treatment, Roman V. Prihod'ko and Nely M. Soboleva
Volume 2013, Article ID 168701, 8 pages

Fenton-Like Oxidation of Malachite Green Solutions: Kinetic and Thermodynamic Study, Saeedeh Hashemian
Volume 2013, Article ID 809318, 7 pages

Editorial

Chemistry, Physics, and Biology of Water

Oleksandr A. Loboda^{1,2} and Vladyslav V. Goncharuk²

¹ *Université de Lorraine, CNRS, SRSMC UMR 7565, 54506 Vandœuvre-lès-Nancy Cedex, France*

² *A.V. Dumansky Institute of Colloid and Water Chemistry, National Academy of Sciences, Boulevard Vernadsky 42, Kyiv 142, Ukraine*

Correspondence should be addressed to Oleksandr A. Loboda; loboda@kth.se

Received 27 October 2013; Accepted 27 October 2013

Copyright © 2013 O. A. Loboda and V. V. Goncharuk. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The aquatic sciences become more important to the research and the public. Water affects almost every aspect of our lives and causes a tremendous interest in its properties. For thousands of years people used to drink only natural water. First water pipelines were made with wood and granite and it was satisfactory because these materials are natural. After replacement of such natural materials by anthropogenic one the new threats to the human health appeared. For instance, ancient Romans used lead pipes and lead tableware which was often the cause of poisoning. This is one of the examples of consequences of anthropogenic approach to a water-supply system and utilization of toxic water. However, the awareness of the whole severity of the problem came only in the 20th century. More than 150 years ago the global industrialization started; megalopolises emerged leading to environmental pollution and numerous ecological problems. The rapid industrial growth prompted people to use chemical reagents for surface water in order to produce drinking water. In 1853 first standards for drinking water were established. By that time the pollution of surface water sources was not so dramatic, therefore, the quality of drinking water was determined only by 9 components. Over past decades chemical composition of water has changed. A vast amount of anthropogenic components have been released into the environment; these substances were made artificially by people and never existed in nature. In peer-reviewed publications more than 35 million of such anthropogenic components were found. Moreover per one year near one and a half millions of new compounds are synthesized and all of them could be found in aqueous medium. Majority of surface water which provides a centralized water supply is characterized by chemical and bacteriological pollution. It

should be noted that among other pollutants the antibiotics are the most dangerous as far as they sterilize the water. Therefore, we hope that the topic of this special issue arrives at a good time and will be of interest for the broad range of readership.

This special issue aims to (a) present new insights in the multifold of data on chemical, physical, and biological properties of water, (b) characterize the state of the water resources, and (c) estimate the quality of natural water and the anthropogenic impact on the water environment. The particular attention paid in this special issue is to the resistance degree of biosystems in respect to the influence of chemical, physical, and some other factors. The general focus of the issue is on the systematic fundamental and applied research work in chemistry, physics, and biology of water.

Of course, the selected papers are not able to fully cover the topic of this special issue; nonetheless they represent the rich and many-faceted knowledge that we are pleased to share with the readers.

This special issue contains six papers, where three papers are related to the oxidation processes and one paper elucidates effective technique for absorption of heavy metals from the wastewaters. The remaining two papers are devoted to the problems of water quality, review the state of the water resources, describe the consequences of the anthropogenic impact on the water environment, and finally address the drinking water standard issue.

In paper entitled “*Fenton-like oxidation of malachite green solutions: kinetic and thermodynamic study*,” J. Hashemian presents oxidation by Fenton-like reactions which is proven to be economically feasible process for destruction of a variety of hazardous pollutants in wastewater. In this study, the

degradation and mineralization of malachite green dye is reported using Fenton-like reaction. The results of experiments showed that the degradation of malachite green dye in Fenton-like oxidation process can be described with a pseudo-second-order kinetic model. It has been shown that the oxidation process occurs spontaneously and endothermically. The obtained results are claimed to be useful for designing the treatment systems of various dye-containing wastewaters.

In the paper entitled "*Photocatalysis: oxidative processes in water treatment*," N. M. Soboleva and R. V. Prihod'ko consider the efficiency of photocatalytic oxidation of various organic compounds. It is shown that photocatalytic methods can significantly increase the speed and depth of decomposition processes of intoxicants. The use of photocatalysis in the creation of low-power water treatment technologies has been concluded by authors as a promising direction in addressing environmental problems of the hydrosphere.

Shvadchina et al.'s paper deals with "*Evaluation of efficacy of anionic surfactant degradation in the presence of concomitant impurities of natural waters*". Y. Shvadchina et al. define the most efficient method of destruction of anionic surfactants in the presence of humic acids and natural organic matter of river waters. Comparison of efficiency of destruction of anionic surfactant-sodium alkylbenzene sulfonate (ABS) in model aqueous solutions by various oxidation methods showed that photocatalytic ozonation is the most effective method of ABS removal from waters containing humic acids or natural organic matter and bicarbonate-ions. Along with a maximum reduction of ABS concentration photocatalytic ozonation also ensured the highest degree of mineralization of organic impurities of all model solutions and river waters.

In the paper entitled, "*Layered double hydroxides as effective adsorbents for U(VI) and toxic heavy metals removal from aqueous media*," G. Pshinko explores high effective adsorbents for U(VI) and other toxic heavy metals in aqueous solution on the basis of layered double hydroxides. The author shows that such adsorbents may be used for sorption of cationic and anionic forms of U(VI) within a technology of purification of highly mineralized water containing carbonate ions. The optimal conditions have been established for adsorption processes, and the studied adsorbents have been shown to be used as potential adsorbents for the recovery of U(VI) and other heavy metals from wastewater of mining and processing plants and other waters containing toxic metals.

V. V. Gonchatuk's paper presents a comprehensive review on "*Water as the earth's buffer and immune system*." The author highlights the relationship between the quality of drinking water and the level of development of human intelligence and its health. The problems of obtaining cytogenetically and physiologically safe high-quality drinking water are discussed along with the problems of its decontamination. The solutions to maintain stable development of aquatic ecosystems are proposed. It is shown that tap water is the habitat of multiresistant genetically mutated microorganisms.

In the final V. V. Goncharuk's paper, he proposes "*The new standard for drinking water*." The author performs analysis of modern critical situation with a quality of drinking water in the world. The author argues and justifies the inefficiency

of existing approaches to the assessment of drinking water in the world. The research work of V. V. Goncharuk reveals the core statements of a new standard for drinking water whereas the key advantage of a new standard is the inclusion to it the integral control methods for the water quality, which is universal for all kinds and types of toxic compounds, irrespective of their origination and type of action.

Acknowledgments

We would like to express our gratitude to the authors for their valuable contributions. Finally, we would like to acknowledge and to thank all reviewers for their criticism, comments, and suggestions.

Oleksandr A. Loboda
Vladyslav V. Goncharuk

Research Article

Layered Double Hydroxides as Effective Adsorbents for U(VI) and Toxic Heavy Metals Removal from Aqueous Media

G. N. Pshinko

*Institute of Colloid and Water Chemistry of the National Academy of Sciences of Ukraine, 42 Vernadsky Boulevard,
Kyiv 03680, Ukraine*

Correspondence should be addressed to G. N. Pshinko; pshinko@ukr.net

Received 31 May 2013; Revised 16 September 2013; Accepted 26 September 2013

Academic Editor: Vladyslav V. Goncharuk

Copyright © 2013 G. N. Pshinko. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Capacities of different synthesized Zn,Al-hydroxalite-like adsorbents, including the initial carbonate $[\text{Zn}_4\text{Al}_2(\text{OH})_{12}]\cdot\text{CO}_3\cdot 8\text{H}_2\text{O}$ and its forms intercalated with chelating agents (ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), and hexamethylenediaminetetraacetic acid (HMDTA)) and heat-treated form $\text{Zn}_4\text{Al}_2\text{O}_7$, to adsorb uranium(VI) and ions of toxic heavy metals have been compared. Metal sorption capacities of hydroxalite-like adsorbents have been shown to correlate with the stability of their complexes with the mentioned chelating agents in a solution. The synthesized layered double hydroxides (LDHs) containing chelating agents in the interlayer space are rather efficient for sorption purification of aqueous media free from U(VI) irrespective of its forms of natural abundance (including water-soluble bi- and tricarbonat forms) and from heavy metal ions. $[\text{Zn}_4\text{Al}_2(\text{OH})_{12}]\cdot\text{EDTA}\cdot n\text{H}_2\text{O}$ is recommended for practical application as one of the most efficient and inexpensive synthetic adsorbents designed for recovery of both cationic and particularly important anionic forms of U(VI) and other heavy metals from aqueous media. Carbonate forms of LDHs turned out to be most efficient for recovery of Cu(II) from aqueous media with $\text{pH}_0 \geq 7$ owing to precipitation of Cu(II) basic carbonates and Cu(II) hydroxides. Chromate ions are efficiently adsorbed from water only by calcinated forms of LDHs.

1. Introduction

Nuclear power engineering is still a potentially hazardous industry worldwide now, which is evidenced by two largest nuclear accidents which occurred in Ukraine and Japan. Uranium mining and processing plants and heat-power engineering facilities add to a list of environmentally hazardous enterprises providing for such negative consequences of their operation as the inevitable pollution of the environment with anionic and cationic radioactive nuclides ($\text{U}_{\text{natural}}$, ^{226}Ra , ^{230}Th , ^{210}Pb , and ^{210}Po) and toxic heavy metals (HM). A prosperous progress in the nuclear industry should be reliably safe, that is, secured on high performance technologies of environmental protection against radioactive nuclides and other heavy metals. Therefore, the issues of environmental protection and rehabilitation are particularly relevant. U(VI) is a most challenging natural radioactive nuclide to be recovered from waste water of uranium-processing plants since it is this radioactive nuclide

that adds most to the overall activity accounting for up to 90% of this activity. Furthermore, this radionuclide features high complexing ability and forms soluble carbonate complexes, $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$, at pH characteristic of natural and waste waters resulting in high migration of its compounds in the environment [1].

Methods of purification of large volumes of water, including coagulation and adsorption methods involving natural cationexchangers, show low efficiency, in particular, when anionic forms of toxicants are present. In such cases, selective synthetic, preferably, inorganic adsorbents characterised with sufficiently high radiation resistance are used. Therefore, generation of inexpensive, efficient, and selective sorption materials designed for the extraction of toxic metals, in particular, in the anionic forms, is a problem of the most immediate interest.

Layered double hydroxides (LDHs) built of positively charged brucite-like layers linked by exchangeable anions are rather promising in this context [2, 3]. Inorganic hydroxalite

adsorbents containing carbonate anions in the interlayer space may be successfully used for sorption of cationic forms of uranyl ions from aqueous media [4, 5]. However, sorption of uranyl ions with such sorbents is substantially reduced in presence of HCO_3^- and CO_3^{2-} in aqueous solutions.

LDHs with chelating ligands in the interlayer space are efficient enough to extract toxic complex-forming metals [6–8]. Increase in the length of methylene chain in ethylenediaminetetraacetic acid (EDTA) homologues to $n \geq 6$ (n is the number of methylene groups) reduces the chelating effect and probability of ring closure. Therefore, the stability constants of the most normal metal chelate complexes with hexamethylenediaminetetraacetic acid (HMDTA) are lower than the stability constants of similar complexes with EDTA [9]. In contrast, diethylenetriaminepentaacetic acid (DTPA), being a potential ligand with an increased number of amine and carboxyl groups, forms more stable, mononuclear complexes than EDTA, with the most complex-forming metals. Moreover, such a chelating agent features higher specificity, in particular, to large cations (including actinides and lanthanides).

This work is aimed at studying U(VI) and HM sorption capacity of calcinated forms of Zn,Al-LDHs and Zn,Al-LDHs, containing different chelating agents in the interlayer space, with chelating agents having similar structure, which differ by the stability of their metal complexes in solution.

In this work, we have studied LDHs intercalated with chelating agents (chelate forms Zn,Al-L) EDTA ($[-\text{CH}_2-\text{N}-(\text{COOH})_2]_2$), DTPA ($[-(\text{CH}_2)_4-(\text{NH})_3-(\text{COOH})_5]$), HMDTA ($[-(\text{CH}_2)_3-\text{N}-(\text{COOH})_2]_2$), CO_3^{2-} ions (carbonate form Zn,Al- CO_3), and calcinated form $\text{Zn}_4\text{Al}_2\text{O}_7$, that may be used to recover U(VI) and heavy metals (Ni(II), Co(II), Pb(II), Cu(II), and Cr(VI)) from aqueous media.

2. Methods

The following reagents were used in the work: $\text{UO}_2(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, K_2CrO_4 , EDTA, HMDTA, and DTPA. Efficiency of U(VI) and HM extraction with different forms of LDHs was studied by using a model water, and the ionic strength (I) was adjusted with NaClO_4 . Besides that, waste water of a uranium-processing plant with $\text{pH} \approx 8$ and increased salt content (1.5 g/dm^3) was used. Concentrations of certain ions in such waters were as follows (mg/dm^3): $\text{HCO}_3^- > 250$, $\text{CO}_3^{2-} \approx 30$, $\text{SO}_4^{2-} > 450$, $\text{Ca}^{2+} \approx 170$, and $\text{Na}^+ \approx 240$ [10].

U(VI) and HM were adsorbed under static conditions with continuous shaking for 1 h; the volume of the aqueous phase was 50 cm^3 and the weights of adsorbent samples ranged from 0.05 g/dm^3 to 6.00 g/dm^3 with $C_{\text{Me}} = 1 \cdot 10^{-4} \text{ M}$. After adsorption equilibrium was achieved, aqueous phase was separated by centrifuging (at 5000 rpm), and equilibrium concentration of U(VI) complex with arsenazo III was determined in a strongly acidic medium (5 M HNO_3); concentration of Cr(VI) complex with diphenylcarbazide was determined by spectrophotometry [11, 12], and concentration

of heavy metals was determined by using C-115-M1 atomic absorption spectrophotometer at the wavelength of $\lambda = 232.0 \text{ nm}$ for Ni(II), $\lambda = 240.7 \text{ nm}$ for Co(II), $\lambda = 283.3 \text{ nm}$ for Pb(II), and $\lambda = 324.7 \text{ nm}$ for Cu(II).

The values of metal sorption (a_s , $\mu\text{mol/g}$) and the degree of purification (DP, %) were calculated according to the formulae

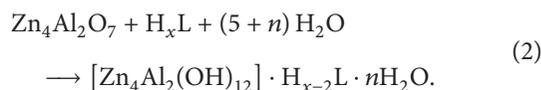
$$a_s = (C_0 - C_{\text{eq}}) \frac{V}{m}, \quad \text{DP} = \frac{(C_0 - C_{\text{eq}})}{C_0} \cdot 100, \quad (1)$$

where C_0 and C_{eq} are initial and equilibrium concentrations of metals, $\mu\text{mol/dm}^3$; V is aqueous phase volume, dm^3 ; m is weight of mineral, g.

3. Results and Discussion

3.1. Synthesis and Analysis of the Chemical Composition of Different Forms of Zn,Al-LDHs. The parameters of synthesis of Zn,Al- CO_3 , $\text{Zn}_4\text{Al}_2\text{O}_7$, and $\text{Zn}_4\text{Al}_2\text{-L}$ hydroxalite-like adsorbents were optimised [13, 14]. Chelate forms of adsorbents were synthesized in three stages: first stage synthesis of $[\text{Zn}_4\text{Al}_2(\text{OH})_{12}] \cdot \text{CO}_3 \cdot n\text{H}_2\text{O}$ (Zn,Al- CO_3), second obtaining $\text{Zn}_4\text{Al}_2\text{O}_7$ of synthesized Zn,Al- CO_3 via its heat treatment at 450°C for 1 to 2 h, and the third stage synthesis of chelate forms of Zn,Al-L via interaction of mixed oxide $\text{Zn}_4\text{Al}_2\text{O}_7$ with aqueous solutions of certain chelating agents containing ammonium hydroxide. In order to avoid formation of byproducts, pH of the initial solution of a chelating agent was adjusted with 20% ammonia to pH ranging 2.5 to 8 prior adding mixed oxide $\text{Zn}_4\text{Al}_2\text{O}_7$. The obtained products were washed with 5 to 7 portions of hot deionized water on a glass filter and dried at 50°C in an oven for 12 h.

Chelate forms of LDHs—Zn,Al-L were synthesized in accordance with the following scheme:



The synthesized products were identified by using chemical analysis of synthesized samples of LDHs after dissolution of adsorbents in diluted (1:1) hydrochloric acid and adding deionized water (free of CO_2) to solutions obtained. Zn and Al contents in an adsorbent sample were determined by using atomic absorption spectrophotometry and total organic carbon (contents of chelating agents) by chromatography [15]. Empirical chemical formulas of LDHs were determined on basis of the results of analysis of molecular ratio of Zn(II) and Al(III) and chelating agents. The content of OH^- ions was determined accounting for the neutrality of adsorbents, and the quantity of molecules of crystallization water was determined on the basis of both thermal and thermogravimetric analyses and by calculating the difference between total weight of adsorbent and its individual components. Values matched in a good way. The results of analysis suggest the following chemical formula of synthesized adsorbents: $[\text{Zn}_4\text{Al}_2(\text{OH})_{12}]\text{L} \cdot 8\text{H}_2\text{O}$.

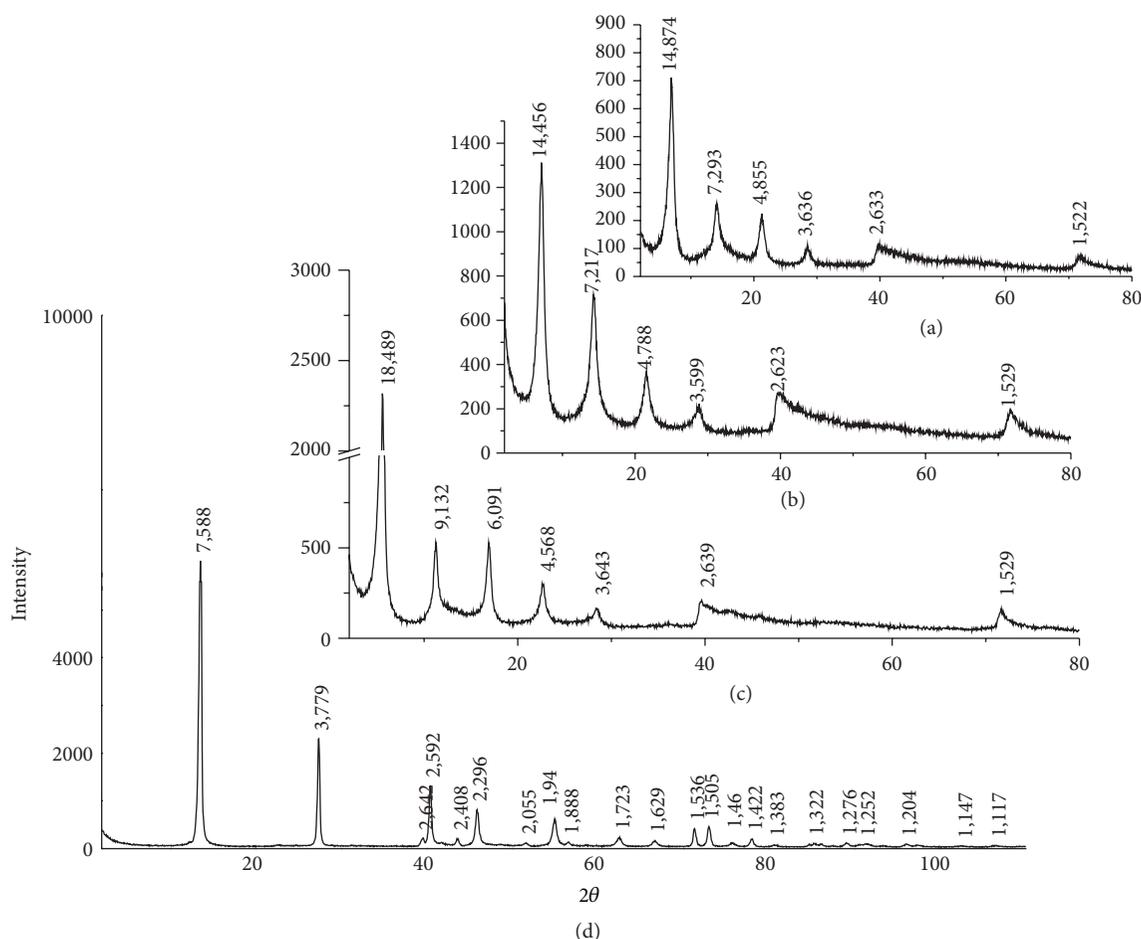


FIGURE 1: X-ray diffraction images of hydrotalcite adsorbents: (a) Zn,Al-EDTA, (b) Zn,Al-DTPA, (c) Zn,Al-HMDTA, and (d) Zn,Al-CO₃.

3.2. X-Ray Investigation of the Adsorbents. Phase composition of Zn₄Al₂(OH)₁₂·CO₃·nH₂O and Zn,Al-L adsorbents was determined by using DRON-2.0 X-ray diffractometer with filtered cobalt emission. Figure 1 shows X-ray diffraction images of Zn,Al-CO₃ and chelate forms (Zn,Al-L). All synthetic sorbents obtained in this work were single-phase ones. The calculated lattice parameters are within experimental error identical with the literature data for Zn,Al-hydrotalcite phase composition [Zn₄Al₂(OH)₁₂]·CO₃·nH₂O (Figure 1(d)) with a Zn:Al ratio of 2:1 [16]. The first four diffraction reflections in the X-ray diffraction image of Zn,Al-EDTA (Figure 1(a)) form a close-to-integer series making it possible to consider them basic 003, 006, 009, and 00.12 reflections of a hydrotalcite-like structure. Spacing between brucite-like layers is 0.975 nm. It has been calculated as the mean of the positions of 006, 009, and 00.12 reflections $(2d_{006} + 3d_{009} + 4d_{00.12})/3 = 1.455$ nm minus the depth of a hydrotalcite layer (0.48 nm). Two broad diffraction lines at high Bragg angle (2θ) seen in the X-ray diffraction images are also attributed to Zn,Al-EDTA.

Five diffraction lines forming an integer series—003, 006, 009, 00.12, and 00.15—are seen in the initial portion of Zn,Al-HMDTA X-ray diffraction image (Figure 1(c)). The value of the first basal reflection is calculated as

the arithmetic mean: $(2d_{006} + 3d_{009} + 4d_{00.12} + 5d_{00.15})/3 = 1.825$ nm. Apart from these basal diffraction reflections, the X-ray image contains also a nonsymmetric diffraction line at 0.2639 nm with a tail extending to larger angles and diffraction line 110 corresponding to interplanar spacing of 0.1529 nm. Such X-ray image is typical for layered hydrotalcite structures. It shows that an intercalation of HMDTA ions into the interlayer space causes an increase in the value of the first basal diffraction reflection characteristic of Zn,Al-hydrotalcite (2:1) from 0.764 to 1.825 nm. Subtraction of the depth of the brucite-like layer gives the value of the depth of the interlayer space occupied with HMDTA anions equal to 1.345 nm.

X-ray diffraction image of Zn,Al-DTPA contains 4 intense diffraction peaks forming a close-to-integer series of reflections corresponding to 14.46, 7.22, 4.79, and 3.60 Å. This makes it possible, on one hand, to assign the observed diffraction lines to basal reflections 001 and, on the other hand, to show that intercalation of DTPA in the interlayer space of an adsorbent structure causes an increase in the interplanar spacing to 9.66 Å. According to [17], the estimated length of DTPA anion is approximately 14 Å along N–C–N–C chain and substantially exceeds the value of the interplanar spacing of the obtained hydrotalcite intercalated with DTPA

anions. Thus, we may conclude that DTPA anions are inclined to the plane parallel to hydrotalcite layers.

The arrangement of intercalated EDTA anions between the charged brucite-like layers is still under discussion in the literature. On the basis of X-ray studies, we have found that vertical anions of chelating agents with the different lengths of ($-N-C\cdots C-N-$) chain are inclined at identical angles to the basal plane of a brucite-like layer in all studied adsorbents intercalated with chelating agents. According to the model described in [6], ligand anions are arranged in a manner that makes ($-N-C-C-N-$) chain perpendicular to brucite layers. According to [7], such vertical arrangement of ligands should provide for the interplanar spacing of 1.12 nm in hydrotalcite layers. The observed lower interplanar spacing (0.977 nm) suggests that EDTA ions are inclined to the brucite-like layers. If we assume that the geometries of anions having the same charge, for example, HMDTA²⁻ and EDTA²⁻, differ only with the values of lengths of their ($-N-C\cdots C-N-$) chains, we can calculate the difference between such lengths along the lines of the same. It has been shown empirically that adding one carbon atom to a paraffin chain lengthens the molecule by 0.126 nm, on average [18]. Therefore, in case of vertical arrangement of similarly charged ligand anions in layered double hydroxides intercalated with chelating agents, the difference between values of interplanar spacing in brucite-like layers should be $0.126 \times 4 = 0.504$ nm. The actually observed value is lower: $1.825 - 1.455 = 0.37$ nm. Such lower value confirms the inclined arrangement of intercalated anions of chelating agents in the interlayer space, and should the molecules of EDTA, HMDTA, and DTPA be tilted at the same angle to the basal plane of a brucite-like layer, such angle is $\alpha \approx 47.2^\circ$ ($\arcsin\alpha = 0.37 \text{ nm}/0.504 \text{ nm}$).

3.3. Uranium(VI) and HM Sorption with Different LDH Forms.

Figure 2 illustrates the influence of pH on U(VI) and Cu(II) sorption with different forms of Zn,Al-LDHs.

Figure 2 shows that maximum values of U(VI) sorption (Figure 2(a)) are achieved in the pH range of 5 to 10 for Zn,Al-EDTA, which testifies the high performance of adsorption of not only cationic but also anionic forms of uranium(VI), for example, soluble carbonate anions formed in more basic range of pH in case of air exposure of an aqueous solution. The virtually full recovery of Cu(II) (Figure 2(b)) is observed for ZnAl-CO₃ at pH > 7 owing to the precipitation of slightly soluble basic carbonates and, partially, hydroxides.

It is known that U(VI) is characterized by the formation of highly soluble UO₂(CO₃)₂²⁻ and UO₂(CO₃)₃⁴⁻ even when the aqueous solution is in contact with air. For Cu(II) at pH > 7, aqueous solution is characterized by formation of poorly soluble hydroxycarbonates and apparently partly hydroxides (Figures 3(a) and 3(b)). Therefore, for U(VI) sorption mechanism is observed by caused complexation on Zn,Al-EDTA and Zn,Al-CO₃ at pH > 7 does remove not U(VI) practically. For Cu(II) at pH > 7, almost complete is observed deposition on ZnAl-CO₃, and in more acidic media more efficient sorption is observed on Zn,Al-EDTA (Table 1).

Sorption performance of Zn,Al-HMDTA and Zn,Al-EDTA in the purification of waste water having the aforementioned composition from U(VI) was analyzed for different doses of adsorbents (Figure 4). It has been shown that Zn,Al-HMDTA provides for 66% to 68% degree of purification (adsorbent dose—1 g/dm³) and Zn,Al-EDTA for 94% to 98% degree of purification; when the adsorbent dose increases to 6 g/dm³, the degree of purification is higher and almost equal for both adsorbents (93% to 98%).

Moreover, sorption isotherms show that sorption capacity of Zn,Al-DTPA is higher in the range of low concentrations of U(VI) in solution (the corresponding isotherm is almost linear, and the rate of recovery of U(VI) is 99.9%) than the sorption capacity of Zn,Al-EDTA and Zn,Al-CO₃ under the same conditions (Figure 5). This is due to a more strong binding of U(VI) with DTPA than with EDTA and CO₃²⁻ ions; maximum values of sorption perfectly correlate with the stability of corresponding complexes; a_{max} , μmol/g, are equal: 131.6, 153.9, 166.7 for Zn,Al-CO₃, Zn,Al-HMDTA, and Zn,Al-HMDTA, respectively (note that isotherm; were described by Freundlich and Langmuir equations in the initial region of the isotherms both equations describe the sorption of metals by these sorbents satisfactorily; the maximum values of sorption were found using the Langmuir equations).

At higher concentrations of U(VI) its sorption is substantially higher on Zn,Al-EDTA and Zn,Al-DTPA owing to coprecipitation of uranium(VI) on the surface of the adsorbent leading to actually full recovery of uranium (irrespective of its concentration in a solution) on this adsorbent [11, 15].

To evaluate the efficiency of U(VI) recovery on Zn,Al-LDH adsorbents intercalated with chelating agents, we have studied the effects of the concentration of carbonate ions in water (Figure 6) [13, 14, 19]. Figure 6 shows that an increase in concentration of carbonate ions in water results in a sharp decrease in U(VI) sorption with synthesized forms of hydrotalcite (Zn,Al-CO₃); that is, carbonate ions in the interlayer space of hydrotalcite are not exchanged with the carbonate forms of U(VI) in solution and no extraction of carbonate forms of radioactive nuclide occurs. In case of Zn,Al-EDTA, increased concentrations of CO₃²⁻ ions cause actually no reduction of the degree of sorption owing to the formation of more strong U(VI) complexes with chelating anions of EDTA in the interlayer space. The results obtained show that this adsorbent may be used for the purposes of purification of uranium-containing water with increased levels of carbonate and hydrocarbonate ions characteristic of natural water.

Furthermore Figure 6 confirms that the sorbent Zn,Al-EDTA is highly effective for the sorption of U(VI) at high concentrations of CO₃²⁻ ions, which is very important for uranium-processing plants wastewater treatment with high content of carbonates and bicarbonates. It is noteworthy that no complexes of uranium(VI) with hydrocarbonate ions have been found; however, such anions play the key role in the formation of strong carbonate complexes of uranium (VI) owing to a shift of carbon-dioxide equilibrium in presence of metal ions.

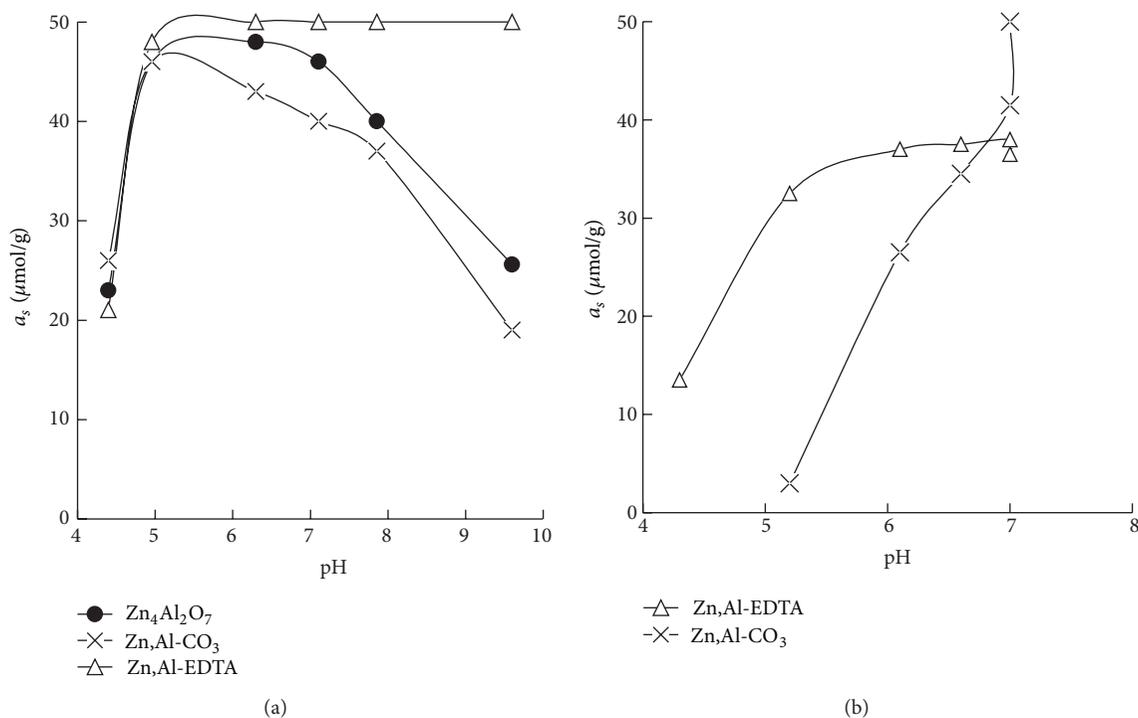


FIGURE 2: Influence of pH_{bal} on U(VI) (a) and Cu(II) (b) sorption with different forms of adsorbents. $C_{\text{U(VI)}} = 100 \mu\text{mol/g}$, $V_{\text{solution}} = 50 \text{ cm}^3$, and $m_{\text{adsorbent}} = 0.100 \text{ g}$.

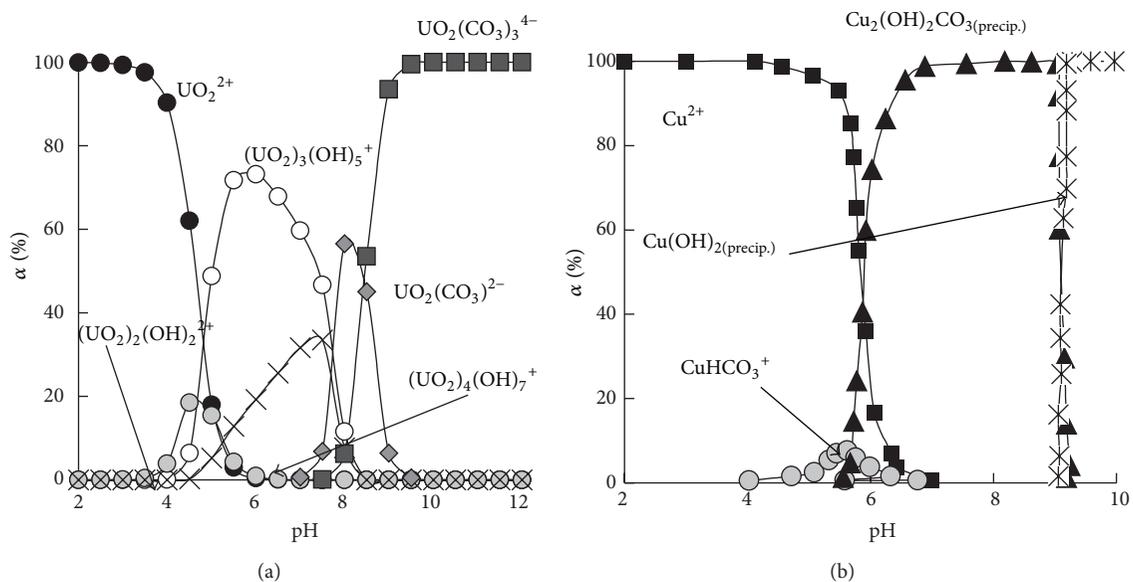


FIGURE 3: The forms of U(VI) (a) and Cu(II) (b) in aqueous solution in the presence of carbonate ions. $C_{(\text{CO}_3^{2-})} = 10^{-3} \text{ M}$; $C_{\text{U(VI)}} = C_{\text{Cu(II)}} = 10^{-4} \text{ M}$.

TABLE 1: The general stability constants of complex compounds ($\lg\beta$) and sediment ($\lg K_s$) formed by sparingly soluble salts and complexes of copper ($\lg K_s$, $I = 0$).

	$\lg\beta$		$\lg K_s$	
OH^-		$\text{H}_4\text{L-EDTA}$	OH^-	CO_3^{2-}
$\text{Cu}(\text{OH})^+$ 6,0;		CuL 18,8; CuHL 21,8;	$\text{Cu}(\text{OH})_2$ 18,2	$\text{Cu}_2(\text{OH})_2\text{CO}_3$ 42,96;
$\text{Cu}_2(\text{OH})_2$ 17,1		$\text{Cu}(\text{OH})\text{L}$ 21,2		$\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ 54,69

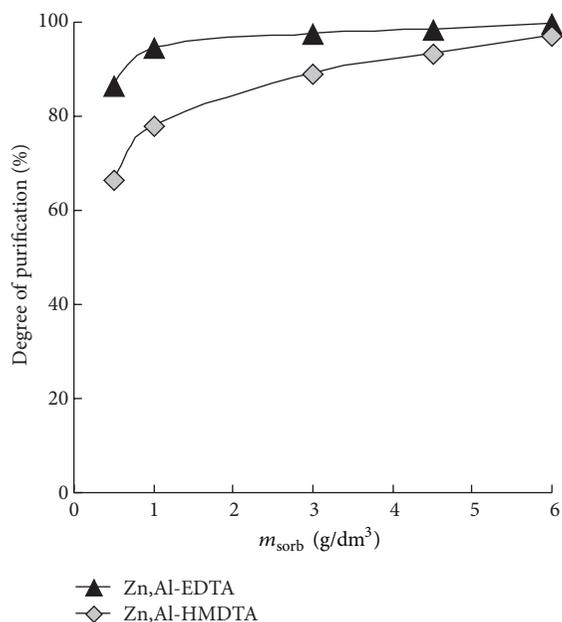


FIGURE 4: Comparative estimation of the recovery efficiencies of U(VI) from waste water with different forms of Zn,Al-L adsorbents.

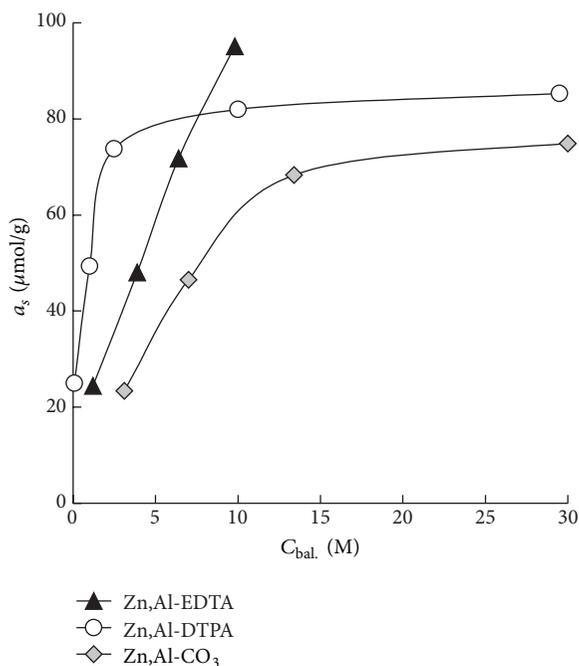


FIGURE 5: U(VI) sorption isotherms for chelate and carbonate forms of adsorbents. pH = 6.5, $V_{\text{solution}} = 50 \text{ cm}^3$, and $m_{\text{adsorbent}} = 0.100 \text{ g}$.

In order to provide for an integral evaluation of the performance of the synthesized adsorbents in the purification of a model solution in deionized water with $I_{(\text{NaClO}_4)} = 0.01$ and $\text{pH}_0 = 7.7$ and plants wastewater having the composition described in [10], the degree of recovery of U(VI) has been estimated at the adsorbent doses of 1 g/dm^3

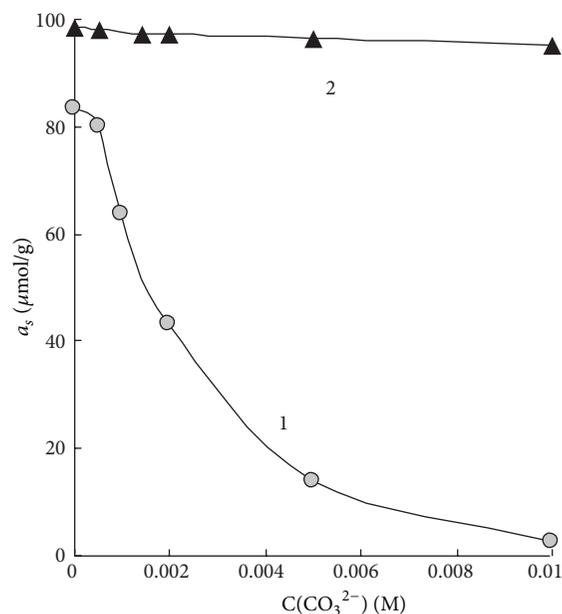


FIGURE 6: Effect of carbonate ion concentration on U(VI) sorption with different forms of adsorbents: (1) Zn,Al- CO_3 and (2) Zn,Al-EDTA. $C_{\text{U(VI)}} = 1 \cdot 10^{-4} \text{ M}$, $V_{\text{sol.}} = 50 \text{ cm}^3$, and $m_{\text{ads.}} = 0.05 \text{ g}$.

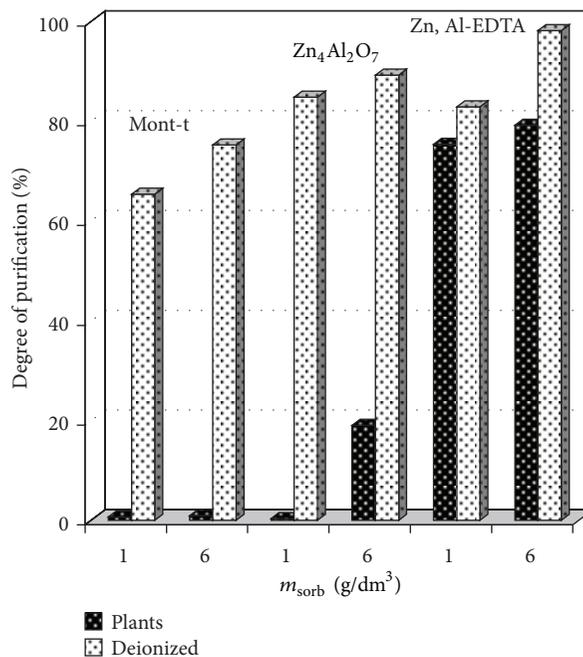


FIGURE 7: Comparative evaluation of the recovery efficiency of U(VI) compounds from aqueous media with different adsorbents, pH 8. $V_{\text{sol.}} = 50 \text{ cm}^3$.

and 6 g/dm^3 (Figure 7). The efficiency of U(VI) recovery with clay mineral montmorillonite having rather high cation exchange capacity of a natural adsorbent of 0.7 mgeq.v/g is shown for reference. Figure 7 shows that montmorillonite is actually inefficient ($<1\%$) for the purification of plants

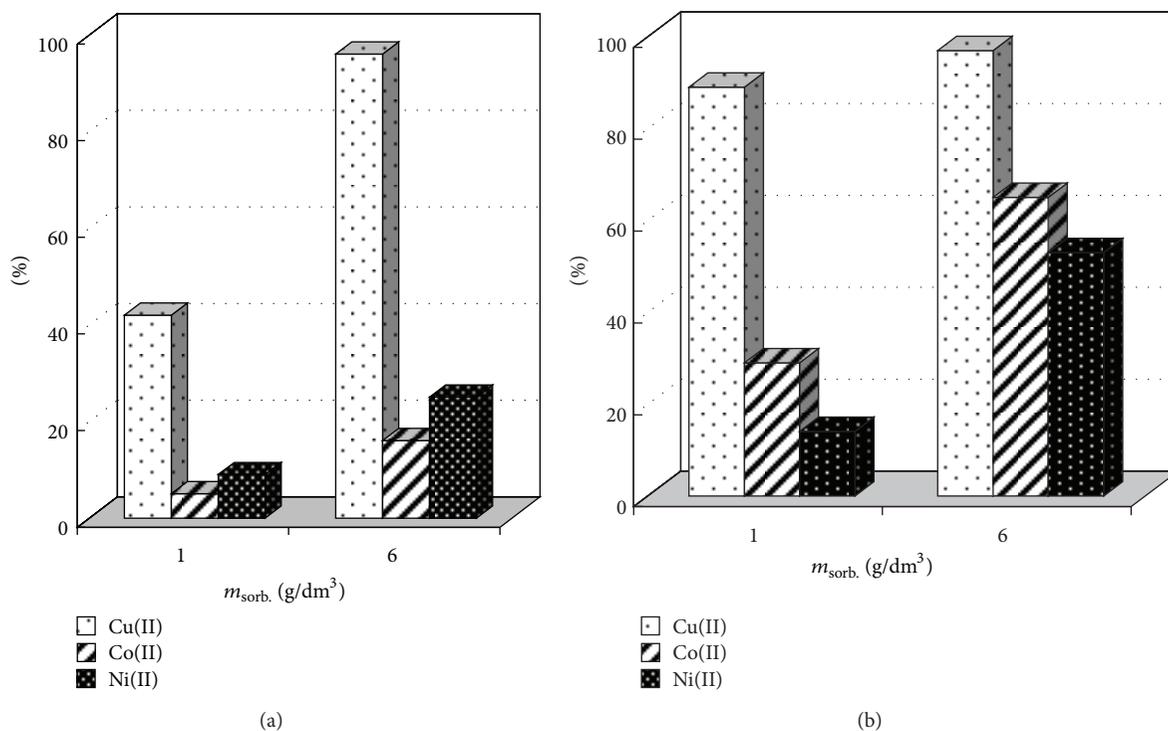


FIGURE 8: Influence of the dose of Zn,Al-CO₃ (a) and Zn,Al-EDTA (b) adsorbents on the degree of purification of aqueous solutions from Cu(II), Ni(II), or Co(II). $I = 0$; $\text{pH}_0 = 3.5$.

wastewater from U(VI) due to the fact that this adsorbent is present in its anionic carbonate forms at the given pH value. Heat-treated form of hydrotalcite, Zn₄Al₂O₇, in the doses of 1 g/dm³ and 6 g/dm³ may provide for 75% to 85% rate of recovery of uranium(VI) from the model solution in deionized water, correspondingly, whereas the rate of recovery from plants wastewater is 19.0% when the adsorbent dose is 6 g/dm³. Meanwhile, Zn,Al-EDTA adsorbent features rather high efficiency of purification of both model and wastewater at the levels of 99.9% and 80%, correspondingly.

Thus, all Zn,Al-L chelate adsorbents are promising in terms of recovery of U(VI) compounds from aqueous media, including those with increased mineralization, in the broad pH range.

Efficiency of heavy metal recovery from aqueous media with adsorbents on the basis of LDH has been studied in the systems with adsorbent doses of 1 g/dm³ and 6 g/dm³ and $\text{pH}_0 = 3.5$, containing actually no hydrolyzed forms of metals (Figure 8). This figure shows that the degree of purification of water from Cu(II) with Zn,Al-CO₃ adsorbent in the dose of 1 g/dm³ is 42% and with Zn,Al-EDTA 90%. An increase in the adsorbent dose to 6 g/dm³ results in actually complete recovery of copper ions with both carbonate form of the adsorbent owing to the precipitation of copper in a form of double salts basic carbonates (increased adsorbent dose results in a more full immobilisation of copper in its basic carbonate form), and EDTA-intercalated form owing to the formation of strong copper complexes with EDTA.

The ionic strength of a solution has actually no effect on Pb(II), Ni(II), Co(II), and Cu(II) sorption with Zn,Al-EDTA testifying to immobilization of metal ions owing to their complex formation with the functional groups of hexadentate ligand (EDTA). Nickel(II) and cobalt(II) sorption on Zn,Al-CO₃ are substantially lower (by the factor of 2 to 3.5) than on Zn,Al-EDTA at both values of ionic strength [20]. This suggests the dominating mechanism of extraction of such ions on account of complex formation with the chelating ligand of adsorbent.

Chelate forms of adsorbents turn out to be particularly promising also for Pb(II) and Cu(II) recovery from aqueous media at $\text{pH} < 7$. A comparison of sorption efficiency of Zn,Al-L for HM recovery from aqueous solutions shows that adsorbent intercalated with DTPA is highly efficient for Pb(II) recovery, evidently, owing to its increased specificity to large cations.

Unlike the aforementioned heavy metals, chromium(VI) occurs in water only in its anionic form. It is toxic for living organisms, and its maximum allowable concentration in potable water is lower than that of Cr(III) by an order of magnitude. Sorption recovery of anionic forms of Cr(VI) from aqueous media is a rather challenging problem. The use of anionic adsorbents may be an appropriate solution [21, 22]. Preliminary studies have shown that chelate and carbonate forms of LDHs are of low efficiency with the rate of recovery of not more than 2% to 3%. Therefore, we have studied Cr(VI) sorption from aqueous media by using calcinated forms of LDHs that have undergone heat treatment directly on the day of sorption measurement.

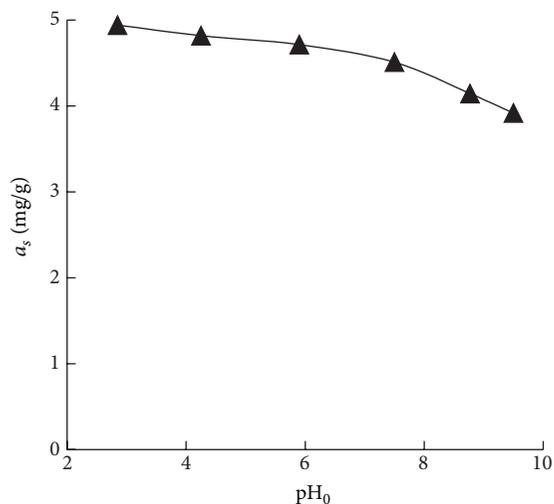


FIGURE 9: Effects of pH on Cr(VI) sorption with $Zn_4Al_2O_7$ from deionized water. $C_{Cr(VI)} = 5.0 \text{ mg/dm}^3$, $m = 0.05 \text{ g}$, and $V = 50 \text{ cm}^3$.

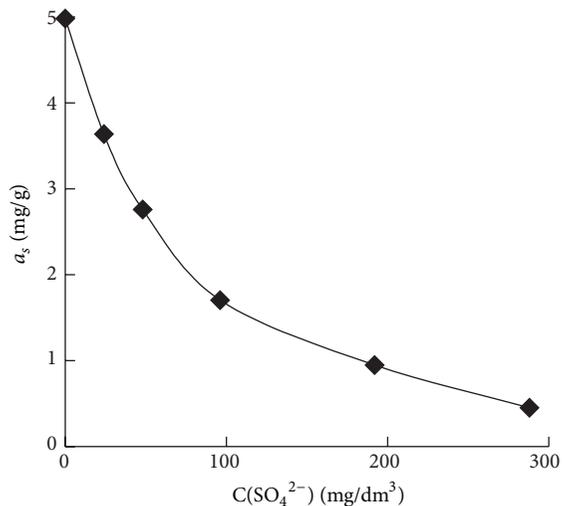
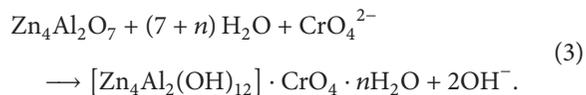


FIGURE 10: Effects of SO_4^{2-} concentration on Cr(VI) sorption on $Zn_4Al_2O_7$ at $pH_0 = 5.0$. $C_{Cr(VI)} = 5.0 \text{ mg/dm}^3$, $m = 0.05 \text{ g}$, and $V = 50 \text{ cm}^3$.

Heat-treated LDH form, $Zn_4Al_2O_7$, placed into an aqueous solution may comprise anions according to the following chemical equation:



Heat-treated form of a LDH is shown in (2) to absorb anions from aqueous media to restore its initial structure, which is confirmed with the results of our X-ray diffraction studies [4, 13]. It has been found that pH_0 values of 3 to 4 are optimal for adsorption (Figure 9), and single-charged anions have less effect on the rate of recovery of chromate ions: they actually cause no reduction in HCO_3^- sorption in the range of up to 7 mgeqv./dm^3 and NO_3^- sorption in the range of up

to 0.2 M , whereas the effects of SO_4^{2-} are more pronounced: sulphate ions in the dose of 30 mg/dm^3 reduce the rate of recovery of Cr(VI) by 20% (Figure 10). The influence of interfering substances on the rate of recovery of chromate ions may be avoided through an increase in the adsorbent weight: actually complete recovery of Cr(VI) from 1 dm^3 of water containing 50 mg/dm^3 of SO_4^{2-} ions is achieved with the adsorbent weight of 2 g. When the level of sulphate ions is below 20 mg/dm^3 , the dose of an adsorbent may be reduced to 1 g/dm^3 .

4. Conclusions

This work suggests that high performance synthetic inorganic adsorbents—layered double hydroxides of zinc and aluminium intercalated with chelating agents—may be used for sorption of cationic and anionic forms of U(VI) within a technology of purification of highly mineralized water containing carbonate ions. It has been shown for the first time that carbonate forms of layered double hydroxides of Zn and Al are more efficient than forms intercalated with EDTA for purification of water with $pH_0 \geq 7$ from Cu(II) owing to the precipitation of slightly soluble compounds, predominantly, basic carbonates and, partially, metal hydroxides on an adsorbent ($K_d = 99,000 \text{ cm}^3/\text{g}$). Zn,Al-EDTA is an efficient adsorbent for Ni(II), Co(II), and Pb(II) sorption via complex formation. The rate of recovery of such elements correlates with the stability constants of their chelate complexes in solution. Only heat-treated (directly prior to sorption) LDH form, $Zn_4Al_2O_7$, is promising for an efficient recovery of chromate ions.

The optimal conditions have been established for adsorption processes, and the studied adsorbents have been shown to be used as potential adsorbents for the recovery of U(VI) and other heavy metals from waste water of mining and processing plants and other waters containing toxic metals.

Acknowledgment

G. N. Pshinko appreciates all kinds of support and advice provided by the Director of the Institute of Colloid and Water Chemistry of the National Academy of Science of Ukraine, a Member of the Academy, Professor V. V. Goncharuk, in carrying out this study.

References

- [1] S. A. Kobets, G. N. Pshinko, and L. N. Puzyrnaya, "Uranium (VI) in natural waters: study of occurrence forms," *Journal of Water Chemistry and Technology*, vol. 34, no. 6, pp. 277–283, 2012.
- [2] F. Cavani, F. Trifirò, and A. Vaccari, "Hydrotalcite-type anionic clays: preparation, properties and applications," *Catalysis Today*, vol. 11, no. 2, pp. 173–301, 1991.
- [3] C. Forano, T. Hibino, F. Leroux, and C. Taviot-Guého, "Layered double hydroxides," in *Handbook of Clay Science*, F. Bergaya, B. K. G. Theng, and G. Lagaly, Eds., Development in Clay Science, chapter 13.1, pp. 1021–1095, 2006.

- [4] T. G. Timoshenko, A. A. Kosorukov, G. N. Pshinko, and V. V. Goncharuk, "Calcinated hydrotalcite—a sorbent for purifying uraniferous waters," *Journal of Water Chemistry and Technology*, vol. 31, no. 4, pp. 250–255, 2009.
- [5] S. A. Kulyukhin, E. P. Krasavina, I. V. Gredina, I. A. Rumer, and L. V. Mizina, "Sorption of U(VI) from aqueous solutions on layered double hydroxides of Mg, Al, and Nd," *Radiochemistry*, vol. 52, no. 6, pp. 653–661, 2010.
- [6] M. R. Pérez, I. Pavlovic, C. Barriga, J. Cornejo, M. C. Hermosín, and M. A. Ulibarri, "Uptake of Cu^{2+} , Cd^{2+} and Pb^{2+} on Zn-Al layered double hydroxide intercalated with edta," *Applied Clay Science*, vol. 32, no. 3-4, pp. 245–251, 2006.
- [7] K. A. Tarasov, D. O'Hare, and V. P. Isupov, "Solid state chelation of metals ions by ethylenediaminetetraacetate intercalated in a layered double hydroxide," *Inorganic Chemistry*, vol. 42, pp. 1119–1127, 2003.
- [8] I. Pavlovic, M. R. Pérez, C. Barriga, and M. A. Ulibarri, "Adsorption of Cu^{2+} , Cd^{2+} and Pb^{2+} ions by layered double hydroxides intercalated with the chelating agents diethylenetriaminepentaacetate and meso-2,3-dimercaptosuccinate," *Applied Clay Science*, vol. 43, no. 1, pp. 125–129, 2009.
- [9] IUPAC Chemical Data Series-No 22, *Stability constants of Metal-Ion Complexes. Part B: Organic Ligands. Compiled by D.D. Perrin*, Pergamon Press, New York, NY, USA, 1979.
- [10] T. G. Timoshenko, A. A. Bogolepov, and G. N. Pshinko, "Treatment of radioactively contaminated waters with an increased content of salts," *Journal of Water Chemistry and Technology*, vol. 31, no. 1, pp. 46–52, 2009.
- [11] A. A. Nemodruk and L. P. Glukhova, "Interaction of Uranium(VI) with Arsenazo III in strongly acid solutions," *Journal of Analytical Chemistry*, vol. 43, no. 1, pp. 93–98, 1963 (Russian).
- [12] Z. Marchenko, *Photometric Determination of Elements*, Mir Publications, Moscow, Russia, 1971.
- [13] G. N. Pshinko, A. A. Kosorukov, L. N. Puzyrnaya, and V. V. Goncharuk, "Layered double hydroxides intercalated with EDTA as effective sorbents for U(VI) recovery from wastewater," *Radiochemistry*, vol. 53, no. 3, pp. 303–307, 2011.
- [14] X. Liang, W. Hou, Y. Xu et al., "Sorption of lead ion by layered double hydroxide intercalated with diethylenetriaminepentaacetic acid," *Colloids and Surfaces A*, vol. 366, no. 1–3, pp. 50–57, 2010.
- [15] A. A. Kosorukov, G. N. Pshinko, L. N. Puzyrnaya, and S. A. Kobetz, "Extraction of U(VI) from aqueous media with layered double hydroxides interacted with chelating agents," *Journal of Water Chemistry and Technology*, vol. 35, no. 3, pp. 188–202, 2013 (Russian).
- [16] I. Pausch, H. H. Lohse, K. Schurmann, and R. Allmann, "Synthesis of disordered and Al-rich hydrotalcite-like compounds," *Clays & Clay Minerals*, vol. 34, no. 5, pp. 507–510, 1986.
- [17] L. A. Kaplan, "Comparison of high-temperature and persulfate oxidation methods for determination of dissolved organic carbon in freshwaters," *Limnology & Oceanography*, vol. 37, no. 5, pp. 1119–1125, 1992.
- [18] A. W. Brindley and A. Brown, *Crystal Structures of Clay Minerals and Their X-Ray Identification*, Mineralogical Society, Berkeley, Calif, USA, 1980.
- [19] V. V. Goncharuk, G. N. Pshinko, and L. N. Puzyrnaya, "Sorption-desorption processes in the system of U(VI)-layered double hydroxide intercalated with EDTA," *Journal of Water Chemistry and Technology*, vol. 34, no. 2, pp. 88–95, 2012 (Russian).
- [20] V. V. Goncharuk, L. N. Puzyrnaya, G. N. Pshinko, A. A. Kosorukov, and V. Y. Demchenko, "Removal of Cu(II), Ni(II), and Co(II) from aqueous solutions using layered double hydroxide intercalated with EDTA," *Journal of Water Chemistry and Technology*, vol. 33, no. 5, pp. 288–292, 2011 (Russian).
- [21] K.-H. Goh, T.-T. Lim, and Z. Dong, "Application of layered double hydroxides for removal of oxyanions: a review," *Water Research*, vol. 42, no. 6-7, pp. 1343–1368, 2008.
- [22] R. L. Goswamee, P. Sengupta, K. G. Bhattacharyya, and D. K. Dutta, "Adsorption of Cr(VI) in layered double hydroxides," *Applied Clay Science*, vol. 13, no. 1, pp. 21–34, 1998.

Research Article

The New Standard for Drinking Water

V. Goncharuk

*A. V. Dumansky Institute of Colloid Chemistry and Chemistry of Water, National Academy of Sciences,
42 Acad. Vernadskoho Boulevard, Kiev 03680, Ukraine*

Correspondence should be addressed to V. Goncharuk; honch@iccwc.kiev.ua

Received 3 July 2013; Accepted 13 September 2013

Academic Editor: Oleksandr A. Loboda

Copyright © 2013 V. Goncharuk. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The main positions of the new standard on drinking water are provided. The inconsistency of existing approaches to the assessment including methodology of drinking water quality was substantiated. The main advantage of the new standard is the inclusion of integral methods of water quality, universal for all kinds and types of toxic compounds, irrespective of their origin and nature of the action.

1. Introduction

Drinking water, that is, the water whose organoleptic, physicochemical, and biological properties meet human biological needs and has neither color nor smell, should have a taste determined by the presence of physiologically necessary salts of calcium, magnesium, sodium, and potassium in corresponding concentrations without which metabolism in the human organism is impossible.

What optimal parameters should the water possess to be completely safe from the biological and physiological points of view?

For the first time in the world in 1853, in Brussels, at the International Congress of Hygienists, an attempt was made to set a standard for drinking water, which would include only nine controllable components. Among them there were vitally important substances such as magnesium, calcium, total mineralization (determined mainly by the presence of salts of sodium and potassium), and the content of oxygen in the water, sulfates, chlorides, nitrates, and ammonium. However, the age of industrialization, a fast development of the agroindustrial complex and the emergence of megapolises with compact settlement of people, whose number dramatically increased, started on the planet. A further development of civilization became impossible without the creation of civilized systems of water supply and a complex of water disposal facilities. In connection with the worsening of the ecological state of surface and underground sources the issue of water quality control, used by people for drinking

purposes, became more acute. As a result of a low quality of drinking water real threats to the sanitary-epidemiological situation in various regions of the planet cropped out. And only early in the 20th century the first standard for drinking water appear in the USA. After almost a century after adoption in Brussels of the first recommendation for drinking water quality a document of the World Health Organization (WHO) was published, which today, at the beginning of the 21st century, proposes to bring under regulation 95 indices of which 26 are toxic substances, whose presence in drinking water is undesirable. The US standard regulates 102 indexes in drinking water, where complete absence is required for as many as 35 toxic indexes.

A high level of technogenic load on water bodies, the use of imperfect technologies of water conditioning, and secondary contamination of the water in distribution networks result in the ingress to the drinking water of a substantial amount of inorganic and organic pollutants whose joint effect on the human organism causes the effect of synergism known in chemistry and biology, posing real threat to human health. In the situation that has taken shape there is in principle no possibility to provide the population of any country or continent with quality and safe for human health drinking water [1–4].

An increase of the quality of the water being controlled by a national standard in various countries of the world does not solve the issue of obtaining safe drinking water at the centralized water conditioning stations either. All this calls

TABLE 1: Microbiological indicators of drinking water quality.

Indicator	Measurement units	Norm, not more than	
		Water of systems of centralized drinking water supply	Water of uncentralized drinking water supply additionally purified (unbottled, bottled)
Number of bacteria in 1 cm ³ of water under study (TMN) at 37°C	CFU/cm ³	100 ^{1*}	20 ^{1*}
Number of bacteria in 1 cm ³ of water under study (TMN) at 22°C	CFU/cm ³	100 ^{1*}	20 ^{1*}
Number of bacteria of the colibacillus group (coliform microorganisms) in 1 dm ³ of water under study (BCG index)	CFU/dm ³	3 ^{2*}	Absence ^{2*}
Number of thermostable colibacillus (fecal coliform—FC index) in 100 cm ³ of water under study	CFU/100 cm ³	Absence ^{3*}	Absence ^{3*}
Number of pathogenic microorganisms in 1 dm ³ of water under study	CFU/dm ³	Ditto ^{3*}	Ditto ^{3*}
Number of coliphages in 1 dm ³ of water under study	PFU/dm ³	“ ”	“ ”
Spores of sulfate-reducing clostridia	Presence (amount)/20 cm ³	Absence ^{4*}	Absence ^{4*}
Blue pus bacillus (<i>Pseudomonas aeruginosa</i>)	CFU/dm ³	Not determined	Absence

^{1*} An excess of the norm shall not be allowed for 95% of water sample in the water supply network that is under investigation during the year.

^{2*} An excess of the norm shall not be allowed for 98% of water samples in the water supply network that is under investigation during the year. In the event the BCG index is exceeded at the stage of colony identification investigations shall be carried out for the presence of fecal coliforms.

^{3*} In the event of the presence of coliform bacteria or coliphages in a water sample their amount shall be immediately determined in repeatedly taken water samples. If in these samples generally coliform bacteria are found in the amount of >2/100³ and (or) thermostable coliform bacteria and (or) coliphages, pathogenic bacteria of the colibacillus group and (or) enteroviruses shall be determined. The investigation of drinking water for the presence of pathogenic bacteria of the colibacillus group and enteroviruses shall also be carried out following the decision of the organs of sanitary supervision in the event of the emergence of the epidemic situation.

^{4*} The control shall be exercised at the outlet from the drinking water conditioning station in the case of using surface sources of water supply or underground ones, which have the hydraulic connection with the surface water body; during the transition period annually the index of the spores of sulfate-reducing clostridia with the norm “absence/20 cm³” shall be controlled.

TABLE 2: Mycological indicators of drinking water quality.

Indicator	Measurement units	Norm	
		Water of systems of centralized drinking water supply	Water of uncentralized drinking water supply additionally purified (unbottled, bottled)
Micromycetes	CFU/100 cm ³	Absence	Absence*

* *Aspergillus fumigatus*, *Aspergillus niger*, and *Penicillium expansum* must not be present at all.

for the ever more expensive equipment and complication of technological processes.

Against the background of such catastrophic changes in the quality of the environment the monitoring of several tens of substances in drinking water causes, to say the least, a surprise. A surprise is also caused by a lack of understanding of the fact that in pursuit of “technical progress,” even increasing the amount of controllable components in drinking water several times as much, one cannot give any guarantees that it is in fact drinking water and safe for human health. Even the use of underground water at present does not always guarantee the quality of the drinking water obtained, especially if one takes into account the fact that an absolute majority of organic matter in the environment under the effect of various physicochemical and ecological factors undergoes biotransformation into unknown and, most often, into unpredictable compounds. According to the aforementioned synergism the effects of two or more

compounds of toxic nature of each individually taken substance increase in that case if this substance initially is not toxic. Hence the senselessness of using classic approaches to the assessment of drinking waters follows. The notion itself of “normalizing maximum allowable concentrations in drinking water of different toxicants” purportedly safe for human health is, as a matter of fact, immoral.

The proposed new standard include fundamentally new, very effective integrated methods of monitoring water quality, which are designed for revealing acute toxicity at the level of organism and finding chronic toxicity at the cellular level using cytogenetic methods on biological objects for this purpose. These methods are universal for all types and kinds of toxic compounds irrespective of their origin and the nature of their effect.

The new Standard for Drinking Water includes three different regulatory documents [5]:

TABLE 3: Toxicity level of drinking water.

Indicator	Measurement units	Norm	
		Water of systems of centralized drinking water supply	Water of uncentralized drinking water supply additionally purified (unbottled, bottled)
Chronic toxicity on <i>Ceriodaphnia affinis</i>	Number of dead individuals and (or) a decrease of the number of newly born individuals in an experiment compared with the reference during 7 ± 1 days	Not determined	Absence of chronic toxicity
Genotoxicity on <i>Drosophila melanogaster</i> Mg	Rate of occurrence of dominant lethal mutations in an experiment compared with the reference during 72 h	Ditto	Genotoxicity absent
Toxicity on <i>Tetrahymena pyriformis</i>	A reduction of the increment coefficient of the number of infusorians in an experiment compared with the reference during the time set—24 hours (a short-term biotesting) or 96% (a long-term biotesting)	“ ”	Toxicity absent
Toxicity on <i>Vibrio fischeri</i>	Reduction of the level of luminescence of bacteria in an experiment compared with the reference over 30 min	“ ”	Toxicity absent
Genotoxicity on <i>Salmonella typhimurium</i>	A deviation of the total mutagenic activity of umuC-gene of bacteria <i>Salmonella typhimurium</i> in an experiment compared with a reference over 4 hours	“ ”	Genotoxicity absent

TABLE 4: Organoleptic indicators of drinking water quality.

Indicator	Measurement units	Norm, not more than	
		Water of systems of centralized drinking water supply	Water of uncentralized drinking water supply additionally purified (unbottled, bottled)
Organoleptic indicators of quality			
Smell at 20°C	Point	2	0
Smell during heating to 60°C	Point	2	1
Smell and taste	Point	2	0
Color	Deg	20	5
Turbidity	NUT	2.5	0.5

- (i) GOST (state all-union standard) for tap water (conditionally drinking);
- (ii) GOST for drinking water of increased quality (the water absolutely safe for human health);
- (iii) GOST for bottled water.

A new concept of providing the population with quality drinking water along with the general provisions and regulation requirements of the quality of drinking water accepted in the European Union, the WHO, and the Codex Alimentarius [6–10] has been taken into account in the development of the standard [11–15].

Such a concept provides for the following. Water safety in terms of toxicological and microbiological indices is prepared at waterworks. This water is suitable for household or domestic use and is fed to the distribution networks. In this case it is obtained mainly from the water of surface sources.

High-quality drinking water in the amount sufficient for satisfying human physiological needs is prepared at the consumption site in the plant of water pump rooms. It is then not fed to the distribution network but is supplied to the consumer by other methods (by gravitation flow or bottling). Such drinking water is obtained mainly from underground water protected against anthropogenic influence or from tap water.

The fundamental feature of the new standard is the regulatory justification of a new conceptual approach to water supply of population with quality drinking water. It provides economic water supply by utilizing the differentiating consumption of drinking water depending on physiological, sanitary-hygienic, and economic needs of human over one 24-hour period in a specific populated area. The necessity of such an approach is determined by the following objective reasons: unjustified use of quality drinking water for sanitary-hygienic needs; unsatisfactory state of transportation and

TABLE 5: Chemical indicators of quality, which affect the organoleptic properties of drinking water.

Indicator	Measurement units	Norm, not more than	
		Water of systems of centralized drinking water supply	Water of uncentralized drinking water supply additionally purified (unbottled, bottled)
Inorganic components			
Hydrogen index (pH)	pH unit	6.5–8.5	6.5–8.5
Dry residue (total mineralization) optimal content	mg/dm ³	1000 (1500)*	1000 100–400
Total hardness, optimal value	mmol/dm ³	7 (10)*	7 1.5–4.0
Total alkalinity, optimal value	mmol/dm ³	6.5	6.5 0.5–5.0
Sulfates	mg/dm ³	250 (500)*	150
Chlorides	mg/dm ³	250 (350)*	150
Total iron (Fe)	mg/dm ³	0.2	Absence
Manganese (Mn)	mg/dm ³	0.05	Ditto
Copper (Cu)	mg/dm ³	1.0	“ ”
Zinc (Zn)	mg/dm ³	5.0	“ ”
Calcium (Ca), optimal value	mg/dm ³	100	100 20–60
Magnesium (Mg), optimal value	mg/dm ³	30	30 6.0–15
Sodium (Na), optimal value	mg/dm ³	200	200 20
Potassium (K), optimal value	mg/dm ³	20	20 2.0–20
Organic components			
Methyl- <i>tert</i> -butyl ether	mg/dm ³	0.015	Absence
Oil products	mg/dm ³	0.05	Ditto
Chlorophenols	mg/dm ³	0.0003	“ ”

*The value in the brackets may be established following the ruling by the Chief State Sanitary Physician in the corresponding area for the specific system of the drinking water supply based on the evaluation of the sanitary-epidemiological state in a town and the technology of drinking water treatment used in a case, when other sources of drinking water supply are inaccessible.

distribution networks of the system of centralized drinking water supply; discrepancy of the technology of drinking water treatment in centralized systems of drinking water supply to the water quality in a water source; unjustified high economic costs for reconstruction and modernization of the systems of centralized drinking water supply for the preparation of high-quality drinking water in a volume substantially exceeding physiological and sanitary-hygienic human needs.

The second fundamental distinction of the new standard is the fact that the main accent was made on new approaches to the assessment of the quality of drinking water in terms of integral indexes of water toxicity, which is set by the methods of biotesting according to standardized techniques. This makes it possible to obtain objective information on the quality of drinking water before the conduction of a detailed analysis by all indices. Such an analysis is expedient in the case of finding toxicity and the necessity of establishing cause of its emergence.

The third fundamental distinction of the new standard is the requirement of complete absence of all toxic chemical and

biological pollutants in drinking water designed for human consumption.

The employment of the methods of assessment of the drinking water quality by the integral indexes makes it possible within short terms and at the lowest economic costs to assess the suitability of drinking water for human consumption.

Unlike the methods of chemical analysis adopted today in the world (more than 100 indexes of water quality), the employment of the integrated methods of biotesting makes it possible to substantially (~ by 3-4 times) reduce the amount of controlled indexes.

It is a well-known fact that in the modern period in all countries of the world units, devices of various powers, and miniplants for add-on treatment of drinking water from various sources of water supply were used on a wide scale including from drinking water of centralized water supply and the center of realization or the pouring of tertiary treated drinking water to the containers of the consumers. An indispensable condition of achieving all regulatory indexes of

TABLE 6: Toxicological indicators of the harmlessness of drinking water chemical composition^{1*}.

Indicator	Measurement units	Norm, not more than	
		Water of systems of centralized drinking water supply	Water of uncentralized drinking water additionally purified (unbottled, bottled)
Inorganic components			
Aluminum (Al)	mg/dm ³	0.2 (0.5) ^{2*}	Absence
Ammonia (by NH ₄ ⁺)	mg/dm ³	0.5 (1.5) ^{2*}	Ditto
Barium (Ba)	mg/dm ³	0.1	0.1
Beryllium (Be)	mg/dm ³	0.0002	Absence
Boron (B)	mg/dm ³	0.5	Ditto
Cadmium (Cd)	mg/dm ³	0.001	“ ”
Arsenic (As)	mg/dm ³	0.01	“ ”
Nickel (Ni)	mg/dm ³	0.1	“ ”
Nitrates (by NO ₃ ⁻)	mg/dm ³	45	5
Nitrites (by NO ₂ ⁻)	mg/dm ³	0.1	0.02
Perchlorates (ClO ₄ ⁻)	mg/dm ³	0.01	Absence
Mercury (Hg)	mg/dm ³	0.0005	Ditto
Lead (Pb)	mg/dm ³	0.01	“ ”
Selenium (Se)	mg/dm ³	0.01	“ ”
Strontium (Sr)	mg/dm ³	7	2
Stibium (Sb)	mg/dm ³	0.005	Absence
Thallium (Tl)	mg/dm ³	0.0001	Ditto
Fluorides (F ⁻) for climatic region:	mg/dm ³		
II		1.5	1.5
III		1.2	1.2
IV		0.7	0.7
Total chromium (CCr)	mg/dm ³	0.05	Absence
Cyanides (CN ⁻), in particular cyanogen chloride	mg/dm ³	0.05	Ditto
Organic components			
Benz(a)pyrene	mg/dm ³	0.00001	Absence
Benzol	mg/dm ³	0.001	Ditto
Pesticides (sum) ^{3*}	mg/dm ³	0.0005	“ ”
Synthetic anionactive surface-active substances (ASAS)	mg/dm ³	0.1	“ ”
Trichloroethylene and tetrachloroethylene (sum)	mg/dm ³	0.01	“ ”
Tetrachloride carbon	mg/dm ³	0.002	“ ”
Integral indicators			
Permanganate oxidizability	mg O/dm ³	2	0.75
Total organic carbon	mg C/dm ³	4	1.5

^{1*}When in drinking water several chemical substances are detected, which refer to the 1st and 2nd classes of safety, and have sanitary-toxicological indicators of hazard, the sum of relationships of concentrations of every one of them determined in water to the standard should not exceed 1.

^{2*}The value in brackets may be set only by the ruling of the Chief State Sanitary Physician in the corresponding area for the specific system of drinking water supply based on the evaluation of the sanitary-epidemiological state in a town and the technology of drinking water treatment used with the account of the specific situation.

^{3*}Pesticides (sum): organic insecticides, herbicides, fungicides, nematocides, acaricides, algicides, bactericides, virucides, rodenticides, slimicides, bound products (in particular growth regulators), and then metabolites and degradation products. The program of control involves only these pesticides, which, most likely, may be contained in this water.

TABLE 7: Substances formed and getting into drinking water during water conditioning.

Indicator ^{1*}	Measurement units	Norm, not more than	
		Water of systems of centralized drinking water supply	Water of uncentralized drinking water supply additionally purified (unbottled, bottled)
Acrylamide ^{2*}	mg/dm ³	0.001	Absence
Bromates	mg/dm ³	0.1	Ditto
Residual chlorine dioxide	mg/dm ³	0.2–0.8	“ ”
Residual ozone, within	mg/dm ³	0.1–0.3	“ ”
Residual polyphosphates (PO ₄ ³⁻)	mg/dm ³	3.5	“ ”
Trihalogenmethanes: chloroform, bromoform, dibromochloromethane, bromodichloromethane (total)	mg/dm ³	0.1	“ ”
Formaldehyde	mg/dm ³	0.05	“ ”
Residual free chlorine, within	mg/dm ³	0.3–0.5	“ ”
Residual bound chlorine, within	mg/dm ³	0.8–1.2	“ ”
Chlorate ion	mg/dm ³	0.7	“ ”
Chlorite ion	mg/dm ³	0.7	“ ”
Chloroform	mg/dm ³	0.06	“ ”
Dibromochloromethane	mg/dm ³	0.03	“ ”

^{1*}The program of control involves specific indicators with the account of the technology of water conditioning from the cited list.

^{2*}The program of control involves specific indicators of using respective reagents and calculating them based on the analysis of the content of the monomer in the commodity flocculant. The reagent doses and the level of the monomer should correspond to the following requirements: at the polyacrylamide dose 1 mg/dm³ the content of acrylamide in it should not exceed 0.05%.

TABLE 8: Reagents permitted as preservatives for drinking water.

Preservatives	Measurement units	Permitted mass fraction of a preservative in water, not more than
Silver (Ag)	mg/dm ³	0.025 (0.05) ^{1*}
Carbon dioxide (CO ₂)	%	0.2–0.6

^{1*}For waters containing chloride ions >50 mg/dm³.

drinking water safety is the setting of certain requirements of drinking water of both centralized and uncentralized systems of water supply.

By microbiological indexes drinking water should conform to the requirements given in Table 1.

By mycological indexes (micromycetes) drinking water should be in line with the norm given in Table 2.

Toxicity of drinking water of uncentralized water supply is an integral (express) quality index of drinking water in the case of suspicion of contamination of a water source or a distribution network with toxic compounds. The list of indices, test objects, and norms for determination of toxicity obtained from the results of biotesting are given in Table 3.

Radiation safety of drinking water shall be determined by the next acceptable levels: total volumetric activity of α -radiators ($\Sigma\alpha$ -activity) not exceeding 0.1 Bq/dm³ and total volumetric activity of β -radiators ($\Sigma\beta$ -activity)—1.0 Bq/dm³.

By organoleptic and chemical quality indexes, which affect organoleptic properties, drinking water should correspond to norms given in Tables 4 and 5.

According to toxicological indices of harmlessness of the chemical composition drinking water should be in line with norms given in Table 6 and the EC directives [6].

For the water supply system, which uses reagent water treatment methods prior to its delivery to the distribution network, during pouring out, transportation, and storage for a set time of suitability and in conducting research the indexes given in Table 7 are additionally taken into account. The content of substances that are formed and enter the drinking water during its treatment should not exceed the norms given in Table 7.

Reagents, introduced as preservatives for drinking water, shall be in accordance with Table 8. Other substances and methods for preservation of add-on purified bottled water from a noncentralized drinking water supply avoid the introduction of carbon dioxide and silver ions.

Thus, the approval and introduction of the new standard will allow us:

- (i) to substantially reduce capital and operational costs for obtaining high-quality drinking water in amounts

- sufficient for meeting physiological needs of the population;
- (ii) to reduce costs for exercising control over the quality of drinking water intended for human consumption as a result of using integral methods of assessing water quality without reequipment of chemical-analytical laboratories with expensive equipment;
 - (iii) to improve the state legislative database for providing the population with good-quality drinking water, safe for human health.

Designations and Abbreviations

BCG: Group of colibacillus bacteria
 Bq: Becquerel
 PFU: Plaque-forming units
 GMN: General microbial number—number of saprophytic microorganisms
 CFU: Colony-forming units
 NUT: Nephelometric unit of turbidity
 ASAS: Anion active surface-active substances
 SSAS: Synthetic surface-active substances
 TCB: Thermotable colibacillus bacteria.

References

- [1] M. F. Falcone-Dias, I. Vaz-Moreira, and C. M. Manaia, "Bottled mineral water as a potential source of antibiotic resistant bacteria," *Water Research*, vol. 46, no. 11, pp. 3612–3622, 2012.
- [2] M. José Figueras and J. J. Borrego, "New perspectives in monitoring drinking water microbial quality," *International Journal of Environmental Research and Public Health*, vol. 7, no. 12, pp. 4179–4202, 2010.
- [3] M. A. Shannon, P. W. Bohn, M. Elimelech et al., "Science and technology for water purification in the coming decades," *Nature*, vol. 19, pp. 295–2301, 2008.
- [4] A. Bosch, S. Guix, D. Sano, and R. M. Pinto, "New tools for the study and direct surveillance of viral pathogens in water," *Current Opinion in Biotechnology*, vol. 452, pp. 301–310, 2008.
- [5] V. V. Goncharuk, "SOS: drinking water," *Journal of Water Chemistry and Technology*, vol. 32, no. 5, pp. 255–283, 2010.
- [6] "The Directive of the European Union Council 98/82/EU concerning water quality designed for human consumption," *The Official Journal of the European Communities*, pp. 2–5, 1998.
- [7] *Guidelines for Drinking—Water Quality*, vol. 1 of *Recommendations*, World Health Organization, Geneva, Switzerland, 3rd edition, 2004.
- [8] CODEX STAN 227-2991, General Standard for Drinking Waters Bottled/Packed (different of mineral waters).
- [9] U.S. Environmental Protection Agency, "National primary drinking water regulations, disinfectants and disinfection byproducts, final rule," *Federal Register*, vol. 63, no. 241, Article ID 69389, 1998.
- [10] Directive of the EU 98/83/EU of November 3, 1998, Drinking Water. Regulatory Documents. Reference Book [in Ukrainian].—Lviv, Leonorm, Part 2.—323 P., 2001.
- [11] V. V. Goncharuk, "A new concept of supplying the population with a quality drinking water," *Journal of Water Chemistry and Technology*, vol. 30, no. 3, pp. 129–136, 2008.
- [12] O. P. Oksiyuk and V. M. Zhukiskii, "Environmental water quality standards for the Ros' River," *Hydrobiological Journal*, vol. 35, no. 6, pp. 16–21, 1999.
- [13] V. V. Goncharuk, A. V. Rudenko, E. Z. Koval et al., "The problem of water infection with pathogens of mycoses and prospects of resolving this problem," *Journal of Water Chemistry and Technology*, vol. 26, no. 2, pp. 1–18, 2004.
- [14] M. Fielding and M. Farrimond, *Disinfection by-Products in Drinking Water: Current Issues*, Royal Society of Chemistry, Cambridge, UK, 1999.
- [15] V. V. Goncharuk, N. A. Klimenko, L. A. Savchina, T. L. Vrabel, and I. P. Kozyatnik, "Water treatment and demineralization technology: current issues in the technology of drinking water conditioning," *Journal of Water Chemistry and Technology*, vol. 28, no. 1, pp. 2–49, 2006.

Review Article

Water as the Earth's Buffer and Immune System

Vladyslav V. Goncharuk

*A. V. Dumansky Institute of Colloid Chemistry and Chemistry of Water, National Academy of Sciences,
42 Academician Vernadskoho Boulevard, Kyiv 03680, Ukraine*

Correspondence should be addressed to Vladyslav V. Goncharuk; honch@iccwc.kiev.ua

Received 31 May 2013; Accepted 29 August 2013

Academic Editor: Oleksandr A. Loboda

Copyright © 2013 Vladyslav V. Goncharuk. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

A comprehensive review on water as a buffer of the planet and its immune system is presented. The relationship between the quality of drinking water, the level of development of human intelligence, and its health is highlighted. The problems of obtaining cytogenetically and physiologically safe high-quality drinking water are discussed along with the problems of its decontamination. The solutions to maintain stable development of aquatic ecosystems are proposed. It is shown that tap water is the habitat of multiresistant genetically-mutated microorganisms.

1. Water Resources of the Planet

The bulk of the planet's water is concentrated in the seas and oceans and constitutes around 1350 million km³. This is salt water, with an average mineralization of 35.0 g/L, which makes it unsuitable not only for drinking but also for agriculture needs. Fresh water is localized mainly in the North and South poles and in the mountains in the form of glaciers. This resource constitutes 30–50 million km³. However, this source of fresh water is almost unobtainable for human use.

The earth's rivers and lakes contain about 0.4 million km³ of fresh water that is accessible for mankind. Subterranean regions of the planet have substantial stocks of water, mainly saline and salt ones. At a depth of 800 m and up to 1600 m, the water resource constitutes around 4 million km³.

Thus, our planet has only 3% of fresh water of its total amount, with its bulk in the pack ice of the Arctic and Antarctic. The resources of fresh water accessible to human constitute only 0.06%, 0.8 million km³.

At present, more than 40 countries of the world experience an absolute water deficiency (e.g., the Near East, Africa, Indochina, and Australia). A fifth of the population in Europe and the Americas drinks contaminated water, which does not meet international standard criterion. According to the World Health Organization (WHO) official data, around 80% of human diseases around the globe are related to the consumption of low-quality drinking water [1].

The first attempts to establish priorities for conservation and functioning resilient natural resources were defined in the documents of the United Nations (UN) conference in Rio de Janeiro (June, 1992) and the World Summit on Sustainable Development in Johannesburg “Johannesburg Agreement on Sustainable Development” (August 2002) [2]. “Every inhabitant of the planet has the right for clean drinking water,” is the formula declared by the UN [3, 4]. This humane statement is unfortunately not supported by any specific actions. An ill-advised economy, the pursuit of profits without accounting for ecological problems, and the harsh competitive struggle of monopolies have resulted in the majority of surface and underground drinking water supply sources being depleted and heavily polluted. As a result, polluted water penetrates rivers, seas, and oceans. A fourfold increase of the world population within the 20th century alone—from 1.5 to 6 billion people—has dramatically exacerbated this deficiency of fresh water, which is used not only for drinking purposes but also for industrial activity. All of this combined has resulted in the worsening of the global ecological situation.

Artesian groundwater is a source of drinking water that is reliably protected from human impacts. We currently know of more than 150 different types of freshwater and saline drinking water treatments.

The most abundant impurities in underground waters are two-valence iron and manganese, fluorine ions, nitrates, ammonia, hydrogen sulfide, hard salts, and an increased

salt content. Normally, these impurities substantially exceed maximum allowable concentrations for drinking water. Their presence is caused by natural factors of a geological nature. At the same time, one has to remember that high-quality water for human health should contain a wide spectrum of micro-impurities, vitally important, biologically active elements, and natural organic compounds. It is these compounds dissolved in water that provide its taste, smell, transparency and physiological properties.

Surface-level fresh waters are the second most common source of the drinking water supply. However, the global nature of human activities in the 20th century in terms of industrial development, progress in agriculture, transportation, urban utilities, the formation of megalopolises, and the growth of cities and settlements resulted in the wide-scale pollution and contamination of surface waters. The composition of wastewaters is constantly changing due to the synthesis of new chemical substances, often possessing toxic, carcinogenic, and mutagenic properties.

One can identify the following most hazardous types of pollutants entering the environment which eventually affect the water supply:

(i) chemical pollutants:

(1) inorganic compounds:

- (a) heavy metal ions,
- (b) salts,
- (c) toxic, biologically active substances,

(2) organic compounds:

- (a) oil products,
- (b) phenols,
- (c) pesticides,
- (d) surface active substances,
- (e) chlorine-containing compounds,
- (f) xenobiotics;

(ii) bactericidal and viral pollutants;

(iii) radioactive substances of natural and anthropogenic origin isotopes of elements;

(iv) mutagenic compounds of organic and inorganic origin;

(v) mycotic pollutants.

Seas and oceans may also serve as the source of drinking water supply. It is known that the average salt content in water constitutes about 35 g/l. It is natural that such water cannot be used for drinking. There are various approaches intended to desalinate water. In practice, desalinization technologies such as distillation, membrane, and electrochemical methods are used.

1.1. Advantages and Drawbacks of Water Desalination by Reverse Osmosis for Drinking Water Purposes. Desalination of sea (ocean) water is one of the fastest growing sectors of the economy. The introduction of reverse osmosis technology has

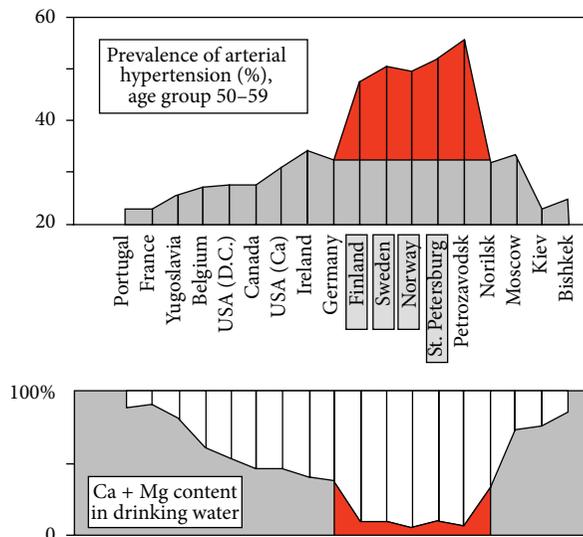


FIGURE 1: Effect of calcium and magnesium in the drinking water on the incidence of hypertonic disease [5].

had a big impact on the rapid development of desalination. Reverse osmosis is used for water treatment and purification of drinking water from heavy metals, nitrates, nitrites, surfactants, phenols, hardness, organic and microbiological contaminants, and organochlorine compounds.

At present, this method is one of the most popular methods of purifying drinking water, including artesian well water for the industrial production of bottled drinking water. The reverse osmosis method of water purification produces water which contains virtually no contaminants. This method has more economical operation and maintenance than any other technology. The effectiveness of using reverse osmosis technology for the desalination of sea water is three times more effective in terms of energy consumption and the degree of purification than the other methods.

At the same time, the obvious disadvantage of reverse osmosis is the lack of selectivity of the membranes to remove contaminants. This means that not only toxic impurities and microorganisms are removed, but also vital minerals and microelements. Will this water fulfill physiological requirements? Of course not! After all, purity of drinking water is not the only criteria of water quality. Also important is the extent to which drinking water is the source of elements necessary for normal body functioning. Water obtained by the reverse osmosis method cannot be called drinking water; one gets somewhat distilled water.

The results of studies on biotesting demineralized (distilled) water show that it affects both the physiological and intracellular processes in the body.

The required presence in the optimal drinking water content of calcium and magnesium is confirmed in Figure 1. Regions supplied by water with a low concentration of calcium and magnesium exhibit a significant (30–40%) increase in the incidence of hypertonic disease (see Figure 1).

It is necessary to do adjustments to the salt composition in water obtained by reverse osmosis [6]. This is achieved by

the introduction of salts required for normal human activity: calcium, magnesium, sodium, and potassium. Taking into account this fact, factories using the reverse osmosis method need to provide special mineralizers, in order to restore the optimal mineral content of water. Thus, an artificial formation of water for drinking purposes is created. This is not the best option, but is vitally necessary where there is no other source of fresh water.

1.2. The Proof of the Failure of World's Approach to Assessing the Quality of Drinking Water and New Scientifically-Based Approaches to Assessing Its Quality. Life on earth is only possible as a result of the presence of water. The emergence and development of biological diversity on our planet is due to the presence of water, which has unique physical and chemical properties. Almost a hundred years it is known that water—not a simple compound where apart of protium there are also heavy isotope patterns however no one has ever thought about why they exist and what their role.

The unique properties of water is determined by its isotope composition and, first of all, by the ratio of protium and deuterium. The natural concentration of deuterium in the world's oceans, in salt and fresh waters varies within the interval 90–180 ppm. The stable optima, concentration of deuterium in water, constitutes 150 ppm. It is within this concentration interval that our ordinary water possesses maximum biological activity both in sea and in fresh water bodies. A decrease or an increase of the deuterium concentration in water results in a radical change of its physicochemical and biological properties [7–9].

Water is currently viewed from fundamentally new positions. The comprehensive study of water has yielded quite new results [10]. It has been found that if the deuterium concentration in water is adjusted, all ideas about its fundamental properties accepted today are changed drastically. Both the melting point and the freezing point, and other water properties, are substantially changed depending on the relation of the isotope composition of hydrogen. If deuterium is completely removed from water, then it will not exist on our planet in its liquid state. Consequently, water structure, just as all physicochemical parameters, is determined by the presence of deuterium. The results regarding the influence of deuterium on water properties became the basis for the discovery of a fundamentally new method for monitoring water quality.

Here, questions arise. What is drinking water? How can the quality of drinking water be assessed? What are the optimal parameters that water should possess in order to be completely safe according to biological and physiological points of view?

The development and the setting of regulations and standards for drinking water quality in different countries since the late 19th and early 20th centuries have changed from simply regulating the macrocomponents of natural water to more insightful knowledge about the impact of anthropogenic contaminants and toxic microcomponents of water on human organisms [11].

In connection with the worsening of the ecological state of surface and underground sources, the issue of water quality

control, used by people for drinking purposes, became more acute [12, 13]. As a result of the low quality of drinking water, real threats to the sanitary-epidemiological situation in various regions of the planet crop out.

An increase of the quality of the matter being controlled in national standards of various countries of the world does not solve the issue of obtaining safe drinking water at centralized water-treatment stations either. All this calls for ever more expensive equipment and the complication of technological processes. Special attention should be paid to the fact that over the last two to three decades, an uncontrolled sharp increase of chemical compounds in the environment took place [11].

While the environment experiences these catastrophic changes, the quality control of dozens of substances in tap water does not guarantee that it really is drinkable and safe for human health. A high level of a technogenic load on water bodies, the use of imperfect technologies of water treatment, and secondary contamination of the water in distribution networks result in the ingress to the drinking water of a substantial amount of inorganic and organic pollutants, whose joint effect on the human organism causes the effect of synergism known in chemistry and biology, threatening human health. In this situation there is no possibility to provide the population of any country and continent with quality drinking water that is safe for human health. In addition, drinking water obtained from surface sources is unsafe due to the presence microtoxins in it of. As a result of our research, we found the presence of toxic micromycetes in surface waters and distribution systems. These micromycetes are not disinfected by current techniques used at centralized water treatment stations, even when chlorinated with high doses.

Hence, classic approaches to the assessment of drinking waters are useless. The notion of “normalizing maximum allowable concentrations in drinking water of different toxicants” purportedly safe for human health, is, as a matter of fact, immoral.

2. Quality of Drinking Water: Problems and Solution

The harmonic development of Homosapiens concurrently with the planet's biosphere calls for the immediate prevention of environmental pollution. Our generation has witnessed qualitative changes of natural and drinking waters. For the first time in the history of mankind, the necessity of introducing quality standards for drinking water has appeared. These standards over time were improved, and new ones were introduced. Substances both of natural and anthropogenic origins were hazardous for human health and were strictly controlled. General human and worldwide approaches for drinking water quality evaluation were established. The first countries in the world that developed state standards for drinking water quality were the USA and the USSR. Owing to a high level of bacterial pollution of surface waters, drinking waters were disinfected with chlorine. This was one of the greatest mistakes of mankind. Since water always contains organic compounds, its chlorination inevitably results in

the formation of very toxic, mutagenic, and carcinogenic organochlorine compounds. For the first time in the history of mankind, people began to drink chlorinated water hazardous for human health—technogenic water!

At the beginning of the 20th century, the level of surface-water contamination with chemical and bacterial components did not achieve a critical state. Therefore, small doses of chlorine, used for disinfection of water, do not lead to the formation of substantial concentrations of hazardous organochlorine compounds. However, the turbulent development of industry, agriculture, the formation of megapolises, and a dramatic increase of the population size of the world (a fourfold rise over the 20th century) resulted in a catastrophic level of bacterial and chemical contamination of water sources used for conditioning drinking water. It entailed the necessity of using large doses of chlorine for the disinfection of water. As a result, there was an increase in the concentration of organochlorine compounds in drinking water. Given such a dangerous factor, new, more sophisticated technologies of water treatment began to be developed. These technologies include preliminary filtration from suspended particles, primary chlorination, and chemical water treatment by coagulation concurrent with aluminum, iron, and flocculants of organic and inorganic origin, then filtration on sand and carbon filters. For suppressing the development of microorganisms in pipelines, the water again is treated with chlorine of such a concentration that at the outlet of the faucet of every consumer the content of residual activated chlorine is within the range of 0.3–0.5 mg/dm³.

Schematic chlorine dioxide, possessing a higher oxidizing potential, is used instead of chlorine in a number of countries, according to regulations. Potentials of some oxidants are given in Table 1.

The current technology has its advantages and disadvantages. Advantages include the fact that the decontamination process occurs more effectively. However, it also means that chlorine dioxide may produce a broader set of organochlorine compounds.

An especially negative side of the abovementioned technologies is the use of coagulants containing aluminum. On the one hand, this final introduction of many types of contaminants into the initial water is a necessary stage of treatment. On the other hand, it introduces a new, very dangerous contamination of drinking water with residual aluminum compounds. It was known for a long time that aluminum ions contained in drinking water are exceptionally toxic and affect human health. Several publications deal with this research. This is why the World Health Organization from year to year toughens the requirements regarding the concentration of residual aluminum in drinking water.

Based on these two important prerequisites, namely, the presence in drinking water of organochlorine compounds and aluminum, I allow myself to discuss drinking water not as tap water but as technogenic water. Never before has mankind consumed water for drinking purposes which contained very toxic organochlorine compounds and also aluminum ions, which are byproducts of the modern water treatment technology.

TABLE 1

Chemical substance and its formula	Oxidizing potential, eV	
Chlorine	Cl ₂	1.36
Chlorine dioxide	ClO ₂	1.57
Hydrogen peroxide	H ₂ O ₂	1.78
Ozone	O ₃	2.07
Atomic oxygen	O	2.42
Hydroxyl radical	HO•	2.80

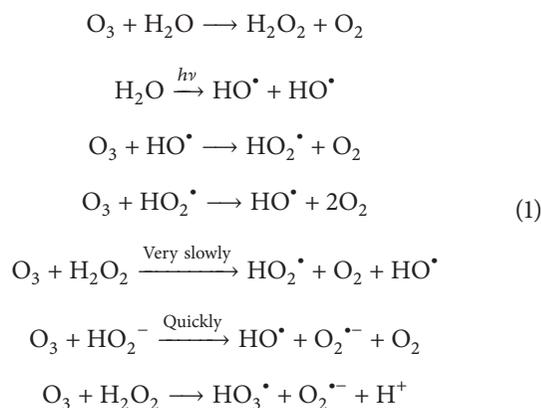
Contaminations of the initial water reached such a level that water treatment facilities built in compliance with the effective world standards already are not capable of preventing the ingress of substances to drinking water. In this regard, their joint effect became a real threat to human health [14].

All this results in the necessity of a search for new alternative water treatment technologies to obtain safe water. Here, first and foremost, one should pay attention to natural, ecologically safe oxidants, which could be used in advanced technologies for obtaining high-quality drinking water from the severely fouled sources.

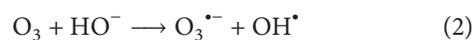
In the last century, for the first time, Russian scientists proposed a fundamentally new approach in water treatment technology—the use of ozone instead of chlorine. The world first ozonizer was developed in Lomonosov Moscow State University, and the first ozonation station for water treatment was built and commissioned in St. Petersburg before World War I. Since then, many years passed before the world community started to treat this technology with due attention.

Below are specified the potential oxidants used today in water treatment, which are the most promising for creating new technologies.

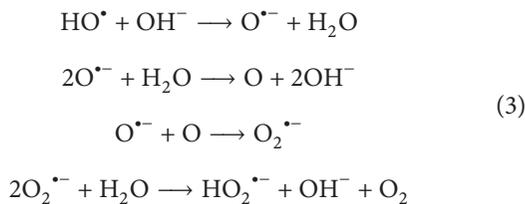
The analysis of the cited data is evidence of the fact that the maximum reactivity is possessed by a hydroxyl radical, which is capable of oxidizing any organic compound into carbon dioxide and water. It is formed in interaction of the ozone with water or hydrogen peroxide with water by the following mechanism:



In aqueous alkaline solutions ozone is decomposed with the formation of O₃^{•-} according to the following reaction:



Then the process follows the schematic with separation of the anion radical of atomic oxygen $O_2^{\bullet-}$ superoxide anion radical $O_2^{\bullet-}$, and then molecular oxygen:

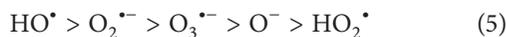


Acid conjugate to anion radical $O_2^{\bullet-}$ that is, radical $HO_2^{\bullet-}$ is a weaker donor of electrons than $O_2^{\bullet-}$, while in the system as following:

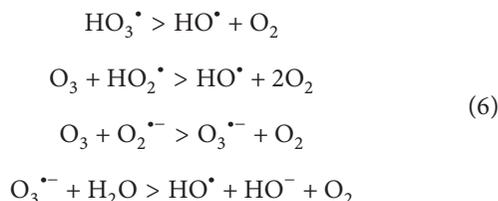


The most active particle is the anion radical of atomic oxygen. Therefore, many reactions of $O_3^{\bullet-}$ are actually reactions of $O^{\bullet-}$. In an aqueous solution, radicals $O_3^{\bullet-}$, $O_2^{\bullet-}$, and $O^{\bullet-}$ are also formed in photolysis or γ -radiolysis.

According to reactivity the active particles may be arranged in the following series:



It has been found that impurities of hydrogen peroxide produce a rather strong catalytic effect on ozone decomposition. Schematically it may be displayed as the following:



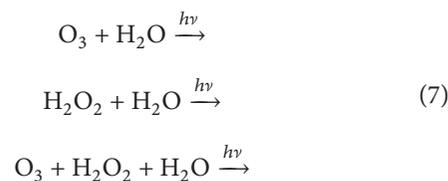
The results of our research confirmed that the identified processes are substantially accelerated in the presence of catalysts (both homogenous and heterogeneous) and under ultraviolet radiation.

It is exactly these results that were used for creating fundamentally new water treatment technologies for any types of pollutants in combination with a set of physical-chemical and biological methods. The research of the kinetics and the mechanism of all processes taking place in aqueous systems provided us with the possibility to develop not only new complex technologies, but new equipment for water treatment. These methods may help obtain high quality drinking water from effectively any source of drinking water supply as far as pollution is concerned. They have an exceptionally great significance for solving the issue of water disinfection from any microbiological and chemical source of pollution.

We offer three ways to solve these problems in the selection of the appropriate parameters—concentration, temperature, pH environment, and other factors.

The first is a simple water treatment with ozone or hydrogen peroxide.

The second is photooxidative disinfection:

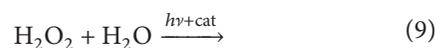


The third is the combined effect of three factors simultaneously:

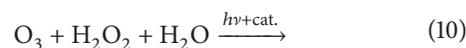
(i) photocatalytic disinfection with ozone



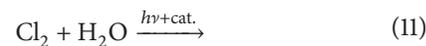
(ii) photocatalytic disinfection with hydrogen peroxide:



(iii) photocatalytic disinfection using the combined effects of ozone and hydrogen peroxide:



(iv) photocatalytic disinfection with chlorine:



To date, we are unaware of more efficient and environmentally friendly methods of water treatment.

3. Water and Human Health

The wide-scale use of chlorine in the technology for centralized drinking water supply stations is determined by the following three main reasons. The use of chlorine ensures:

- (i) primary decontamination of raw water;
- (ii) substantial improvement of the coagulation process whereby phyto- and zooplankton and many organic and inorganic substances are removed from water;
- (iii) prevention of the biological fouling of treatment facility tanks, filtering media, water system networks and equipment.

However, as was indicated above, water treatment with chlorine is accompanied by the formation of a whole range of highly toxic halogen-containing organic compounds such as chlorinated methanes, phenols, aldehydes, ketones, acids and especially hazardous polychlorinated biphenyls up to dioxins—the most toxic matter known on earth. Many years of medical-biological research demonstrated that the long-term use of such drinking water results in an emergence of neurotoxins, cardiovascular diseases, and oncological diseases of liver, kidneys, and the hematopoietic system of human and produces mutagenic effects. It is these compounds that lead to the development of impotence. Therefore, the technology of water ozonation has been used increasingly in water treatment systems all over the world. Ozone as

an alternative reagent simultaneously plays both the role of a disinfectant and an oxidant. In addition, as was noted above, it possesses a higher oxidizing potential, especially the products of its interaction with water. Therefore, the rate of its interaction with all classes of organic compounds is very high. It decolorizes water very well, eliminates fetid smells and odors, removes iron and manganese, suppresses the growth of algae, and so forth. At the same time, one should remember that the use of ozone in the technology of water treatment is possible only in conjunction with other physicochemical methods.

3.1. Ecology—The Health of Human. Having addressed all the above problems, the world-wide issue of determining the degree of risk in the ecology-health system becomes a high-priority one [4]. The hygienic standards and regulations for the levels of environmental pollutants effective today are mostly of a declarative nature. In each specific country, in every region of the world, one needs to assess the priorities of pollutants by the risk levels to human health.

As sources of the risk I would separate four factors playing the most important part in the life of human:

- (1) drinking water,
- (2) air,
- (3) soil,
- (4) foods.

It is necessary to carry out a complex monitoring of all environmental aspects. Why is monitoring needed? First of all, for finding priority pollutants in each specific region that produces maximum negative impact on human health. Certainly, one may follow the path of eliminating all types of pollutions, but this requires fantastically large financial costs. The most expedient formula of the ecological policy in every country should be the following: minimum costs → maximum results, starting from that of the highest priority, the most dangerous pollutants to human health.

One should isolate such main priorities of risk levels:

- (i) chemical pollutants,
- (ii) bacterial pollutants,
- (iii) radioactive and isotopic pollutants,
- (iv) mutagenic pollutants.

One should not forget that complex pollution of the environment with different classes of toxic substances very often results in synergism of their effects, when each toxicant's individual effect is much weaker than a blend of different toxicants. The most glaring among the known examples of the synergetic effect is a joint presence of radioactive matter and asbestos, which strengthen the negative effect of each other sixfolds.

As risk indicators let us point out the following five factors whose presence may help unambiguously assess the state of the environment:

- (i) genetic violations,
- (ii) disease incidence,

- (iii) birth rate,
- (iv) death rate,
- (v) average longevity.

3.2. Bottled Water: Issue of Disinfection and Preservation.

Over the last two decades, the technology of water bottling and its sale through a wide network of shops has become very popular [14, 15]. There are just a few who would think about the enormous scientific and technical issues of preserving the quality of such waters. First of all, the water being subjected to bottling should be immaculate in terms of chemical, biological, and organoleptic indicators and in addition should preserve its qualities in a closed state.

We talked about the issue of water disinfection above, but the issue of its preservation requires a more detailed consideration. Carbon dioxide is the most common preservative, which diluting in water, forms carbonic acid. The taste of such acid water is experienced by everybody who drank aerated water in their lifetime. This water is used for extreme situations of quenching one's thirst rather than for its systematic consumption.

The other effective reagent preserving water is silver or, to be more accurate, silver ions. Since ancient times, the technology of water storage in silverware has been known. Such water can be drunk without worry since the concentration of silver ions is meaningless, but the disinfection process is rather lengthy. It can be amplified a thousand times using the electrochemical technology of silvering water. However, the excessive silver concentration is dangerous. Over time, silver ions are adsorbed on the walls of the vessel and rather quickly lose their disinfecting properties. Under these conditions, secondary bacterial contamination is possible.

Unscrupulous companies may use as preservatives special chemical substances whose functional properties have effects similar to those of antibiotics, which suppress or destroy microorganisms. These substances present enormous hazard for human health. The consumption of such water by drinking leads to the sterilization of the digestive tract causing a known disease—dysbacteriosis.

The chemical nature of the containers used is a very serious issue in the process of water bottling. There are a sufficiently large number of investigations, whose results are an evidence of the toxicity of polymer containers. The safest containers are glassware, glass containers, and enameled and ceramic ware.

4. “Green” Chemistry

The contemporary world early in the 20th century found itself on the verge of the global ecological crisis, which threatens the very existence of civilization. Industrial production still remains high-waste. That is why a new science has appeared and continues to develop effectively. This is the science of ecological economy, which tries to unite social, economic, and ecological systems. Ecological economy should take into account ecological costs when assessing the economic performance of production. A modern economy should develop with the account of ecological factor.

It is quite clear that the correction of the current unfavorable situation does not look to be an easy or quickly resolved issue. This results from the impossibility of allocating sufficient investments for the solution of the ecological issues.

In the world science, this area of science and technical investigations has been referred to as “green chemistry”.

When we talk about drinking water quality we, first of all, should think and care about the quality of drinking water supply sources, and this is almost the entire water basin of the planet. The solution to the existing issue of protecting the whole ecosystem from the products of mankind’s life activity lies in the quest for fundamentally new technical solutions. These solutions aim not only to overcome the consequences, but should prevent the causes, leading to the unfavorable ecological aftermath.

The most widely known water contamination, referred to as water “color,” is caused by blue-green algae—cyanobacteria. An important adverse influence on the water basin is related to their ability to synthesize biologically active substances possessing very high toxicity. The ingress to water of such biogenic elements as phosphorus, nitrogen, potassium, sulfur, and also organic matter from industrial, domestic, rainfall, and waste waters of the agricultural production created the prerequisites for intensive development of algae of various systematic groups, which results in the formation of water “color”.

The facts of the formation of toxins by algae have been known for a rather long time, as early as the 1960s, while the systematic research of the causes of this phenomenon and factors increasing the toxicity started about 20 years ago. The most serious attention at present has been drawn to the toxicant microcystine, produced by cosmopolite cyanobacteria, causing water “blooming” in water bodies of virtually all countries of the world. In terms of biological activity, toxins of cyanobacteria surpass by many times such known substances as strychnine, curare, a range of fungi toxins, and potassium cyanide. They exceed the toxicity of potassium cyanide by as much as 50–1000 times. Such a strong poison as curare exceeds them by least 10 times. Hence, it is quite obvious that such water presents a serious threat to the life of fish, birds, and humans. Even swimming in “blooming” water pools is dangerous for human health, not to mention the use of this water as a source of drinking water supply.

All these facts indicate the necessity of forming the Global World Program for the Protection of the Planet’s Water Basin against Pollution.

5. The Biosphere and Civilization—The Issue of Compatibility

The biosphere in its classical state no longer exists. We are witnessing the apocalypse of the biosphere, which started in the middle of the 20th century. Transforming the environment—the biosphere, whose part is human himself—society underestimated the fact that creating the technogenic environment by its existence violates the basic laws of the biosphere, the laws of the universe.

Nowadays we live in the transition period of the coexistence of two worlds—the biosphere and the noosphere.

There is no return to the biosphere. Man as a creature of the biosphere origin should find new ways for his survival and development. The gene pool of the biosphere has started to intensively rearrange itself—the turbulent process of evolution has begun, which has given birth to ecological changes on a global scale. Mass extinction of the existing species and emergence of new ones are observed across the board. Especially intensive is the evolution of infections. This is evidenced by a widely known fact of the adaptation of pathogenic microflora to antibiotics. This is an illustrative manifestation of mutagenesis—the emergence of a new, earlier absent quality—resistance to antibiotics. Complex genomes are created by nature during millions of years, while in modern laboratories they are created within a year. Man has designed a new artificial habitat, the TechnoSphere, kept safe from all biological processes of the biosphere, without connection with which he simply cannot exist.

The issues of nuclear energy and its impact on the environment bear a complex nature. Since the radioactivity phenomena have been discovered, the irreversible processes of dramatic increase of background radiation all over the planet have been seen [16].

The intensive development of the nuclear industry led to the emergence of a considerable number of objects presenting potential radiation danger: nuclear power plants with reactors of various types, chemical mining plants, and plants for processing nuclear fuel. The radionuclide compositions of pollutants emitted to the environment during the operation and also in emergency situations substantially differ, which makes the use of a single flow chart of purification impossible in all mentioned cases.

Among the numerous aspects of protecting the water basin from technogenic pollutants, one of the most important aspects is achieving the effective purification of various types of pollutants, including radioactive pollutants. Achievement of this task is hampered by the general worsening of the ecological situation, accompanied by the appearance in the waters of an ever larger amount of various toxicants of organic and inorganic nature. Together with the necessity of development and the employment of more complex and sophisticated technologies to achieve purification levels to meet the existing standards, this begs the question of the applicable range of the standards themselves. Here the ever increasing restraint, which currently manifests itself despite the sufficient theoretical and practical substantiation at the moment of adoption, is determined by insufficient accounting of the possibility for aggravation of the adverse influence of toxicants on live organism in their synergetic effect. The synergetic effect of pollutants of various types and radionuclides seems to be one of the most dangerous for human health.

The adverse effect of radioactive elements of the environment is of a complex nature. Despite the fact that it is well studied, the issue of the processing and burial of radioactive waste, which today like “a nuclear gene” are either on the sea bottom or in the mines under earth and are waiting for their time, is still outstanding.

There is one more aspect of this issue which has not been sufficiently studied yet. I mean the issue of the impact of non-radioactive isotopes on the development of biological objects

and, first of all, hydrogen isotopes, in particular, deuterium. The impact of the isotopic composition of substances on kinetic characteristics of numerous reactions has been known for a long time.

It turns out that deuterium strongly affects the chemical parameters of chemical and biological processes since it forms a stronger bond with oxygen in a water molecule, unlike light hydrogen—protium. It is also known that an increased concentration of deuterium in drinking water results in acceleration of the organism aging process. Deuterium manifests toxic properties with respect to living organisms [17].

Nowadays, one of the most serious issues is increased levels of background radioactivity and an increase of the concentration of heavy isotopes with respect to their light prototypes. First of all, it concerns vitally important elements such as hydrogen, oxygen, and carbon, which are a basis of protein life in our biosphere and affect the mechanism of biological evolution.

Thus, ecology is a science studied, strictly speaking, the state of the biosphere, where human is its indispensable part. However, today, when it is quite obvious that the biosphere is being transformed, in an increasing degree, to the noosphere transforming into the TechnoSphere, one cannot help taking into consideration that the world has really changed. It is necessary to have a clear notion of the place of human in a quickly changing world. Ecology transforms into a new geological phenomenon, into a new branch of science investigating the interaction of three globally coexisting constituent components of the universe: biosphere, noosphere, and TechnoSphere. The decisive role in their interaction is played by human. The future of our civilization is determined by the level of the awareness of the changes that have taken place in the environment.

6. A New Approach to the “Environment-Human Health” Problem

Nature built up self renewing systems in the process of evolution supporting life activity of all live bodies. Gastrointestinal tract (GI) is the most impressive system of people and animals. Actually this is a flow-through bioreactor inhabited by many microorganisms. Total number of microorganisms exceeds number of macroorganism's own cells and makes up about 10^{14} – 10^{15} cells [18]. Total weight of microorganisms amounts to 3–4 kg. Intestinal tract of healthy people contains more than 500 types of microorganisms. In the different gastrointestinal tract segments, number of bacteria is different and correlate with the state of digestive system (Table 2).

Set of genes being a part of bacterial metagenome exceeds approximately 100 times set of genes of human organism [20]. Number of bacteria differs in the various segments of gastrointestinal tract. Number of microorganisms in the mouth cavity in acid environment conditions is little and makes up from 0 to 10^3 CGU (colonies of generatrices units) as per one milliliter of environment. In the lower sections of gastrointestinal tract number of microorganisms is much higher. The main factors determining reproduction of bacteria in the environment in the upper sections of

gastrointestinal tract is a fast movement of food, secretion of bile and pancreatic juice. Environmental conditions in the colon are diametrically opposite, that is why number of bacteria in this section of gastrointestinal tract amounts to 10 CGU per one milliliter. *Bifidobacteria* and *Bacteroids* dominate among several hundreds of bacteria in the intestinal tract which share constitutes 25 and 30%, correspondingly, with regard to the total number of anaerobic bacteria. Intestinal tract of a child contains no bacteria before his birth. Fast innidiation of child's intestine with bacteria which are a part of the composition of intestinal and vaginal flora of the mother takes place at the moment of birth. As a consequence it is formed complicated community of microorganisms consisting of *Bifidobacteria*, *Lactobacteria*, *Enterobacteria*, *Clostridia*, and Gram-positive cocci.

Then composition of microbial population is subject to changes due to the influence of several factors of the environment, the most important of which is child's feeding. As early as 1900 Tissier proved that the main components of intestine microflora of the breastfed children are *Bifidobacteria*. Such bifidodominant microflora exercises protective functions and is instrumental in maturation of the mechanisms of child's immune response. On the other hand, artificially fed children have much less *Bifidobacteria* in the colon, and species' composition of intestine microflora is less diversified.

Composition of intestine microflora is fairly individual and is formed from the first days of child's life, nearing indices of an adult person by the end of the 1st–2nd year of life, and undergoes some changes at the elderly age (Table 3).

Numerous research works revealed that there is a connection between composition of intestine microflora and children's immune resistance [21–24]. Distribution of microorganisms in the gastrointestinal tract has quite exact laws. Most microorganisms (about 90%) are presented constantly in one or another section of gastrointestinal tract and represent the main (resistant) microflora, facultative (supernumerary, accompanying) microflora (makes up 10%), and 0.1–0.02% is accounted for accidental (transit or residual) microorganisms. Thus, the basic microflora in the colon is represented by anaerobic microorganisms, while aerobic bacteria make up an accompanying microflora. *Staphylococci*, *Clostridium*, *Proteus*, and Fungi belong in the colon to the residual microflora (Tables 2 and 3). Besides, there are about 10 intestine viruses and certain representatives of the nonpathogenic protozoa in the intestine. The quantity of strict and facultative anaerobes is always one order more than aerobes in the colon, and obligate anaerobes are immediately adhesived on epithelial cells, facultative anaerobes are located higher, followed by aerobic microorganisms. Thus, anaerobic bacteria (mainly *Bifidobacteria* and *Bacteroides*), which on the whole constitute about 60% of the total number of anaerobic bacteria, represent the most permanent and numerous group of intestine microflora carrying out the basic functions.

The whole complex of microorganisms and macroorganisms creates specific symbiosis. Recently some microbiologists declared a man and his microbes as one whole symbiotic superman. Progress in the development of methods of molecular biology thrust the scientists forward to the new level of understanding of processes of symbiosis of a man

TABLE 2: Composition of the intestinal organisms of the human [19].

Types of bacteria	Average concentration of microorganisms (as per 1 mL or 1 g)			
	Intestine	Small intestine	Twisted intestine	Colon
Total number	0–10 ³	0–10 ⁵	10 ² –10 ⁷	10 ¹⁰ –10 ¹²
Anaerobes				
<i>Bacteroides</i>	Seldom	0–10 ³	10 ³ –10 ⁷	10 ¹⁰ –10 ¹²
<i>Bifidobacteria</i>	Seldom	0–10 ⁴	10–10 ⁹	10 ⁸ –10 ¹²
<i>Enterococci</i>	Seldom	0–10 ³	10 ² –10 ⁶	10 ¹⁰ –10 ¹²
<i>Clostridia</i>	Seldom	Seldom	10 ² –10 ⁶	10 ⁶ –10 ³
<i>Eubacteria</i>	Seldom	Seldom	Seldom	10 ⁹ –10 ¹²
Aerobes				
Enterobacteria	0–10 ²	0–10 ³	10 ² –10 ⁷	10 ⁴ –10 ¹⁰
<i>Streptococci</i>	0–10 ²	0–10 ⁴	10 ² –10 ⁶	10 ⁵ –10 ¹⁰
<i>Staphylococci</i>	0–10 ²	0–10 ³	10 ² –10 ⁵	10 ⁴ –10 ⁹
<i>Lactobacteria</i>	0–10 ²	0–10 ⁴	10 ² –10 ⁵	10 ⁴ –10 ¹⁰
Fungi	0–10 ²	0–10 ²	10 ² –10 ⁴	10 ⁴ –10 ⁶

TABLE 3: Composition of intestine microflora in various age groups.

Name of the group of microorganisms	Children of the first year of life	Adult people	People at the elderly age
<i>Bifidobacteria</i>	10 ¹⁰ –10 ¹¹	10 ⁹ –10 ¹⁰	10 ⁹ –10 ¹⁰
<i>Lactobacteria</i>	10 ⁶ –10 ⁷	10 ⁷ –10 ⁸	10 ⁶ –10 ⁷
<i>Bacteroides</i>	10 ⁷ –10 ⁹	10 ⁹ –10 ¹⁰	10 ¹⁰ –10 ¹¹
<i>Fusobacteria</i>	<10 ⁶	10 ⁸ –10 ⁹	10 ⁸ –10 ⁹
<i>Veillonella</i>	<10 ⁵	10 ⁵ –10 ⁶	10 ⁵ –10 ⁶
<i>Eubacteria</i>	10 ⁶ –10 ⁷	10 ⁹ –10 ¹⁰	10 ⁹ –10 ¹⁰
<i>Peptostreptococcus</i>	<10 ⁵	10 ⁹ –10 ¹⁰	10 ¹⁰
<i>Clostridium (lecithinpositive)</i>	<10 ⁵	<10 ⁵	<10 ⁶
<i>Clostridium (lecithinnegative)</i>	<10 ⁷	10 ⁷ –10 ⁸	10 ⁸ –10 ⁹
Enterobacteria: <i>Escherichia coli</i> (with typical properties)	10 ⁷ –10 ⁸	10 ⁷ –10 ⁸	10 ⁷ –10 ⁸
	<10 ⁴	<10 ⁷	<10 ⁷
<i>Enterococci</i>	10 ⁶ –10 ⁷	10 ⁷ –10 ⁸	10 ⁶ –10 ⁷
	<10 ⁵	<10 ⁴	<10 ³
<i>Staphylococci: Staphylococci epidermidis; Staphylococci aureus</i>	<10 ¹	<10 ²	<10 ²
Aerobic bacteria	<10 ³	<10 ⁵	<10 ⁵
Fungi pertaining to <i>Candida</i> genus	<10 ³	<10 ⁴	<10 ⁴

and his microflora. There seemed that processes of symbiosis of a man and his microflora were well studied and their further study will not give any specific surprise. However, quick growth of the speed with simultaneous fall of cost of methods of sequence analysis for deoxyribonucleic acid (DNA) (determining its nucleotide sequence), simultaneous growth of PC capacity, and development of Internet made it possible to analyze information about large areas of genomes. New (population) approach appeared in genetics of microorganisms after decoding of chromosomes of hundreds of types of certain bacteria: analysis of genes of all bacteria inhabiting a certain natural area at once. The population of “human bioreactor” is of course one of the most important for the investigation of microbial population. The first study made to look in a new way at the intestinal microbiota was published in 1999 by the group of scientists from the National Institute for Agronomic Research (France) and University of Reading

(Great Britain). The authors decided to apply method of sequence analysis of genes of 16S RNA for the investigation of microbial population of intestines (16S RNA is certificate of identity of bacteria). Since Pasteur times the first and obligatory stage of identification of microorganisms was their cultivation in culture media. But a great number of important (useful and pathogenic) microbes do not grow in any media. Due to the development of bioinformatics and appearance of modern methods of molecular biology, it has become possible to study before inaccessible and uncultivated bacteria and to begin to put in order ultraentangled classification of already known prokaryotes [20].

It was established using new methods that only 24% of obtained sequences of 16S RNA belonged to the already known microorganisms. Three fourths of microflora in the intestine of each person avoided attention of the researchers armed by the methods of classic microbiology for more than

one-hundred years! The scientists just could not select conditions for cultivation of these bacteria because the most capricious inhabitants of intestine refused to grow in traditional microbiological media. Just the same situation is observed in the chlorinated water of the water supply system. For the time being it was established by means of molecular method that in the microbiota of an adult person are presented 10 out of 70 large bacterial taxons. About 90% of our microbes belong to Firmicutes type (to them belong, e.g., known by everybody as Lactobacteria responsible for milk souring) and Bacteroidetes—strict anaerobes (organisms able to live only in absence of oxygen). The last are often used as indicators of contamination of natural waters by sewage runoff. Remaining populations (10%) are divided between taxa Proteobacteria (among others intestinal bacteria (*Escherichia coli*) belong to them), Actinobacteria (from one of actinomycetes types was obtained antibiotic streptomycin), *Fusobacteria* (usual inhabitants of mouth cavity and are frequent cause of periodontosis), Verrucomicrobia (not long ago a type of these microbes was found in geothermal spring feeding methane which is more than enough in intestine due to the vital functions of other microorganisms), Cyanobacteria (they are often called “blue-green algae”), Spirochaetes, Synergistes, and VadinBE97.

Feeding of microorganisms inhabiting intestine are provided at the cost of so-called nutrients coming from superposed sections of gastrointestinal tract, which are not digested with their own enzymatic systems and are not soaked in the thin intestine. Proteins and carbohydrates not soaked in the thin intestine are exposed to deeper bacterial decomposition in the blind intestinal—mainly by intestinal bacteria and anaerobic microorganisms. These agents are needed to provide energy and flexible requirements of microorganisms. Ability to use nutrients for its vital functions depends on the enzymatic systems of various bacteria. According to this, the following types of bacteria are conditionally marked out:

- (i) mostly with saccharolytic activities, carbohydrates are basic energy substrates which is characteristic for the saprophyte flora;
- (ii) mostly with proteolytic activities which are used with proteins for energy goals (representatives of pathogenic and conditionally pathogenic flora);
- (iii) bacteria with mixed activities.

Accordingly, predominance in food of one or another nutrient and violation of their digestion will stimulate growth of various microorganisms [25, 26]. Carbohydrate nutrients are especially needed for the normal vital functions of intestinal microflora. They were considered as “ballast”, but later it was found out their importance for the intestinal microflora and people’s health on the whole. According to the modern definition, prebiotics are partly or fully indigestible food which selectively stimulates growth and metabolism of one or several groups of microorganisms, providing normal composition of microbiocenosis [27–30].

Microflora of the gastrointestinal tract performs the following functions [31–35].

- (i) Morphokinetic and energy effects (energy supply of epithelium, regulation of intestinal peristalsis, organism’s thermal supporting, regulation of the differentiation, and regeneration of epithelial fabrics).
- (ii) Forming of protective barrier of mucous membrane of intestine, suppression of growth of pathogenic microflora.
- (iii) Immunogenic role (stimulation of immune system, stimulation of tissue immunity including generation of immunoglobulins).
- (iv) Modulation of functions of cytochromes P450 in the liver and generation of P450-like cytochromes.
- (v) Detoxication of toxic substances and compounds.
- (vi) Production of various biologically active compounds, promotion of certain medicaments.
- (vii) Mutagenic/antimutagenic activity (growth of resistance of increase of epithelial cells to the mutagens (carcinogens), destruction of mutagens).
- (viii) Regulation of cavities’ gas composition.
- (ix) Regulation of behavioral reaction.
- (x) Regulation of replication and gene expression of prokaryotic and eukaryotic cells.
- (xi) Regulation of the programmed death of eukaryotic cells (apoptosis).
- (xii) Depository of microbial genetic material.
- (xiii) Participation in etiopathogenesis of the diseases.
- (xiv) Participation in water-salt metabolism, sustention of organism’s ionic homeostasis.
- (xv) Forming immunological tolerance to the food and microbial antigens.
- (xvi) Participation in colonization resistance.
- (xvii) Providing homeostasis of symbiotic relations of prokaryotic and eukaryotic cells.
- (xviii) Participation in the metabolic activity: metabolism of proteins, lipo (delivery of lipogenesis substrates), and carbohydrates (delivery of gluconeogenesis substrates) and regulation of bile acids, steroids, and other macromolecules.

Thus, gastrointestinal tract bioreactor is represented with sequencing circuit of microorganisms’ specific communities each of which performs certain functions and transfers to the following community substances required for its life activity and functioning. Gastrointestinal tract bioreactor is now the most advanced advice providing complete destruction of the wide range of organic and inorganic matters.

Aerotanks and digestors are used in the practice of water treatment where aerobic and anaerobic processes take place. However, each reactor works individually and, what is extremely important, a limited number of microorganisms participate in their work.

Creation of communities’ chain of microorganisms where conditions necessary for their normal life activity (gastrointestinal tract type) will be will allow in the visible future

to develop an universal bioreactor for destruction of the wide spectrum of organic and inorganic matters in the waste waters.

7. Tap Water Is the Medium for Multiresistant Microorganisms—Mutants

As it is known, the main task of chlorine treatment of the drinking water is water sterilization against pathogenic microorganisms. However, this task is not fulfilled to the full extent because of high adaptive capacities of single-celled animals (protozoa).

Scientists of the Swiss Federal Institute for water supply problems found out with the new method of microbiologic control based on flow cytometry that the content of microorganisms 100–1000 times higher in the sanitarily pure drinking water than the standard method. What is happening with the chlorinated water in the obsolete water distribution systems of the centralized water supply of the people? Under these at-first-sight aseptic conditions, the conglomerate of various microorganisms multiresistant to chlorine and its compounds is developed. One-celled organisms, having large adaptive flexibility, completely adapt to the habitation in the tap water. They are developing and propagating themselves in the water and educe their metabolic by-products having toxicant properties into aqueous media. Thus, in the water supply lines of the water distribution systems is forming their own “microcosmos” of the communities of multiresistant microorganisms, including pathogenic ones. They die in the dechlorinated aqueous media.

Emergence of adaptation by combinative way sometimes results in the new mutations which being included into system of genotype changes a phenotype. This path is called the adaptation of a combinative. The use of sublethal concentrations of disinfectants in water treatment processes to the emergence of strains of microorganisms, resistant to chlorine and chlorine compounds.

Adaptation emerging in the combinatorial way sometimes leads to the new mutation which, being included in the genotype system, changes the phenotype. Application of sublethal concentrations of disinfecting agents used during drinking-water treatment contributes to the appearance of microorganism strains, resistant to chlorine and its compounds. This phenomenon is proved by the studies of Mokiyenko and colleagues [36, 37], who considered very important medical problem “drinking water—water-caused infections.” The authors concern themselves with the nature of bacteria resistance to the biocides effect, including chlorine and its compounds. In this connection they take notice of deterioration of the situation with infectious diseases in Ukraine on account of the drinking water of poor quality [38]; they make a hypothesis of chlorine resistance of bacteria which rests on very complicated process. It consists of two stages: information-spatial interaction of the receptive body and a substrate [39, 40].

According to this hypothesis the problem of bacteria's adaptive multiresistance to chlorine is closely connected with hormesis. This phenomenon is determined with two-phase effect of chemical matters directed to the water disinfection.

Small doses produce stimulating effect, and large doses result in the inhibition of biological processes. hormesis connections “dose-effect” are observed in the biota representatives of all levels of organization starting from viruses and bacteria and ending with endotherms and human beings within the wide range of doses [41, 42].

In the papers [43, 44], investigating dynamics of microbial cenosis in the bottled slightly carbonated and strongly carbonated mineral waters, the scientists come to conclusion as to inadequacy of the carbonation methods in question. It was noted substantial increase of saprophyte microorganisms even after the first month of storage of these waters. Saturation, according to the authors, does not guarantee sanitarian safety of the waters. The data is provided which testifies about adaptation of microorganisms to the high concentrations of carbon dioxide.

The mechanism of adaptation of microorganisms to the aggressive environment is based on the process of adaptation development. Process of adaptation development, as any other process, is inconsistent internally. It consists of interaction of two counter-parties: of partial disorganization of already fully formed norm of organism's and species' reaction and its next new organization [45, 46].

In the process of adaptation of microorganisms, takes place a change in the structure and physiological processes under the influence of the environmental factor. Degree of adaptation of microorganisms to the new conditions depends on resistance of this culture to the intensity of impact of external environmental factors. Some species of microorganisms, for example, acid-alcohol-alkali-resistant, diphtheritic group and fungi, are changeable somewhat less than typhous group, round bacteria, and anaerobes. The last adapt easier to the disturbing factors of the environment. Adaptation of the microorganisms is expressed mostly in the attitude to the temperature and availability of oxygen. The better and more perfect adaptation is realized, the slowly and gradually increases impact of the new factors [47].

New conditions can make microorganisms to become less demanding to the environment, limit their physiological requirements or sporulate. Thus, the morphology of microbial cell and its structure sometimes is changes.

Mutations lead to the emergence of bacteria strains with new properties. Mutagenic effect takes place often in case of encountering harmful chemical compounds in the environment where microorganisms usually reproduce themselves; a part of them die and the most stable survive and produce multiresistant strains, sometimes even towards antibiotics and immune serum.

The primary effect of mutagenic agent does not necessary lead to the true mutation. A new phenotype shows up only when changed gene starts to function. There is a possibility to accumulate and to highlight mutants with various defects: with violation of processes of transport or usage of the substrate, with the defects of intermediate metabolism, hypersensirivity to the temperature, and so on [48].

Theoretically, mutations provoked by radiations, chemical matters or other factors could lead to the extinction of bacterial population; however, there are biochemical mechanisms in any living cell that are able to fully or partially restore

parent structure of DNA. Complex of ferments catalyzing reactions of corrections of DNA damage make up systems of repair. They differ fundamentally as to their biochemical mechanism of genome reconstruction. There are three known main mechanisms of correction of DNA defects: immediate reversion from DNA damage to the initial structure, excision (falling out) of damaged initial structure with the further reconstruction, and activation of mechanisms providing immunity to damage.

Thus, there is a high-scale possibility of formation in the tap water of multiresistant populations to the chloride and its compounds. It is largely due to the fact that prokaryotes are the most ancient living organisms on the Earth. They successfully existed during various eras owing to their unique adaptability to the drastic change of physical-chemical factors of media. They are widely presented in these latter days which are described dangerously increasing anthropogenic pollution of the environment.

Microorganisms adapt easily to the aggressive media because they have high mutagenic properties. They are agamic and are reproducing themselves by cell division that is also a positive factor for their adaptive possibilities. Thus, if in the changed media conditions survives at least one cell-mutant, in case of intensive division it forms a new population of microorganisms with changed phenotypic characteristics. Animal unit in such population of microorganisms differ from the natural forms by the appearance, structure of colonies, and physiological characteristics.

An important factor influencing the adaptation of *microbiotas* to biocides as well as to chloride is hormesis. It allows microorganisms to stimulate its biological activity on exposure of small doses of decontaminant. Such "training" increases immunity of the cells to the higher doses and increases number of mutations in the population holding out hope to the survival of microbiota in the aggressive media.

It is necessary to change from time to time decontaminant substances to make the process of adaptation of microorganisms to the tap water more difficult or impossible. For this purpose, it is necessary to use a set of biocides differing as to chemical composition and mechanism of action. But realization of such technological process of decontamination of drinking water at the water treatment works of the centralized water supply is not a trivial task.

8. Toxic Influence of Bacteria on Test Organisms in the Drinking Water

The influence of *Escherichia coli* bacteria and products of their metabolism on the toxic level of the drinking water was not studied before. As a result of our last research work [49] it was found that the drinking water including bottled water contains *colibacillus*. Standard research as to the usage of *Escherichia coli* bacteria as an index of sanitary-hygienic condition of the water does not include toxic evaluation of the water bacterized with *Escherichia coli*.

It is established that metabolites of *Escherichia coli* bacteria separated in the aqueous media considerably deteriorate its quality, inhibit roots' growth on the plant body,

demonstrate chronic toxicity on hydra, and provoke acute toxicity on *Ceriodaphnia*.

The obtained results on the cellular level showed that deviations from control were observed starting from the concentration of microorganisms in the amount of 10^2 . Even in case of finding few bacteria, the inflammatory processes affect hematological indices in the leucocytes of fish blood.

The leucocytes play a very important role for the protection of the organism against bacterial and mycotic infections. Growth of neutrocytosis in the blood is a response of the organism to the bacterial and many other infections. Lymphopenia (decrease of the number of lymphocytes) is typical for the initial stage of infectious-toxic process and is related with their migration from the vessels to the tissues (inflammatory tissue).

In the studied samples of the bottled drinking water with different concentrations of bacteria, significant increase of nucleus rate of the fish tissues is observed. Structural and quantitative changes of cell nucleus were observed in case of bacteria concentration equal to *Escherichia coli* 10^2 . Changes in the components of cell nucleus which are carriers of genetic information leads to the mutation of cells. This can be a reason for error exclusion of one or another disease and lead to the proliferation of oncologic cells.

According to WHO acting hygienic requirements to the water quality from the centralized drinking water supply systems, total number of *E. coli* in 1 mL of water should not exceed 3 CGU. Our research proved that existence of bacteria *E. coli* in the drinking water is inadmissible.

References

- [1] World Health Organization, *Guidelines on Drinking Water Quality Control. Recommendation*, vol. 1, World Health Organization, Geneva, Switzerland, 2004.
- [2] United Nations, *Report of the World Summit on Sustainable Development*, United Nations, New York, NY, USA, 2002.
- [3] World Water Day, "Clean Water for a Healthy World," 2010, <http://www.unepcom.ru/?go=razdel&level=2&cid=66>.
- [4] Global Environment Outlook, *GEO4. Environment For Development. United Nations Environment Programme*, Prog Press, Valletta, Malta, 2007.
- [5] "How to turn water into the water," Mineral additive, "SEVERYANKA", 2011, <http://www.koshcheev.ru/2011/10/20/severyanka/>.
- [6] V. V. Goncharuk, "SOS: drinking water," *Journal of Water Chemistry and Technology*, vol. 32, no. 5, pp. 255–283, 2010.
- [7] V. N. Lobyshev and L. P. Kalinichenko, *Izotopnyye Effekty D₂O V Biologicheskikh Sistemakh (Isotope Effects of D₂O in Biological Systems)*, Nauka, Moscow, Russia, 1978.
- [8] G. Somlyai, G. Laskay, T. Berkenyi et al., "The biological effects of deuterium-depleted water, a possible new tool in cancer therapy," *Zeitschrift fur Onkologie*, vol. 30, no. 4, pp. 91–94, 1998.
- [9] V. V. Goncharuk, A. A. Kavitskaya, I. Y. Romanyukina et al., "Revealing water's secrets: deuterium depleted water," *Chemistry Central Journal*, vol. 7, no. 1, pp. 103–108, 2013.
- [10] V. V. Goncharuk, V. B. Lapshin, T. N. Burdeinaya et al., "Physicochemical properties and biological activity of the water depleted of heavy isotopes," *Journal of Water Chemistry and Technology*, vol. 33, no. 1, pp. 8–13, 2011.

- [11] M. J. Figueras and J. J. Borrego, "New perspectives in monitoring drinking water microbial quality," *International Journal of Environmental Research and Public Health*, vol. 7, pp. 4179–4202, 2010.
- [12] M. A. Shannon, P. W. Bohn, M. Elimelech, J. G. Georgiadis, B. J. Mariñas, and A. M. Mayes, "Science and technology for water purification in the coming decades," *Nature*, vol. 452, no. 7185, pp. 301–310, 2008.
- [13] C. A. Stedmon, B. Sereďnyška-Sobecka, R. Boe-Hansen, N. Le Tallec, C. K. Waul, and E. Arvin, "A potential approach for monitoring drinking water quality from groundwater systems using organic matter fluorescence as an early warning for contamination events," *Water Research*, vol. 45, no. 18, pp. 6030–6038, 2011.
- [14] S.-L. Loo, A. G. Fane, W. B. Krantz, and T. Lim, "Emergency water supply: a review of potential technologies and selection criteria," *Water Research*, vol. 46, no. 10, pp. 3125–3151, 2012.
- [15] C. Reimann, M. Ayräs, A. Chkushin et al., *Environmental Geochemical Atlas of the Central Barents Region. Special Publication of the Central Kola Expedition, Geological Survey of Finland and Geological Survey of Norway*, Schweizerbart Science, Stuttgart, Germany, 1998.
- [16] E. V. Sobotovich and V. V. Dolin, Eds., *Tritij Y Biosferi (Tritium in the Biosphere)*, Nauk Dumka, Kyiv, Ukraine, 2012.
- [17] In Search of the Fountain of Youth, "Preliminary analysis of deuterium's role in DNA degradation," 2003, http://www.springboard4health.com/notebook/health_deuterium_analysis.
- [18] V. V. Goncharuk, *Nauka O Vode*, Naukova Dumka, Kiev, Ukraine, 2010.
- [19] I. A. Meshkov, M. M. Anikhovskaya, M. Y. Yakovleva et al., "Intestinal endotoxin in regulation of hemostasis activity and in pathogenesis of the DIC syndrome," *Human Physiology*, vol. 131, no. 6, pp. 91–96, 2005.
- [20] G. A. Zavarzin, *Bacteria and Composition of Atmosphere*, Nauka, Moscow, Russia, 1984.
- [21] S. V. Belmer, T. V. Gasilina, and A. V. Malkoch, "Znachenije prebiotikov dlya funktsionirovaniya kishhechnoi mikroflory (Importance of prebiotics for functioning of intestinal microflora)," *Russkiy Meditsinskiy Zhurnal*, vol. 3, pp. 151–153, 2008.
- [22] S. V. Belmer and A. V. Malkoch, "Kishechnaia mikroflora y znachenije prebiotikov dlya eyo funktsionirovaniya (Intestinal microflora and importance of prebiotics for its functioning)," *Lechshchiy Vrach*, vol. 4, pp. 25–29, 2006.
- [23] V. Poroyko, "Glubokouvazhayemy microb (Dear microbe)," *Populyarnaya Mekhanika*, vol. 4, pp. 44–47, 2008.
- [24] P. L. Stark and A. Lee, "The microbial ecology of the large bowel of breast-fed and formula-fed infants during the first year of life," *Journal of Medical Microbiology*, vol. 15, no. 2, pp. 189–203, 1982.
- [25] S. Salminen, C. Bouly, R. M. C. Boutron et al., "Functional food science and gastrointestinal physiology and function," *British Journal of Nutrition*, vol. 80, supplement 1, pp. 147–171, 1998.
- [26] A. I. Khavkin, "Microbiotsenos kishhechnika y immunitet (Intestine's microbiocenosis and immunity)," *Russkiy Meditsinskiy Zhurnal*, vol. 11, no. 3, pp. 1–16, 2003.
- [27] G. R. Gibson and M. B. Roberfroid, "Dietary modulation of the human colonic microbiota: introducing the concept of prebiotics," *Journal of Nutrition*, vol. 125, no. 6, pp. 1401–1412, 1995.
- [28] S. Salminen, R. Tanaka, H. Takayama et al., "Effects of administration of TOS and *Bifidobacterium breve* 4006 on the human faecal Hoga," *Bifidobacter Microflora*, vol. 2, pp. 17–24, 1983.
- [29] B. Björkstén, E. Sepp, K. Julge, T. Voor, and M. Mikelsaar, "Allergy development and the intestinal microflora during the first year of life," *Journal of Allergy and Clinical Immunology*, vol. 108, no. 4, pp. 516–520, 2001.
- [30] S. V. Belmer and T. V. Gasilina, "Ratsionalnoye pitaniye y sostav kishhechnoy mikroflory (Balanced feeding and composition of intestine microflora)," *Voprosy Detskoy Diyetologii*, vol. 1, no. 5, pp. 17–20, 2003.
- [31] A. F. Voronin and B. A. Tenderov, *Funktsionalnoye Pitaniye (Balanced Feeding)*, Koloss-Press, Moscow, Russia, 2002.
- [32] S. V. Belmer, A. V. Malkoch, and O. N. Minushkin, "Znachenije prebiotikov dlya funktsionirovaniya kishhechnoy mikroflory (Importance of prebiotics for the functioning of intestine microflora)," in *Proceedings of the 13th Congress Detskikh Gastroenterologov, Aktualniye voprosy abdominalnoy patologii u ditey*, Moscow, Russia, March 2006 2006.
- [33] R. D. Rolfe, "Interactions among microorganisms of the indigenous intestinal flora and their influence on the host," *Reviews of Infectious Diseases*, vol. 6, supplement 1, pp. S73–S79, 1984.
- [34] D. A. Jenkins, C. W. C. Kendall, and V. Vuksan, "Inulin, oligofructose and intestinal function," *Journal of Nutrition*, vol. 129, no. 7, pp. 1431–1433, 1999.
- [35] C. A. Edwards and A. M. Parrett, "Intestinal flora during the first months of life: new perspectives," *British Journal of Nutrition*, vol. 88, supplement 1, pp. S11–S18, 2002.
- [36] A. V. Mokiienko, A. I. Gozhenko, N. F. Petrenko et al., "Water and water caused infections Voda y vodnoobuslovlennyye," *Odessa, ART-B*, 2: 288, 2008.
- [37] A. V. Mokiienko, A. I. Gozhenko, and N. F. Petrenko, "Water chlorination: disinfection or adaptiveness, inactivation or stimulation?" *Vesnik NAN Ukrainy*, vol. 1, pp. 32–40, 2012.
- [38] M. A. Anfrychik, "Infectious diseases and demographic crisis in Ukraine," *Journal of Academy of Medical Sciences*, vol. 13, no. 3, pp. 533–542, 2007.
- [39] A. V. Mokiienko, A. I. Gozhenko, and N. F. Petrenko, "Mechanism of formation of adaptive multiresistance of bacteria to biocides from the point of view of contribution of fundamental basis of supramolecular chemistry," *Vesnik NAN Ukrainy*, vol. 8, pp. 49–56, 2010.
- [40] A. V. Mokiienko, A. I. Gozhenko, and N. F. Petrenko, "Adaptive multiresistance of bacteria to the analysis of contribution to the evolution of epidemiological process," *Preventive Medicine*, vol. 2, pp. 90–95, 2011.
- [41] L. M. Shafran, A. I. Gozhenko, N. F. Petrenko et al., "For the substantiation of hormesis as a fundamental medical paradigm (review of literature and results of own research)," *Present Day Problems of Toxicology*, vol. 2, no. 3, pp. 13–23, 2011.
- [42] A. V. Mokiienko and N. F. Petrenko, "hormesis as trigger mechanism of regulatory mutations and its role in the formation of multiresistance bacteria," *Contemporary Problems of Industrial Toxicology*, vol. 5, pp. 47–52, 2011.
- [43] O. M. Khmelevska, A. V. Mokiienko, and S. I. Nikolayenko, "Hygienic evaluation of dynamics of microbial coenosis of the bottled slightly carbonated water," *Medicine Today and Tomorrow*, vol. 4, no. 49, pp. 161–165, 2010.
- [44] O. M. Khmelevska, A. V. Mokiienko, and S. I. Nikolayenko, "Hygienic evaluation of illustratory microorganisma from the bottled on-carbonated, slightly carbonated and highly carbonated mineral waters of Ukraine," *Hygiene of Population Centers*, no. 58, pp. 122–126, 2011.
- [45] E. V. Ermilova, *Molecular Aspects of Adaptation of Prokaryote*, Khimizdat, Sankt-Peterburg, Russia, 2012.

- [46] V. L. Petukhov, V. S. Korotkevich, and S. Z. Stambekov, "Genetics. Sem.GPI, Novosibirsk," 2007.
- [47] L. S. Buzoleva, *Adaptation of Pathogenic Bacteria to the Environmental Abiotic factors*, Press, Vladivostok, Russia, 2001.
- [48] S. N. Schelkunov, *Genetic Engineering*, Siberian University Edition, Novosibirsk, Russia, 2004.
- [49] V. V. Goncharuk and M. R. Vergolyas, "Toxic influence of bacteria on test organisms in the drinking water," *Journal of Water Chemistry and Technology*, 2013.

Research Article

Evaluation of Efficacy of Anionic Surfactant Degradation in the Presence of Concomitant Impurities of Natural Waters

Yuliya Shvadchina, Vera Vakulenko, Elena Alekseenko, and Anatoliy Sova

A. V. Dumansky Institute of Colloid Chemistry and Water Chemistry, National Academy of Sciences of Ukraine, 42 Vernadsky blvd., 03680 Kyiv-142, Ukraine

Correspondence should be addressed to Vera Vakulenko; vakulvera@ukr.net

Received 31 May 2013; Accepted 3 August 2013

Academic Editor: Oleksandr A. Loboda

Copyright © 2013 Yuliya Shvadchina et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The efficacy of anionic surfactant—sodium alkylbenzene sulfonate (ABS) degradation in the river waters and model solutions containing humic acid by various oxidation processes has been compared. The most effective method is photocatalytic ozonation ($O_3/TiO_2/UV$) which ensures maximum reduction of ABS concentration (94%–95% over 20–30 min) from $\sim 5 \text{ mg/dm}^3$ to values not exceeding the MPC ($<0.5 \text{ mg/dm}^3$) and the highest degree of total organic carbon (TOC) removal (up to 74%) at the lowest values of specific ozone consumption per 1 mg/dm^3 of TOC compared to ozonation and O_3/UV . Photocatalytic oxidation with air oxygen ($O_2/TiO_2/UV$) and O_3/UV treatment provides a smaller decrease in ABS concentrations (86%–93% and 71%–87% within 20–30 min, resp.) and significantly lowers TOC removal (up to 57% and 47%, resp.). Ozonation and UV irradiation, used separately, are inefficient methods for ABS degradation ($<40\%$), and for TOC removal ($<15\%$).

1. Introduction

Synthetic surface-active substances (SAS), due to the wide application in industry and household and shortcomings of existing methods of wastewater treatment, find their way into natural waters [1–3] and have a negative impact on the environment and aquatic biota [1]. Different types of anionic, nonionic, and cationic surfactants have been detected in sewage effluents with concentrations up to 1090, 332, and $62 \mu\text{g/dm}^3$, respectively [1]. The concentrations of SAS in river waters depend upon a percent removal at the sewage treatment plants (STPs), sorption, solids settling, and degradation in stream. Linear alkylbenzene sulfonates (LAS) have been reported in surface waters at concentrations up to $416 \mu\text{g/dm}^3$ [1]. Very low concentration ($<0.1 \text{ mg/dm}^3$) of LAS is discharged in rivers after aerobic STPs such as activated sludge process or trickling filter. Higher concentrations of anionic surfactants ($0.36\text{--}0.49 \text{ mg/dm}^3$) were predicted in the Hindon River (India) from up flow anaerobic based STPs [2]. The average annual concentrations of anionic surfactants in the waters of the Dnieper River and some of its tributaries ($0.07\text{--}0.11 \text{ mg/dm}^3$ and $0.21\text{--}0.32 \text{ mg/dm}^3$, resp.

[3]) were below the maximum permissible concentration (MPC = 0.5 mg/dm^3 [4]), but their content in some samples exceeded the MPC by a factor of 1.5–2. In a shallow urban stream receiving untreated household wastewaters, LAS were found between 0.43 and 1.9 mg/dm^3 [5]. Strongly polar metabolic intermediates of LAS—sulfophenyl carboxylates were detected in river water ($14\text{--}155 \mu\text{g/dm}^3$) and in drinking water ($1.6\text{--}3.3 \mu\text{g/dm}^3$) [6]. Some types of surfactants and their metabolites are compounds with estrogenic activity known as endocrine disrupting chemicals (EDCs) [7]. So reliable removal of surfactants from the real water systems is an important ecological task, and complex composition of organic and inorganic substances in natural and wastewaters and the processes occurring in them must be taken into account.

The major organic impurities in surface waters—humic and fulvic acids (HA and FA) can fix organic xenobiotics (e.g., pesticides, petroleum products, surfactants, etc.) through different mechanisms, through formation of strong chemical bonds (such as ionic, hydrogen, and covalent), charge transfer or weak interactions (such as van der Waals forces, ligand exchange, hydrophobic links) [8–11]; therefore,

they may significantly affect the properties and behavior of xenobiotics in the processes of natural water or sewage treatment [12, 13]. In particular, HA are able to bind anionic surfactants (ASAS) through hydrophobic interactions, significantly distorting their quantification by standard extraction-photometric method with methylene blue [8, 14]. The binding of surfactants with mentioned natural organic matter (NOM) depends on the structure of the substrate and NOM and a number of other factors (such as pH, ionic strength, and duration of exposure) [8, 10, 11]. It was shown that HA have a greater affinity for binding surfactants and other xenobiotics than less hydrophobic FA [8–10, 13].

Therefore, the HA and FA, along with some inorganic ions, affect the kinetics, mechanism, content of intermediate products, the degree of organic xenobiotics detoxification, and decomposition in natural and wastewater by photolytic and oxidation methods [12, 13, 15–23]. The degree of degradation of xenobiotics [24, 25] and specific consumption of oxidizer [18] greatly depend on the qualitative composition of organic impurities of water matrix and their total concentration. In low concentrations (up to 3 mg/dm³ as dissolved organic carbon (DOC)) HA and FA can sensitize photolytic degradation of certain organic xenobiotics [20, 26] as well as initiate a decomposition of ozone molecules resulting in the hydroxyl radicals generation, which accelerate the oxidation of resistant impurities [12]. For example, the destruction of sodium dodecylbenzene sulfonate (ASAS) under ozonation or catalytic ozonation of the solution ($C_0 = 0.028 \text{ mmol/dm}^3$, pH 7) in the presence of 1 mg/dm³ HA was accelerated 1.7 times [12]. HA and Fe³⁺ ions have a synergistic effect on photolytic degradation of 4-*n*-nonylphenol (metabolite of nonionic SAS (NSAS) related to EDCs) [26]. In the presence of HA (1 mg/dm³ as DOC) and 2 mg/dm³ Fe³⁺ the duration of irradiation ($\lambda > 300 \text{ nm}$) needed for reduction of initial concentration of 4-*n*-nonylphenol ($C_0 = 2 \text{ mg/dm}^3$) by 96%–97% declined 9.5 times (from 19 to 2 hours).

However, according to [17, 21] rate constants of photolytic and photocatalytic (O₂/TiO₂/UV) degradation of some other xenobiotics in the presence of even a little amount of NOM (0.5–1 mg/dm³ as DOC) were decreased by 25%–57%. HA and FA at elevated concentrations are powerful scavengers of •OH radicals and retard the chemical and photocatalytic degradation of resistant xenobiotics in natural and wastewaters [13, 15–20, 23]. For example, in the presence of 30 mg/dm³ FA or HA (DOC ~ 16 mg/dm³), rate constants of oxidation of some aromatic hydrocarbons by Fenton reagent (Fe²⁺/H₂O₂) were decreased by 45%–90% [13]. Photocatalytic degradation of some synthetic compounds at high concentrations of HA or NOM was retarded 2–10 times [16, 17, 24, 25].

Nevertheless, analysis of published works [12, 13, 15–18, 22, 24–26] indicates that various catalytic and photocatalytic processes are promising methods of destruction of resistant organic xenobiotics, even if they are present in a complex matrix of natural and wastewaters. However, the rate of xenobiotics oxidation in real waters is considerably reduced. Therefore, higher concentrations or doses of oxidizers [15, 18] and longer treatment time [25] are required for their effective destruction.

The degree of destruction of surfactants and their metabolites by various methods in real waters currently has not been researched thoroughly [12, 22, 25]. According to [22] a concentration of two NSAS (Tergitol and Triton X-100) during photochemical oxidation (H₂O₂/UV, $C_{\text{H}_2\text{O}_2} = 600 \mu\text{mol/dm}^3$, $\lambda = 254 \text{ nm}$) of their model solutions in distilled water ($C_0 = 5 \mu\text{mol/dm}^3$, pH 6.7–6.9) was reduced by 97% within 10 min, whereas in tap water, purified wastewater and untreated wastewater (DOC—0.7, 3.5 and 22–27 mg/dm³, resp.), only by 73%–76%, 58%–62%, and 12%–15%, respectively. The oxidation of model NSAS solutions with photo-Fenton (H₂O₂/Fe²⁺/UV) also provided a reduction of their concentration by 94%–96% within 10 min at a lesser concentration of oxidizing agent ($C_{\text{H}_2\text{O}_2} = 100 \mu\text{mol/dm}^3$, $C_{\text{Fe}^{2+}} = 25 \mu\text{mol/dm}^3$, $\lambda = 254 \text{ nm}$). However, the NSAS removal from tap, purified wastewater and untreated wastewater using the mentioned method was decreased to 60%–64%, 24%–35%, and 12%–25% over 10 min, respectively [22].

The purpose of this work was to define the most efficient method of destruction of anionic surfactants in the presence of HA and NOM of river waters.

2. Materials and Methods

As objects of the research we used sodium alkylbenzene sulfonate (ABS) of the averaged composition C₁₂H₂₅-C₆H₄-SO₃Na, commercial humic acid from Fluka Co. (elemental composition (%): C—46.63, H—4.3, N—0.72, ash content ~ 20), and the Dnieper and Desna Rivers waters, sampled in winter and summer seasons, as well as a sample of fulvic acid separated from the Dnieper River water (elemental composition (%): C—36.8, H—3.9, O—56.2, N—1.2, and S—1.9). Humic acid from Fluka Co. consists mainly of high molecular weight (MW) fractions (content of fractions with MW > 50 kDa is ~95%) [27]. The fractions of compounds with MW up to 10 kDa are dominant in NOM of the Dnieper River water with MW of main fraction—0.5–1 kDa [28, 29]. The river waters contain mainly fulvic acids whose contents are ~20–40 times as high as those of humic acids. Characteristics of model solutions of ABS, HA, FA, and river waters are listed in Table 1.

Commercial TiO₂ Degussa P-25 (81% of anatase, 19% of rutile; $S_{\text{BET}} = 56 \text{ m}^2/\text{g}$, size of particles ~ 30 nm) [30] was used as a photocatalyst at a concentration of 0.5 g/dm³.

Model solutions in distilled water containing ABS and HA simultaneously and separately at initial concentrations 5 mg/dm³ and 10 mg/dm³, respectively, as well as river waters and solutions of ABS ($C_0 = 5 \text{ mg/dm}^3$) in river waters sampled in winter, were oxidized by various methods (O₃, O₃/UV, O₃/TiO₂/UV, O₂/TiO₂/UV, and O₂/UV) at room temperature ($18 \pm 2^\circ\text{C}$) on a laboratory facility equipped with a computer system of recording of ozonation parameters [31], in a quartz reactor ($d = 3.6 \text{ cm}$, $V = 0.44 \text{ dm}^3$) equipped with a dispenser at the bottom for feeding an ozone-air mixture (OAM) or air, spherical defoamer ($V \sim 1 \text{ dm}^3$) at the top and peristaltic pump for ensuring slurry circulation from bottom

TABLE 1: Characteristics of initial solutions of ABS, humic, or fulvic acids and river waters.

Object of research	Colour value, degr.	A_{254} , cm^{-1}	TOC, mg/dm^3	pH	Concentration of HCO_3^- , $\text{mg-eq}/\text{dm}^3$
ABS solution in distilled water	—	0.04	3.6	5.7	0
HA solution in distilled water	68	0.35	3.8	7.2	0
ABS and HA solution in distilled water ($t = 0$ or 14 days)	67–71	0.34–0.39	6.1–6.3	7.2	0
Desna River water (winter)	18	0.22	7.6	8.0	3.7
Solution of ABS in the Desna water (winter)	24	0.27	9.4	8.2	3.7
Dnieper River water (winter)	38	0.38	12.4	7.9	3.1
Solution of ABS in the Dnieper water (winter)	38	0.42	16.1	7.8	3.1
Dnieper River water (summer)	43	0.43	17.9	8.3	2.75
Desna River water (summer)	30	0.27	14.7	8.6	3.7
Solution of FA in model water	72	0.60	16.4	8.2	2.0
Solution of FA in distilled water	58	0.54	15.8	6.0	0

Note: Initial concentration of ABS and HA—5 and 10 mg/dm^3 , respectively.

upwards with fixed rate of 0.15 dm^3/min [32]. The applied ozone dosage (ν_{oz}) was 0.8–2.0 $\text{mg}/(\text{dm}^3 \cdot \text{min})$ at constant flow rate of OAM (0.07 dm^3/min) and the range of ozone concentration in OAM was 4.9–12.7 mg/dm^3 .

UV irradiation of solution or suspension was carried out by a low-pressure mercury-quartz lamp DB-15 ($\lambda_{\text{max}} = 254 \text{ nm}$) located outside and parallel to the axis of the reactor at a distance of 5 cm from the wall. The UV radiation intensity (I_{UV}) entering the solution was 5.2 mW/cm^2 .

The water of Dnieper River sampled in the winter and model solutions of FA were also treated in another reactor ($d = 4.0 \text{ cm}$, $V = 0.36 \text{ dm}^3$) [31] at higher applied ozone dosage and UV radiation intensity ($\nu_{\text{oz}} = 3.1\text{--}3.7 \text{ mg}/(\text{dm}^3 \cdot \text{min})$, I_{UV} about 8 mW/cm^2 ($\lambda = 254 \text{ nm}$)). In addition, river waters, sampled in the summer, were oxidized by O_3/UV in the reactor ($V = 0.625 \text{ dm}^3$) with an immersed source of UV radiation (DRB-8) in the following parameters: $\nu_{\text{oz}} = 1.9 \text{ mg}/(\text{dm}^3 \cdot \text{min})$, $I_{\text{UV}} = 2.72 \text{ mW}/\text{cm}^2$, a thickness of layer irradiated (l)—1.5 cm, and a temperature of 27°C.

After oxidation within 20–30 min the photocatalyst was separated from model solutions and river waters by centrifugation (8000 rpm).

Change in ABS concentration during oxidation was monitored by standard extraction-photometric method with methylene blue (EPh) or advanced sorption-photometric (SPh) technique with methylene blue (determination limit of 0.05 mg/dm^3 and 0.02 mg/dm^3 , resp.) [8, 14]. The latter method allows to significantly improve the accuracy of the ASAS control in waters with high content of the NOM. For example, sorption-photometric (SPh) technique allowed to determine ~80% of initial concentration ($C_0 = 0.14 \text{ mg}/\text{dm}^3$) of sodium dodecyl sulfate (SDS) in the lake water containing HA (15.3 mg/dm^3) and FA (33.5 mg/dm^3) after the sample storage during 14 days, whereas the SDS recovery by standard (EPh) technique declined with time of ~30% [8].

The degree of destruction of HA, FA, and NOM was estimated in terms of the discoloration (ΔA_{364}) of model

solutions or river waters and the variation of optical density in UV region (A_{254}) specifying the decomposition of aromatic structure. Absorption spectra of river waters and model solutions were recorded using a spectrophotometer Shimadzu UV-2450. Change of total concentration of organic compounds in the reaction mixtures was evaluated by reduction of total organic carbon (TOC) concentration which was determined using a Shimadzu TOC-VCSN analyzer.

3. Results and Discussion

Previously, it was found [8] that the binding of ASAS to humic acids depends on the duration of their contact. Humic acids at a concentration of more than 5 mg/dm^3 essentially associated ASAS through 7–14 days. Therefore, to assess the impact of HA on the degree of ABS degradation, model solutions containing ABS and HA simultaneously ($C_{\text{ABS}} = 5 \text{ mg}/\text{dm}^3$, $C_{\text{HA}} = 10 \text{ mg}/\text{dm}^3$, pH 7.2) were oxidized by various methods directly after preparation and after a prolonged (14 days) storage.

Analysis of the data (Table 2) shows that the presence of HA in a fresh prepared model solution at a ratio of $\text{TOC}_{\text{HA}}/\text{TOC}_{\text{ABS}} \sim 1$ did not influenced the degree of photocatalytic transformation of ABS by ozone or oxygen and values of specific ozone consumption (i.e., absorbed ozone dose needed to reduce ABS concentration at 1 mg/dm^3). Photocatalytic oxidation of fresh model solution by ozone or oxygen reduced the concentration of ABS by 94%–95% and 92%–93%, respectively, regardless of the concentrations of HA (0 or 10 mg/dm^3).

Residual concentration of ABS and specific ozone consumption increased slightly during photocatalytic oxidation of model solution containing ABS and HA after prolonged (14 days) storage (see Table 2). However, residual concentration of ABS in all model solutions after photocatalytic oxidation

TABLE 2: Effect of humic acid on reduction of ABS concentration and values of specific ozone consumption under oxidation of model solutions by various methods.

The content of model solution	Oxidation method	C_{ABS} , mg/dm ³		ΔC_{ABS} , %		$D_{\text{oz}}/\Delta C_{\text{ABS}}$, mg/mg	
		EPh	SPh	EPh	SPh	EPh	SPh
ABS ($C_0=5$ mg/dm ³)	—	5.43	5.06	—	—	—	—
	O ₃	4.35	4.45	20	25	2.4	4.3
	O ₃ /UV	0.68	0.64	87	87	2.5	2.7
	O ₃ /TiO ₂ /UV	0.34	0.27	94	95	2.0	2.1
	O ₂ /TiO ₂ /UV	0.49	0.41	91	92	—	—
ABS ($C_0=5$ mg/dm ³) + HA ($C_0=10$ mg/dm ³) (fresh)	—	4.90	5.20	—	—	—	—
	O ₃	3.35	3.45	32	34	5.2	4.6
	O ₃ /UV	0.60	0.75	88	86	2.7	2.6
	O ₃ /TiO ₂ /UV	0.40	0.29	92	94	2.2	2.0
ABS ($C_0=5$ mg/dm ³) + HA ($C_0=10$ mg/dm ³) (storage over 14 days)	—	2.18	4.85	—	—	—	—
	O ₃	1.06	3.3	51	32	6.4	4.6
	O ₃ /UV	0.28	0.61	87	87	6.5	2.9
	O ₃ /TiO ₂ /UV	0.46	0.48	79	90	6.6	2.6
	O ₂ /TiO ₂ /UV	0.28	0.51	87	89	—	—

Note: Duration of treatment (t)—20 min, $v_{\text{oz}} = 0.8$ mg/(dm³·min), $I_{\text{UV}} = 5.2$ mW/cm², $T = 18 \pm 1$ °C.

by ozone or oxygen did not exceed the MPC (MPC of ASAS = 0.5 mg/dm³ [4]).

Residual concentration of ABS was slightly above the MPC after O₃/UV treatment of three model solutions and significantly (7–9 times) higher than the MPC—after ozonation of them. Smaller residual ABS concentration (by ~1 mg/dm³) in ozonated fresh prepared model solution containing ABS and HA simultaneously, as compared to that in ozonated net solution of ABS (see Table 2), apparently was due to the ability of HA at low concentrations to induce the formation of high reactive $\cdot\text{OH}$ radicals. As it is known rate constants of ABS interaction with $\cdot\text{OH}$ radicals are several orders of magnitude higher than those with O₃ molecules [12].

Both techniques (EPh and SPh) used for monitoring of residual ABS concentrations in the course of oxidation of fresh model solutions by various methods gave similar results (see Table 2). At the same time, it was shown that the correctness of ABS determination by standard extraction-photometric technique (EPh) in the initial and ozonated model solutions, containing both ABS and HA after prolonged storage (14 days), significantly decreased and was 45% and 32%, respectively, compared with sorption-photometric technique (SPh) (see Table 2). Therefore, the use of a standard (EPh) method for monitoring of ASAS concentration during oxidative treatment of natural waters with high content of HA can lead to inaccurate assessment of degree of ABS removal and errors in calculating of values of specific ozone consumption.

Maybe, correctness of ABS determination by standard extraction-photometric technique (EPh) in ozonated model solution was reduced due to its insufficient discoloration and therefore incomplete destruction of the associates, formed by

HA and ABS, in contrast to solutions, oxidized photocatalytically by ozone or oxygen (Table 3).

Along with a maximum reduction of ABS concentration, photocatalytic ozonation also provided the highest degree of destruction (mineralization) of organic impurities in all model solutions (by 67%–74% in terms of TOC) at minimum values of specific ozone consumption compared with other oxidation processes studied in this research (see Table 3). A substantial degree of HA destruction (by 68% in terms of TOC) and some lesser degree of mineralization of organic impurities (by 51%–57% in terms of TOC) of three model solutions, containing ABS, were achieved by photocatalytic oxidation with oxygen. The degree of mineralization of organic impurity by ozonation and O₃/UV treatment of model solutions was, respectively, 3.9–5.5 and 1.6–3.5 times lower than under photocatalytic ozonation.

Analysis of values of specific ozone consumption per 1 mg/dm³ of TOC degraded (see Table 3) indicates that the mineralization of HA under oxidation by ozone or O₃/UV was lighter than that of ABS. For example, value of specific ozone consumption during O₃/UV treatment of model solutions containing HA and ABS was higher than that during oxidation of HA solutions. On the contrary, almost equal values of specific ozone consumption were needed for the mineralization of HA and ABS with photocatalytic ozonation, which also somewhat decreased during oxidation of model solutions containing HA and ABS simultaneously. Perhaps, humic acids are the sensitizers of ABS photocatalytic destruction by ozone.

The use of photocatalyst (TiO₂) together with both O₃ and UV radiation reduced values of specific ozone consumption needed for mineralization of HA and ABS in model solutions 1.5–4 times (see Table 3).

TABLE 3: The degree of destruction of organic contaminants of model solutions containing ABS and HA under oxidation by various methods.

The content of model solution	Oxidation method	Discoloration, %	Δ TOC, %	D_{oz}/Δ TOC, mg/mg
ABS ($C_0=5$ mg/dm ³) + HA ($C_0=10$ mg/dm ³) (fresh)	O ₃	74	18	7.4
	O ₃ /UV	84	21	8.9
	O ₃ /TiO ₂ /UV	84	70	2.3
	O ₂ /TiO ₂ /UV	68	57	—
ABS ($C_0=5$ mg/dm ³) + HA ($C_0=10$ mg/dm ³) (storage over 14 days)	O ₃	54	13	9.0
	O ₃ /UV	62	20	10.3
	O ₃ /TiO ₂ /UV	75	71	2.6
ABS ($C_0=5$ mg/dm ³)	O ₂ /TiO ₂ /UV	75	51	—
	O ₃	—	0	—
	O ₃ /UV	—	25	13.4
ABS ($C_0=5$ mg/dm ³)	O ₃ /TiO ₂ /UV	—	67	4.3
	O ₂ /TiO ₂ /UV	—	53	—
	O ₃	65	16	14.5
HA ($C_0=10$ mg/dm ³)	O ₃ /UV	69	47	6.1
	O ₃ /TiO ₂ /UV	78	74	4.0
	O ₂ /TiO ₂ /UV	74	68	—

Note: $t = 20$ min, $v_{oz} = 0.8$ mg/(dm³·min), $I_{UV} = 5.2$ mW/cm², $T = 18 \pm 1^\circ$ C.

TABLE 4: Reduction of ABS concentration in the course of oxidation of its solutions in natural waters by various methods.

Object of research	Oxidation method	t , min	v_{oz} , mg/(dm ³ ·min)	C_{ABS} , mg/dm ³		ΔC_{ABS} , %		$D_{oz}/\Delta C_{ABS}$, mg/mg
				EPh	SPh	EPh	SPh	
Solution of ABS in Desna River water	—	0	—	4.97	—	—	—	—
	O ₃ /UV	20	0.9	1.43	—	71	—	3.3
	O ₃ /TiO ₂ /UV		0.9	0.29	—	94	—	2.8
	O ₂ /TiO ₂ /UV		—	0.68	—	86	—	—
Solution of ABS in Dnieper River water	—	0	—	4.90	4.95	—	—	—
	O ₃		1.6	3.60	3.65	27	26	19.1
	O ₃ /UV	30	1.3	0.85	0.90	83	82	5.5
	O ₃ /TiO ₂ /UV		1.3	0.26	0.26	95	95	5.3
	O ₂ /TiO ₂ /UV		—	0.55	0.60	89	88	—
	O ₂ /UV		—	3.25	3.10	37	39	—

Note: Initial ABS concentration—5 mg/dm³, $T = 20 \pm 1^\circ$ C.

Thus, the presence of humic acids at the ratio $TOC_{HA}/TOC_{ABS} \sim 1$ did not affect the reduction of ABS concentration up to MPC during photocatalytic oxidation of neutral model solutions by ozone and oxygen. The values of specific ozone consumption per 1 mg/dm³ of ABS or per 1 mg/dm³ of TOC obtained in this study were close to the values established earlier [32] at a higher (10 times) initial concentration of substrate (2.3 mg O₃/mg ABS and 4.0 mg O₃/mg TOC).

Oxidation of solutions of ABS in the Dnieper and Desna River waters by various methods made it possible to assess the overall influence of the matrix of natural waters (NOM and mineral impurities) on efficiency of ASAS removal (Table 4). Mentioned model solutions are characterized by a higher concentration of concomitant organic impurities (ratio $TOC_{NOM}/TOC_{ABS} = 2.1-3.5$) and contain more than

3 mg-eq/dm³ of bicarbonate ions, which are scavengers of \cdot OH radicals (see Table 1).

Efficiency of photocatalytic removal of ABS from the Desna River water by two methods (O₃/TiO₂/UV, O₂/TiO₂/UV) (Table 4) was close to efficiency of its removing from fresh model solution containing ABS and HA simultaneously at similar oxidation parameters (see Table 2), but value of specific ozone consumption increased. At the same time, O₃/UV treatment of ABS solution in the Desna River water provided significantly less reduction of its concentration compared both with photocatalytic ozonation of mentioned solution and with O₃/UV treatment of model solution containing ABS and HA simultaneously (by 23% and 17%, resp.) (see Tables 2 and 4).

Oxidation of ABS solution in the Dnieper River water was conducted at higher applied ozone dosage and prolonged

TABLE 5: The degree of destruction of organic contaminants during oxidation of river waters and model ABS solutions in them by various methods.

Water sample	Oxidation method	t , min	ν_{oz_2} , mg/(dm ³ ·min)	Discoloration, %	Δ TOC, %	D_{oz}/Δ TOC, mg/mg
Desna River (winter)	O ₃ /UV	20	0.9	87	28	6.1
	O ₃ /TiO ₂ /UV		0.9	93	33	4.9
	O ₂ /TiO ₂ /UV		—	50	5	—
ABS solution in Desna River water	O ₃ /UV	20	0.9	83	18	6.8
	O ₃ /TiO ₂ /UV		0.9	88	26	5.5
	O ₂ /TiO ₂ /UV		—	55	16	—
Dnieper River (winter)	O ₃		2.0	75	14	12.8
	O ₃ /UV	30	2.0	87	40	7.5
	O ₃ /TiO ₂ /UV		2.0	91	47	6.0
	O ₂ /TiO ₂ /UV		—	68	17	—
	O ₂ /UV		—	114	4	—
ABS solution in Dnieper River water	O ₃		1.6	70	13	11.8
	O ₃ /UV	30	1.3	91	29	4.8
	O ₃ /TiO ₂ /UV		1.3	91	33	4.7
	O ₂ /TiO ₂ /UV		—	62	26	—
	O ₂ /UV		—	108	2	—
Dnieper River (winter)	O ₃ /TiO ₂ /UV*	30	3.7	97	70	7.9
	O ₂ /TiO ₂ /UV*		—	74	27	—
Dnieper River (summer)	O ₃ /UV**	30	1.9	98	47	3.1
Desna River (summer)	O ₃ /UV**	30	1.9	97	53	3.2

Note: * $I_{UV} = 8 \text{ mW/cm}^2$ (lamp DRB-15), ** $I_{UV} = 2.72 \text{ mW/cm}^2$ (lamp DRB-8).

contact time, due to higher concentration of NOM (see Table 1). At photocatalytic ozonation the concentration of ABS in the Dnieper River water was reduced by 95% (below MPC) over 30 min (see Table 4). Photocatalytic oxidation by oxygen and O₃/UV treatment also were quite effective (ΔC_{ABS} was equal 88% and 82% over 30 min, resp.). Ozonation and UV irradiation, used separately, were inefficient to remove ABS from the Dnieper River water, its concentration was reduced only by less than 40% within 30 min (see Table 4).

It should be noted that since the $\text{TOC}_{\text{NOM}}/\text{TOC}_{\text{ABS}}$ ratio in river waters was 2–3.5 times higher compared with model solutions containing ABS and HA, values of specific ozone consumption per 1 mg/dm³ of ABS significantly increased in the course of oxidation of ABS solutions in rivers waters by all methods used in our research, but they were lowest during photocatalytic ozonation (see Tables 2 and 4).

Assessments of efficiency of ABS removal from the Dnieper River water by a variety of oxidative methods based on monitoring its residual concentrations by two techniques (EPh and SPh) are almost equal. Fulvic acids are the dominant fraction of NOM in the Dnieper River water [28], these substances poorly affected the correctness of ASAS monitoring by standard technique [8].

River waters are poorly coloured during the winter season (see Table 1). Therefore, all methods of oxidation, except UV irradiation, ensured a satisfactory degree of discoloration of river waters and model solutions of ABS in them over 20–30 min (the residual colour value was above 15 grad) (Table 5). The UV irradiation of the Dnieper River water

within 30 min enhanced the intensity of its colour. However, the degree of complete degradation of organic contaminants of river waters (the degree of TOC mineralization), due to the presence of > 3 mg-eq/dm³ of bicarbonate ions, was much smaller compared to oxidation of model solutions of ABS and HA in distilled water (see Tables 3 and 5). The TOC content of the Dnieper and Desna River waters and ABS solutions in them in the course of photocatalytic ozonation, O₃/UV treatment, and photocatalytic oxidation with oxygen within 20–30 min was reduced by 33%–47%, 18%–40%, and 5%–26%, respectively (see Table 5). Efficiency of photocatalytic mineralization of NOM of the Dnieper River water was significantly enhanced (above 1.5 times) by increasing applied ozone dosage and UV radiation intensity. Thus, due to replacement of air oxygen by ozone, the degree of TOC removal in the course of photocatalytic oxidation of river waters was increased 2.6–6.6 times. Ozonation and UV irradiation, used separately, as expected, had little effect on NOM mineralization of river waters.

It should be noted a marked increase of values of specific ozone consumption, reducing concentrations of ABS below MPC in the Desna River water compared with those obtained when model solutions of ABS and HA were oxidized, and a significant increase of these parameters during oxidation of ABS solution in the Dnieper River water (see Tables 2 and 4). The values of specific ozone consumption per 1 mg/dm³ of TOC of natural waters also varied significantly (see Tables 3 and 5). Mentioned difference in the values of specific ozone consumption under oxidative treatment of the Desna and

TABLE 6: Effect of bicarbonate ions on the degree of destruction of fulvic acid by various methods.

Characteristic of fulvic acid solution	Oxidation method	ν_{oz} , mg/(dm ³ ·min)	Discoloration, %	Δ TOC, %	D_{oz}/Δ TOC, mg/mg
TOC ₀ —16.4 mg/dm ³ , pH 8.2, 2 mg-eq/dm ³ HCO ₃ ⁻	O ₃ /UV	3.2	94	35	10.1
	O ₃ /TiO ₂ /UV	3.4	98	60	6.7
	O ₂ /TiO ₂ /UV	—	92	30	—
TOC ₀ —15.8 mg/dm ³ , pH 6, 0 mg-eq/dm ³ HCO ₃ ⁻	O ₃ /UV	3.1	86	51	7.3
	O ₃ /TiO ₂ /UV	3.2	94	85	4.6
	O ₂ /TiO ₂ /UV	—	95	53	—

Note: $t = 30$ min; $I_{UV} = 8$ mW/cm²; $T = 18 \pm 1$ °C.

Dnieper River waters (see Tables 4 and 5) appeared to have been caused by a change of both quantitative and qualitative contents of NOM in them. As it is known the composition of organic impurities of the river waters varies seasonally. In winter, the river waters contain more weakly coloured krenic acids which are resistant to oxidation, while in summer more intensely coloured and easily oxidizable apokrenic acids dominate in content of NOM [33]. As one can see from the Table 5, O₃/UV treatment of the Dnieper and Desna River waters sampled in summer at $\nu_{oz} = 1.9$ mg/(dm³·min) and $I_{UV} = 2.72$ mW/cm² ensured a higher degree of mineralization of organic impurities with less values of specific ozone consumption compared with oxidation of water sampled during winter.

Effect of bicarbonate ions on the degree of NOM destruction illustrates the data obtained in the course of O₃/UV treatment and photocatalytic oxidation (O₃/TiO₂/UV, O₂/TiO₂/UV) of model solutions of fulvic acids separated from the Dnieper River water (Table 6). The degree of mineralization of fulvic acids in model water containing 2 mg-eq/dm³ HCO₃⁻ ions was reduced by 1.4–1.8 times, while the values of specific ozone consumption increased 1.4–1.5 times.

4. Conclusions

Comparison of efficiency of destruction of anionic surfactant—sodium alkylbenzene sulfonate (ABS) in model aqueous solutions by various oxidation methods (O₂/UV, O₃, O₃/UV, O₂/TiO₂/UV, O₃/TiO₂/UV) showed that photocatalytic ozonation (O₃/TiO₂/UV) is the most effective method of ABS removal from waters containing HA or NOM and bicarbonate ions. ABS concentration ($C_0 = 5$ mg/dm³) during photocatalytic ozonation of all model solutions with a ratio $TOC_{NOM}/TOC_{ABS} \sim 1$ –3.5 was reduced by 94%–95% over 20–30 min to values not exceeding the MPC (<0.5 mg/dm³).

Along with a maximum reduction of ABS concentration photocatalytic ozonation also ensured the highest degree of mineralization of organic impurities of all model solutions and river waters compared with other oxidation processes investigated in this research at the lowest values of specific ozone consumption per 1 mg/dm³ of TOC.

Values of specific ozone consumption significantly depended on the qualitative and quantitative contents

of concomitant organic impurities and concentration of bicarbonate ions.

The degree of mineralization of organic impurities can be significantly enhanced by changing the parameters of photocatalytic ozonation (applied ozone dosage and UV radiation intensity) at a constant treatment time.

ABS concentration was reduced quite effectively also during photocatalytic oxidation with air oxygen and O₃/UV treatment of model solutions (by 86%–93% and 71%–87% within 20–30 min, resp.), but the degree of mineralization of organic impurities by specified methods was lower compared to photocatalytic ozonation.

Ozonation and UV irradiation, used separately, were inefficient methods for ABS degradation (<40%) and for TOC removal (<15%).

Acknowledgment

The authors express their sincere gratitude to their supervisor Professor V. V. Goncharuk for substantial support and very useful comments when discussing the results of this study.

References

- [1] G.-G. Ying, "Fate, behavior and effects of surfactants and their degradation products in the environment," *Environment International*, vol. 32, no. 3, pp. 417–431, 2006.
- [2] A. K. Mungray and P. Kumar, "Fate of linear alkylbenzene sulfonates in the environment: a review," *International Biodegradation and Biodegradation*, vol. 63, no. 8, pp. 981–987, 2009.
- [3] M. Yu. Antomonov and I. V. Mudryi, "Prognostication of anthropogenic chemical pollution of the Dnepr River," *Hygiene and Sanitation*, no. 6, pp. 15–17, 1996 (Russian).
- [4] *Sanitary Regulations and Standards for Protection of Surface Waters from Pollution (SanPiN No. 4830-88)*, USSR Health Ministry Publications, Moscow, Russia, 1988, (Russian).
- [5] Y. Hirayama, H. Ikegami, M. Machida, and H. Tatsumoto, "Simple and rapid determination of linear alkylbenzene sulfonates by in-tube solid-phase microextraction coupled with liquid chromatography," *Journal of Health Science*, vol. 52, no. 3, pp. 228–236, 2006.
- [6] P. Eichhorn, S. V. Rodrigues, W. Baumann, and T. P. Knepfer, "Incomplete degradation of linear alkylbenzene sulfonate surfactants in Brazilian surface waters and pursuit of their polar metabolites in drinking waters," *Science of the Total Environment*, vol. 284, no. 1–3, pp. 123–134, 2002.

- [7] J. Lintelmann, A. Katayama, N. Kurihara, L. Shore, and A. Wenzel, "Endocrine disruptors in the environment: (IUPAC technical report)," *Pure and Applied Chemistry*, vol. 75, no. 5, pp. 631–681, 2003.
- [8] S. A. Dolenko, E. Yu. Alekseenko, and N. F. Kushchevskaya, "The impact of water-soluble humic acids on extraction-photometric determination of anionic SAS with methylene blue in natural waters," *Journal of Water Chemistry and Technology*, vol. 33, no. 3, pp. 183–186, 2011.
- [9] R. Vinken, A. Höllrigl-Rosta, B. Schmidt, A. Schäffer, and P. F.-X. Corvini, "Bioavailability of a nonylphenol isomer in dependence on the association to dissolved humic substances," *Water Science and Technology*, vol. 50, no. 5, pp. 277–283, 2004.
- [10] M. M. Yee, T. Miyajima, and N. Takisawa, "Study of ionic surfactants binding to humic acid and fulvic acid by potentiometric titration and dynamic light scattering," *Colloids and Surfaces A*, vol. 347, no. 1–3, pp. 128–132, 2009.
- [11] L. K. Koopal, T. P. Goloub, and T. A. Davis, "Binding of ionic surfactants to purified humic acid," *Journal of Colloid and Interface Science*, vol. 275, no. 2, pp. 360–367, 2004.
- [12] J. Rivera-Utrilla, M. Sánchez-Polo, J. D. Méndez-Díaz, M. A. Ferro-García, and M. I. Bautista-Toledo, "Behavior of two different constituents of natural organic matter in the removal of sodium dodecylbenzenesulfonate by O_3 and O_3 -based advanced oxidation processes," *Journal of Colloid and Interface Science*, vol. 325, no. 2, pp. 432–439, 2008.
- [13] M. E. Lindsey and M. A. Tarr, "Inhibited hydroxyl radical degradation of aromatic hydrocarbons in the presence of dissolved fulvic acid," *Water Research*, vol. 34, no. 8, pp. 2385–2389, 2000.
- [14] S. A. Dolenko, E. Yu. Alekseenko, and N. F. Kushchevskaya, "Determination of anionic surface-active substances in waters," *Journal of Water Chemistry and Technology*, vol. 32, no. 5, pp. 297–302, 2010.
- [15] W. Song, V. Ravindran, and M. Pirbazari, "Process optimization using a kinetic model for the ultraviolet radiation-hydrogen peroxide decomposition of natural and synthetic organic compounds in groundwater," *Chemical Engineering Science*, vol. 63, no. 12, pp. 3249–3270, 2008.
- [16] C. Lin and K.-S. Lin, "Photocatalytic oxidation of toxic organohalides with TiO_2 /UV: the effects of humic substances and organic mixtures," *Chemosphere*, vol. 66, no. 10, pp. 1872–1877, 2007.
- [17] T. E. Doll and F. H. Frimmel, "Photocatalytic degradation of carbamazepine, clofibric acid and iomeprol with P25 and Hombikat UV100 in the presence of natural organic matter (NOM) and other organic water constituents," *Water Research*, vol. 39, no. 2–3, pp. 403–411, 2005.
- [18] K. Kosaka, H. Yamada, H. Tsuno, Y. Shimizu, and S. Matsui, "The effects of dissolved organic matter on the decomposition of di-*n*-butyl phthalate by ozone/hydrogen peroxide process," *Water Science and Technology*, vol. 49, no. 4, pp. 57–62, 2004.
- [19] A. Latifoglu and M. D. Gurol, "The effect of humic acids on nitrobenzene oxidation by ozonation and O_3 /UV processes," *Water Research*, vol. 37, no. 8, pp. 1879–1889, 2003.
- [20] O. Mihas, N. Kalogerakis, and E. Psillakis, "Photolysis of 2,4-dinitrotoluene in various water solutions: effect of dissolved species," *Journal of Hazardous Materials*, vol. 146, no. 3, pp. 535–539, 2007.
- [21] L. Zhou, Y. Ji, C. Zeng, Y. Zhang, Z. Wang, and X. Yang, "Aquatic photodegradation of sunscreen agent *p*-aminobenzoic acid in the presence of dissolved organic matter," *Water Research*, vol. 47, no. 1, pp. 153–162, 2013.
- [22] P. M. Nagarnaik and B. Boulanger, "Advanced oxidation of alkylphenol ethoxylates in aqueous systems," *Chemosphere*, vol. 85, no. 5, pp. 854–860, 2011.
- [23] L. Chen, H.-Y. Zhou, and Q.-Y. Deng, "Photolysis of nonylphenol ethoxylates: the determination of the degradation kinetics and the intermediate products," *Chemosphere*, vol. 68, no. 2, pp. 354–359, 2007.
- [24] F. J. Benitez, J. L. Acero, F. J. Real, G. Roldan, and F. Casas, "Comparison of different chemical oxidation treatments for the removal of selected pharmaceuticals in water matrices," *Chemical Engineering Journal*, vol. 168, no. 3, pp. 1149–1156, 2011.
- [25] W. Zhang, Y. Li, Y. Su, K. Mao, and Q. Wang, "Effect of water composition on TiO_2 photocatalytic removal of endocrine disrupting compounds (EDCs) and estrogenic activity from secondary effluent," *Journal of Hazardous Materials*, vol. 215–216, pp. 252–258, 2012.
- [26] M. Martínez-Zapata, C. Aristizábal, and G. Peñuela, "Photodegradation of the endocrine-disrupting chemicals 4-*n*-nonylphenol and triclosan by simulated solar UV irradiation in aqueous solutions with Fe(III) and in the absence/presence of humic acids," *Journal of Photochemistry and Photobiology A*, vol. 251, no. 1, pp. 41–49, 2013.
- [27] A. Kerc, M. Bekbolet, and A. M. Saatci, "Effects of oxidative treatment techniques on molecular size distribution of humic acids," *Water Science and Technology*, vol. 49, no. 4, pp. 7–12, 2004.
- [28] P. N. Linnik and T. A. Vasilchuk, "The role of humic substances in the processes of complexation and detoxication (by the example of the Dnieper reservoirs)," *Hydrobiological Journal*, vol. 38, no. 5, pp. 82–97, 2002.
- [29] N. A. Klimenko, E. A. Samsoni-Todorova, L. A. Savchina, I. A. Lavrenchuk, and T. N. Zasyad'ko, "Seasonal variations of characteristics of organic matter in the Dnieper River water," *Journal of Water Chemistry and Technology*, vol. 34, no. 3, pp. 154–161, 2012.
- [30] Yu. O. Shvadchina, V. F. Vakulenko, E. E. Levitskaya, and V. V. Goncharuk, "Photocatalytic destruction of anionic SAS with oxygen and hydrogen peroxide in the TiO_2 suspension," *Journal of Water Chemistry and Technology*, vol. 34, no. 5, pp. 218–226, 2012.
- [31] V. V. Goncharuk, V. F. Vakulenko, T. N. Sitnichenko, Yu. O. Shvadchina, and A. N. Sova, "Photocatalytic destruction of fulvic acids by ozone and oxygen," *Journal of Water Chemistry and Technology*, vol. 35, no. 2, pp. 62–70, 2013.
- [32] Yu. O. Shvadchina, V. F. Vakulenko, A. N. Sova, and V. V. Goncharuk, "The photocatalytic degradation of anionic surfactants by ozone and oxygen," *Journal of Water Chemistry and Technology*, vol. 35, no. 5, pp. 351–365, 2013 (Russian).
- [33] M. A. Shevchenko, P. V. Marchenko, P. N. Taran, and V. V. Lizunov, *Oxidants in Technology of Water Treatment*, Naukova Dumka Publications, Kiev, Ukraine, 1979, (Russian).

Review Article

Photocatalysis: Oxidative Processes in Water Treatment

Roman V. Prihod'ko and Nely M. Soboleva

Dumanskii Institute of Colloid and Water Chemistry, National Academy of Sciences of Ukraine, Kiev, Ukraine

Correspondence should be addressed to Roman V. Prihod'ko; r.v.prihodko@icccw.kiev.ua

Received 30 May 2013; Revised 26 July 2013; Accepted 18 August 2013

Academic Editor: Oleksandr A. Loboda

Copyright © 2013 R. V. Prihod'ko and N. M. Soboleva. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The efficiency of various homogeneous and heterogeneous systems photocatalytic processes destructive oxidation of organic compounds of different classes is considered. It is shown that photocatalytic methods can significantly increase the speed and depth (up to complete mineralization) of decomposition processes of toxicants. The use of photocatalysis (PC) in the creation of low-power water treatment technologies is a promising direction in addressing environmental problems of the hydrosphere.

1. Introduction

A global character of the human activity with respect to development of industry, agroindustrial complex, and transportation poses the ecological problems as the most topical. By the middle of the last century, the scale of the impact on the environment began to exceed the adaptive capacity of the biosphere which caused disturbances in a number of places natural evolution of the ecological balance, the deterioration of living conditions for living organisms, and eventually the disappearance of the biological species. Currently, anthropogenic factor was to play a decisive role in the genesis not only of continental but also of marine aquatic ecosystems.

In the anthropogenesis impacts, contamination of natural water by the nonpurified waste effluents of industrial and agricultural production, including water pollution by harmful microorganisms, plays an essential role. Under action of different external factors (light, temperature, humidity, etc.), there comes to pass degradation of toxicants and formation of new substances including the more toxic ones. Alongside with the biological processes, there run a number of the physicochemical processes in hydrosphere, namely, adsorption, ion exchange, oxidation-reduction reaction, catalysis, synthesis of new compounds, and so forth [1–3].

Great scientific and practical interest in the system under consideration in the environmental aspect is due to the possibility to carry out the oxidation of organic matter to a high degree of mineralization at relatively low temperatures,

especially in the presence of oxygen, ozone, and hydrogen peroxide with a significant reduction of energy consumption of the process when using sunlight [4].

Among photocatalytic processes that play an important role in the natural self-purification of water by solar light are those that are initiated by complexes of transition metal (TM) (iron, copper, chromium, etc.), for which photoreactivity is of crucial environmental importance. The main sources of TM compounds in surface waters are the processes of dissolution and destruction of rocks and minerals, waste of the steel, metal, and chemical plants, oil refineries, mines, and so forth. The use of waste water in agricultural engineering is also a threat of pollution of the biosphere. TM content in surface freshwater changes from a few to several hundred micrograms per liter. The most common TM pollutants of soils and natural waters include iron and copper, which are also in nutrients, due to the participation in the synthesis of proteins, enzymes, photosynthesis, and so forth.

Compounds of Fe(III) and Cu(II), as being thermodynamically more stable, are more common than Fe(II) and Cu(I). The coordination interaction of TM ions is particularly important in the photochemical processes of transformation of organic compounds in surface waters. In this case, there is usually extension to longer wavelengths of the spectral range of utilization of solar radiation reaching the Earth's surface [2].

Studies on the effect of ions on the kinetics of the TM and the mechanism of chemical transformation of the organic

component of the hydrosphere facilities to suit different synergistic and antagonistic effects provide important information as to the environmental aspect and from the point of view of increasing the efficiency of the advanced oxidation process (AOP) technologies, based on the new photooxidation systems. The interactions of TM ions with organic pollutants in natural and waste waters play a significant role in the environmental photocatalysis. Under solar irradiation, TM ions are photoreduced by organic matter and reoxidized by molecular oxygen. The photoreduction is accompanied by simultaneous oxidation of organic matter. They also affect the efficiency of photooxidation methods used in water treatment technology. The kinetics of these processes are largely determined by the nature of the TM and organic substrate and physicochemical parameters of objects of the hydrosphere: pH, redox potential of the medium, and so forth.

Due to the increasing complexity of wastewater, in particular through the stubborn biological, toxic, and organic compounds, the most promising methods for water treatment are those based on the use of foremost photocatalytic oxidation processes.

The use of photocatalytic processes in the water treatment is a relatively new area with great features which will be implemented in the near future [5–9].

The photocatalytic oxidative degradation of anthropogenic and natural organic contaminants (pesticides, surfactants, organic fertilizers, humic matter, etc.) in the photic layer of surface waters is of great importance among the vast number of physicochemical transformations occurring in hydrosphere. The importance of environmental photochemical processes is ever growing due to intensification of the UV component of solar radiation reaching the Earth surface that is caused by growth of the ozone holes in the stratosphere.

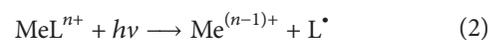
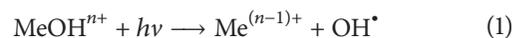
Modern homo- and heterogeneous photocatalytic methods of water purification from organic compounds—pollutants of natural and man-made origin—are based on the oxidation of the latter by molecular oxygen, ozone, and hydrogen peroxide under the influence of artificial UV light or sunlight in the presence of dissolved, suspended or immobilized PCs [10]. It is already known advantages that contribute to their promise, which include simplicity, efficiency, and the possibility of using solar light. Due to the ongoing depletion of world reserves of fossil fuel energy production, the application of photocatalytic processes occurring under the influence of solar radiation, of course, will be a priority in the development of technology and industry.

2. Homogeneous Photocatalysis

Among homogeneous photocatalytic processes that are of crucial environmental importance and play an important role in the natural self-purification of water by ultraviolet (UV) component of solar light are those that originated on hydrocomplexes of TM (iron, copper, chromium, etc.) in higher oxidation state [2, 5, 11].

Thus, generated hydroxyl radicals react with the substrate, which leads to accumulation in the solution of various organic radicals. One-channel flow photochemical process in this case is the oxidation of the substrate hydroxyl radicals

that are formed as a result of phototransfer charge in the hydraulic field inside the metal ions (Me) in a higher valence state. Consider



Under the action of atmospheric oxygen the original form of TM is regenerated with simultaneous formation of superoxide ions, peroxylic radicals, and radical oxidation of the substrate degradation products. Interactions of organic pollutants with hydroxyl radicals formed by the photoreaction (1), in the presence of molecular oxygen, are accompanied by the generation of hydrogen peroxide (Figure 1).

The photochemical process can be carried by photoinduced inner-sphere electron transfer from ligand to metal ion with the formation of organic radicals and reducing of TM ions (2). Formed in the early stages of the photoreaction, the reduced form of the metal, organic radicals, and radical ions are involved in the subsequent thermal reactions.

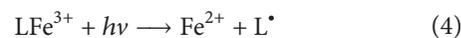
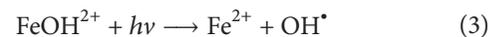
The formation of H_2O_2 in the photooxidation of alcohols in the presence of molecular oxygen is independent of the method of generating HO^{\bullet} radicals, initiating the regeneration process under consideration.

Thus, accumulation of H_2O_2 is observed during photooxidation of ethanol in aqueous solutions of salts of iron (III), in which HO^{\bullet} generation is effected by photoinduced electron inner-aqua Fe^{3+} ions [12–14].

This primarily includes oxidation of organic matter of hydrosphere in the system Fe^{2+} (Fe^{3+})- H_2O_2 -UV (photo-Fenton system), which has been widely used in photochemical methods of water treatment [5].

Fenton's reagent oxidation with additional exposure to UV radiation is one of the most promising ways to clean heavily soiled AOP drains.

Substrates and intermediate destruction products forming complexes with Fe^{3+} may act as light-sensitizing agent. The effect of light is formed in the system of a relatively high concentration of the active catalyst Fe^{2+} ions due to photoreduction of trivalent iron complexes with aqua (3) and organic (4) ligands via intraspherical electron transfer with formation of secondary hydroxyl radicals with a quantum yield of $\Phi = 0.14$ (313 nm) and 0.017 (360 nm)



The photoactive ions are Fe^{3+} , FeOH^{2+} , and $\text{Fe}_2(\text{OH})_2^{4+}$ whose contribution is determined by the pH value and the wavelength of the light source used.

When the quantum yield in the photooxidation of ligands is higher than in reaction (3), this process will predominate in the system as was the case in the oxidation of oxalic acid and 2,4-xylene. Photoreduction of Fe^{3+} in its complexes with citric and oxalic acids in the near-UV region is reported to proceed with high quantum yields.

In the processes occurring in the system H_2O_2 - Fe^{2+} - $h\nu$, we must also consider proceeding with a high quantum

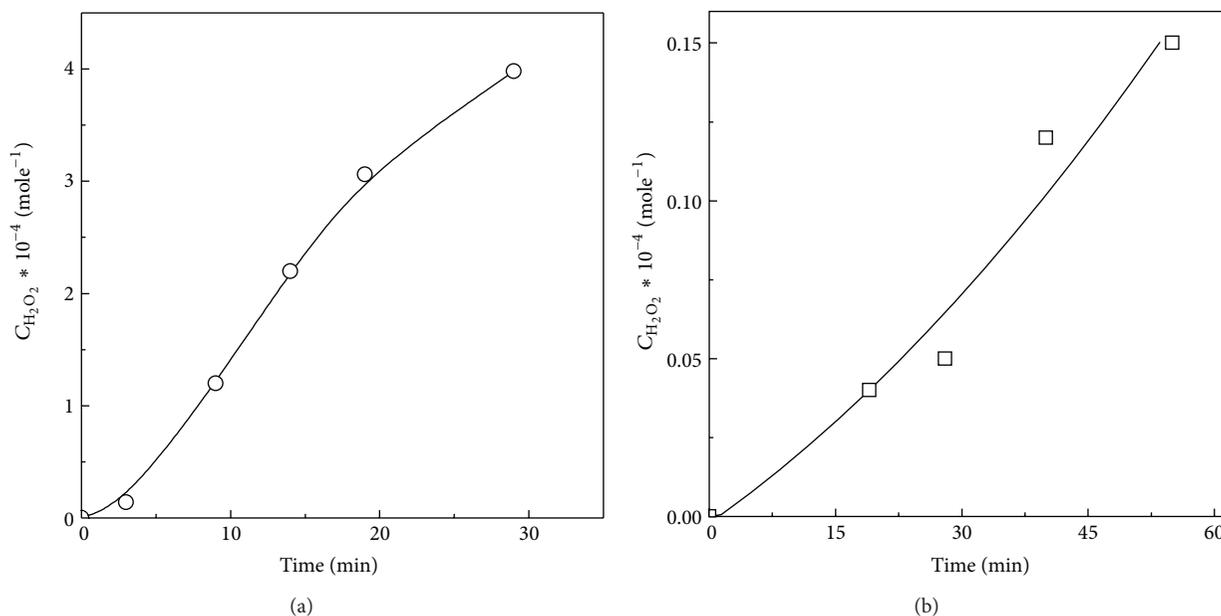
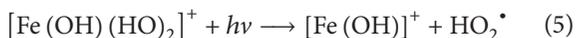


FIGURE 1: Generation of H_2O_2 in the photooxidation of tert-butyl alcohol ($\text{Co} = 1.0 \cdot 10^{-3} \text{ M}$) by Fe^{3+} ($1.0 \cdot 10^{-4} \text{ mole}^{-1}$) (a), and Cu^{+2} ($1.0 \cdot 10^{-3} \text{ mole}^{-1}$) (b) in an aqueous solution ($1.18 \cdot 10^{-3} \text{ M HClO}_4$) under the action of UV light.

yield (1.32) photo-induced decomposition of complex ions $[\text{Fe}(\text{OH})(\text{HO})_2]^+$ (5) to form hydroperoxide radicals, far inferior of hydroxyl radicals as oxidative agents:



This process competes with the oxidation of organic compounds by Fe^{3+} ions according to (4), which reduces the efficiency of the cleaning process itself.

Effect of various physicochemical factors on the efficiency of the oxidation process flowing in the photo-Fenton is system generally similar to that observed in the case of Fenton's reagent.

Destruction of toxic substances in both cases increases with the growth of the temperature and the drop of pH.

The increase of the degree of mineralization of pollutants contributes to the phased introduction in the system of hydrogen peroxide.

Application of photo-Fenton system provides more complete removal of several classes of organic compounds as compared with conventional oxidation methods. TOC removal degree in photochemical mineralization of 4-chlorophenol and waste water components using different dye oxidation systems is reduced in sequence $\text{UV}/\text{H}_2\text{O}_2/\text{Fe}^{2+} > \text{UV}/\text{O}_3 > \text{UV}/\text{H}_2\text{O}_2 = \text{UV}/\text{TiO}_2$ [1, 11].

Interaction of pyridinecarboxylic (PA) and dichloropycolinic (DCPA) acids with the hydrogen peroxide at pH 2–9 in the absence of iron ions does not cause oxidation said compound.

Under the action of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ and $\text{H}_2\text{O}_2/\text{Fe}^{3+}$ systems oxidation of DCPA and PA at pH 4 effectively carried out; moreover, the reaction rate increases with increasing concentration of hydrogen peroxide and iron ions [15].

The presence of the oxidation products NH_4^+ ions indicates the occurrence of deep destruction of DCPA and PA, degradation process cannot achieve a quantitative removal of these compounds from the reaction mixture.

Pyridinecarboxylic acid oxidation in Fenton system can be intensified by additional using of natural solar radiation ($\lambda > 310 \text{ nm}$). The time required for substantially complete removal of these compounds is significantly reduced.

Destructive oxidation of acids proceeds by photocatalysis mechanism according to which the role of the solar radiation is in the regeneration of Fe^{2+} by photoreduction of Fe^{3+} , consequently, maintaining a certain ratio of the valence forms involved in catalytic decomposition of hydrogen peroxide.

Under the reaction conditions, the Fe^{2+} ions (Fe^{3+}) form chelates with DCPA and PA, and therefore, it can be assumed that the latter plays an important role in photoreproduction of an active form of catalyst.

Under the reaction conditions, the formation of chelate compound of Fe^{2+} (Fe^{3+}) ions with DCPA and PC takes place and therefore can suggest a role of these complexes in processes of photogenerated active form of the catalyst.

It was shown that irradiation in the absence of acid solutions of iron oxidation with hydrogen peroxide is not observed; therefore, the effect of radiation on the rate of degradation is only due to the influence of the catalyst. Improving the effectiveness of Fenton's reagent in the processes of oxidative degradation under the influence of solar radiation, as we observed in an example of pyridinecarboxylic acids, will expand the scope of this oxidation system.

Waste water from dyeing and finishing factories is a dangerous source of environmental contamination with pollutants characterized by high levels of chemical and biochemical oxygen demand, color, concentration of suspended solids

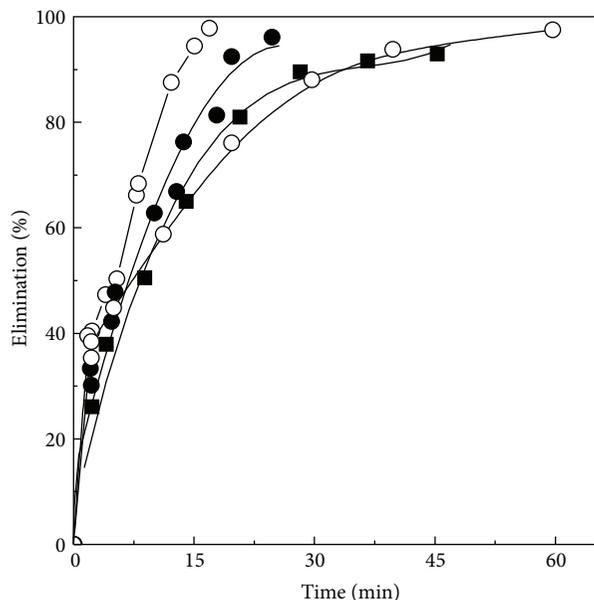


FIGURE 2: Sunlight influence on the AYL ($5.8 \cdot 10^{-5}$ M) oxidation with Fenton's reagent $[\text{H}_2\text{O}_2]_0$ (M): $1 \cdot 10^{-3}$ (circle) (dark conditions); $1 \cdot 10^{-3}$ (box); $5 \cdot 10^{-4}$ (black circle) (\bullet), $3.3 \cdot 10^{-4}$ (black box) (\blacksquare).

and so on. The reduction of color produced by residual dyes causes the most difficulties.

To intensify the bleaching of aqueous solutions of azo dyes by Fenton's reagent, we studied the effect of exposure to natural sunlight on the rate of discoloration of azo dye active yellow lightfastness AYL [6]. The results of experiments using solar radiation show the efficiency of such influence in the oxidation by Fenton's reagent (Figure 2).

Accelerating action of light to be seems apparently due to photoreduction of the Fe^{3+} ion in the system with renewal of Fe^{2+} ions, which, compared with the first, are more active catalysts of the hydrogen peroxide decomposition, resulting in formation of a hydroxyl radical.

The accelerating action of light, apparently, is due to photoreduction of Fe^{3+} ions to Fe^{2+} ions, that are more active catalysts of the hydrogen peroxide decomposition.

As a result the intensification of the process takes place as previously observed for a system substrate- H_2O_2 - Fe^{2+} -sunlight, wherein the substrate was the components of sewage of waste water.

Increasing the speed of the process as previously observed for a system of substrate- H_2O_2 - Fe^{2+} -sunlight, wherein the substrate, the components of sewage of textile production.

Thus, in this case, we have the rate increase as a result of photoreduction of $\text{Fe}^{3+}(\text{L}) \rightarrow \text{Fe}^{2+}(\text{L}^*)$ for the substrate- H_2O_2 - Fe^{2+} -sunlight system, where the substrate was 3,6-diechloropyridine-2-carboxylic acid or sewage components from textile factories.

These studies show that it is possible to reduce the specific consumption of H_2O_2 to bleach azo dye solutions by selecting the appropriate initial concentration of the oxidizing agent.

Application of aeration at certain stages of the process reduces the hydrogen peroxide consumption and reduces

thereby the economic costs of this method in water treatment. Due to regeneration of Fe^{2+} ions in the reaction, original amount of the catalyst can be significantly reduced.

The Cu^{2+} ions in substrate- H_2O_2 - Cu^{2+} -light system also can be photoreduced. Formed Cu(I) ions are also capable of catalyzing the formation of reactive hydroxyl radicals through the decomposition of hydrogen peroxide via Fenton-type reaction.

The principal vulnerabilities of photo-Fenton system include high costs of H_2O_2 storage and of additional acidification and neutralization systems as well as usage of UV-lamps and electric power, and high salinity of the water under treatment because of addition of reagents used to adjust pH and formation of hydroxide slurries that need to be utilized or buried.

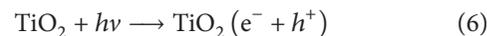
The costs of treatment by the methods under consideration can be reduced, for example, by on-site synthesis of H_2O_2 by means of electrochemical reduction of oxygen and by replacing ultraviolet sources with solar light in oxidation by Fenton's reagent.

3. Heterogeneous Photocatalysis

Heterogeneous photocatalytic water treatment technologies are in the early stage of practical use. But known advantages that contribute to their promising future, which include simplicity, efficiency, and the possibility of using solar light.

The heterogenic photocatalysis on semiconductor materials has been used on the evergrowing scale in the processes of water purification of pollutants and contaminants of natural and man-made origin, artificial photosynthesis, developing methods of storing the energy of sunlight and photochemical water decomposition, and so forth [1, 16–18].

Most papers consider heterogenic systems based on high disperse titanium dioxide with a crystalline modification of anatase (Degussa, Hombikat, Aldrich, etc.). Practical use of other semiconductors (WO_3 , Fe_2O_3 , ZnO , CdS , ZnS , SnO_2 , SrTiO_3 , etc.) has been complicated by their solubility in water or toxicity thanks to which they are substantially inferior to titanium dioxide in terms of technology. Titanium dioxide is a highly active, cheap, nontoxic, and chemically stable product of heavy duty production. Photocatalytic properties of TiO_2 are determined by the features of its electronic structure [17, 19], namely, the existence of a valence and conductance zones in it (Figure 3). When a quantum of light is absorbed—a free electron (e^-) and an electronic vacancy—a hole are formed and they recombine or migrate in a semiconductor being partially localized on structural defective centers of its crystalline lattice:



Probability of electron transfer in PC-adsorbate (oxidant, substrate) system is determined by a relative position of the valence and conductance zones of PC and the value of the oxidation-reduction potential (ORP) of the oxidant and the substrate. The photogeneration of electrical charges is in dynamic equilibrium with their recombination substantially reducing the quantum yield of the photocatalytic process.

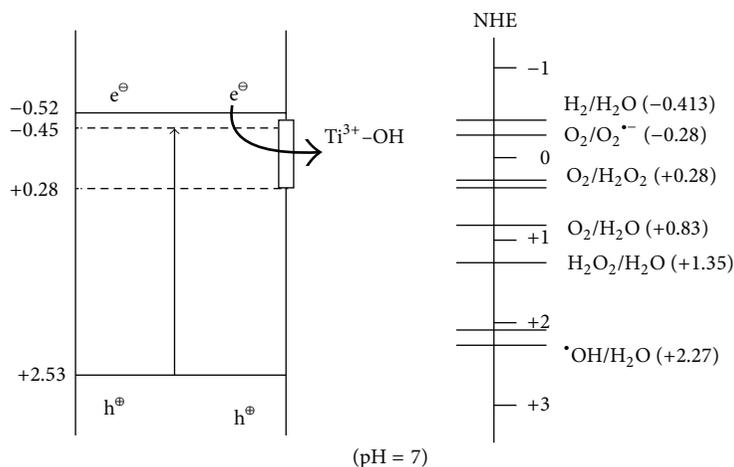
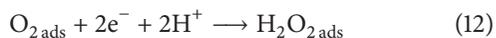
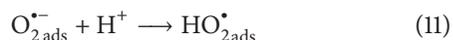
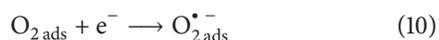


FIGURE 3: Schematic of photogenerating initial oxidizing agents on the TiO_2 surface in the presence of electron-donor (D) and electron-acceptor (A) compounds.

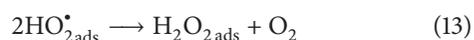
The ORP of water oxidation, the hydroxylic ions, and most organic compounds in a wide range of pH is below of the photogenerated holes (Figure 1), whereby the formation of hydroxyl radicals and organic cation radicals on the surface of PC are thermodynamically possible processes:



The redox potential for conduction band electrons equals -0.52 V, which is negative enough to evolve hydrogen from water. However, even after trapping, a significant number of electrons are still able to reduce dioxygen to superoxide radicals $\text{O}_2^{\bullet-}$ or to hydrogen peroxide. Depending upon the conditions, the holes, OH^{\bullet} and $\text{O}_2^{\bullet-}$ radicals, H_2O_2 , and O_2 itself can all play important roles in the photocatalytic reaction mechanisms. Reduction of oxygen with electrons results in the formation of superoxide, hydroperoxide radicals, and hydrogen peroxide:



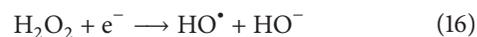
Hydrogen peroxide is also formed during interaction of hydroperoxide radicals and recombination of hydroxylic radicals:



Under the action of UV light, (<300 nm) hydrogen peroxide dissociates with the formation of hydroxylic radicals:



Hydrogen peroxide is an effective scavenger of photogenerated electrons:



As in the case of homogenous photocatalytic systems used in the water treatment technologies, in the heterogeneous photocatalytic reactions, hydroxylic, hydroperoxide, and peroxide radicals are the main highly effective oxidizing agents.

The photocatalytic process is performed by the direct oxidation of the substrate by the holes of TiO_2 on the surface of the latter's and by oxidation of the pollutant highly active oxygen radicals in the solution layer contiguous to TiO_2 [20, 21].

In addition to the above energy factors of the rate of the photocatalytic process substantially depends on the specific surface of a catalyst, the nature of surface active centers, the localization degree of photogenerated charges and other parameters of the system, which are determined by a crystalline structure, the synthesis method, and subsequent treatment of TiO_2 . Thanks to amphoteric properties of TiO_2 , the rate of a photoreaction depends also on the acid-base equilibrium in the system.

The designing of new highly effective photocatalytic system based on semiconductor materials is possible only with the account of thermodynamic, crystallochemical, and photo- and electrophysical properties of PC on a molecular cluster level [19].

An increase of photocatalytic activity of semiconductor materials is achieved by doping them with TM (Pt, Pd, Au, Ni, Cr, Mo, Nb, W, Mn, Fe, Ce, Co, etc.), by grafting to the surface of PC polymers and dyes, by the use of mixed double and triple metal-oxide systems, nanosized TiO_2 , and so forth.

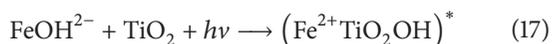
Nanodimensional particles of TiO_2 in combination with oxides and sulfides of other elements (Si, Ce, Zr, Nb, etc.) are incorporated in the composition of the series of composites that possess higher photocatalytic properties and thermal and chemical stability as compared with initial TiO_2 .

Sol-gel methods were developed for obtaining new nanostructural semiconductor composites based on silicate

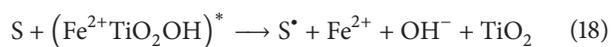
materials with incorporated nanoparticles of sulfides of silicon and zinc. A positive effect when using the above systems is determined by stabilization of electrons photogenerated in one of the component systems (e.g., CdS, ZnS, ZnSe, etc.) as a result of transition to a conductance zone of other component (e.g., TiO₂, ZnO, etc.). Activity of TiO₂ increases after its preliminary thermal treatment (400–700°C) and also when ultrasound affects the medium being radiated [22, 23].

The rate of oxidizing photodestruction of organic pollutants substantially increases with simultaneous use of the homogenous (in the presence of Fe³⁺, Cu²⁺, Ag⁺, Hg²⁺, Cr⁶⁺, Pt⁴⁺, Au³⁺ ions, etc.) and heterogenous catalysis [1]. As the oxidizer ORP increases from some threshold (−0.3 V) the degree of substrate decomposition increases [17].

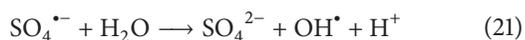
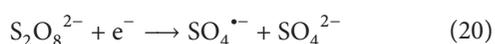
In result of phototransfer of charge in hydrocomplexes an excited cluster (Fe²⁺TiO₂OH) containing hydroxyl radical is formed, which thus provides sensibilization of the heterogeneous-homogenous catalytic system:



Organic radicals, generated as a result of the transfer of the radical state from the excited cluster to the substrate (S), participate in further oxidizing processes leading to the formation of the products (P) of their mineralization through an intermediate buildup in the system of hydroperoxides:



When oxidizers (H₂O₂, S₂O₈²⁻, ClO⁻, O₂, etc.) are introduced to the system, the rate of recombination of electron-hole pairs in PC decreases and additional channels for generating radicals from there:



Oxidation of substrate on the surface of PC goes on the two different mechanisms: that of Langmuir-Hinshelwood and that of Eley-Rideal. The Langmuir-Hinshelwood mechanism according to the process of substrate absorption on the PC surface is followed by its oxidation with holes. The photoreaction rate (ν) is proportional to the degree of binding the PA adsorption centers with the substrate, which depends on the concentration of the latter (Cs) and the constant of adsorption equilibrium (K):

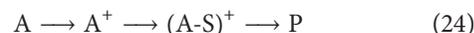
$$\nu = \frac{kKCs}{1 + KCs}, \quad (22)$$

where k is the constant of the photoreaction rate.

The product of substrate oxidation (S_{ads}⁺) is reduced with the electrons of the valence zone until the initial state or is transformed to reaction products:



According to the Eley-Rideal mechanism, oxidation is implemented through the initial stage of forming active centers (A⁺) as a result of capturing the holes with the defects of the catalyst surface (A) on which substrate chemisorption takes place:



Indirect oxidation is brought about during interaction of the substrate with hydroxylic radicals adsorbed and being in solution:



Adsorption properties of PC may be substantially increased by introducing it in the form of strutting off poles in the interlayer space of disperse aluminosilicates. The interlayer surface of the latter in most cases has a hydrophobic nature, which is conducive to adsorption and concentration of the substrate. A high degree of removing pollutants, especially at their low concentration, is achieved by TiO₂, impregnated into mesoporous zeolite with a high specific surface (>100 m²/g). The shift of spectral bands being observed in the spectra of TiO₂ fixed clays with the particles size <10 nm is determined by the quantum-size effect resulting in the increase of PC activity.

In photoreactors, using suspended TiO₂, the penetration depth of effective light in a great measure decreases due to absorption of radiation by the components of the medium. In addition, the use of the suspended PC in water treatment is linked with the necessity of its separation at the end of the technological cycle. The indicated drawbacks of the reactors of this type may be ruled out by using PC in the form of pallets or immobilized on various carriers (glass, ceramic, oxide metallic, fabric, etc.). Light penetration depth in the reactor increases when using a glass fiber as a carrier for TiO₂.

The efficiency of the photodestruction process may be increased also by using combined methods of water treatment according to which water is preliminary purified by filtering through membranes or photocatalytic decomposition of the pollutants precedes biological water treatment.

The vast majority of works devoted to the photocatalytic degradation of water pollutants here studied heterogeneous systems based on highly semiconductor PCs (mainly involving the dispersion of titanium dioxide). In practical terms, these systems are attractive because they can relatively easily achieve separation of the components, especially in the case of the PC supported on the stationary substrate.

Various physical and chemical factors (pH, the initial concentration of the oxygen pressure, the nature and amount of additives, the wavelength of the excitation light, etc.) have an impact on the efficiency of photocatalytic processes.

The maximum speed of the process achieved by the simultaneous presence of O₂ and H₂O₂; small additions of TM ions (Fe³⁺, Fe²⁺, Zn²⁺, Cu²⁺, etc.) increase the reaction rate. The highest speed of the process is observed in the presence of TiO₂ with doped zinc ions.

The efficiency of polycrystalline technical modification of titanium oxide (anatase) in DCPA destructive oxidation in

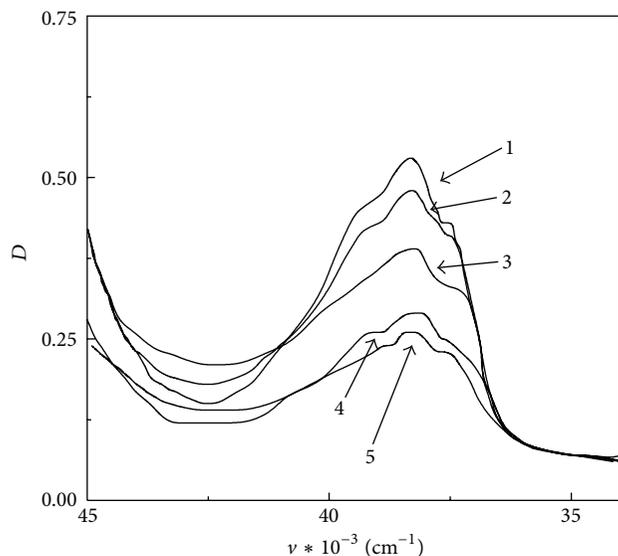


FIGURE 4: An effect of the photocatalyst (TiO_2) on the photolysis kinetics of CPB: 1—spectrum of the feed solution; 2—the same after irradiating by UV light in the absence of TiO_2 ; 3—the same by using the nonmodified TiO_2 ; 4 and 5—the TiO_2 samples alloyed by correspondingly iron and platinum.

aqueous media is commensurate with the reference sample Degussa P25.

Introduction TM ions TiO_2 lattice (Fe, Cr, Ce, Mo, Nb, Ni, Mn, etc.), in most cases, allows to increase the efficiency of photocatalytic process by increasing chemisorption of pollutants on the surface of the photocatalyst and the expansion of the range of the spectral sensitivity of the latter in the long wavelength region of the spectrum.

As shown in [1, 17], of the tested PC oxidative degradation (and recorded in the electronic spectrum of the products of its photolysis), DCPA is most effective in visible light polycrystalline technical modification of TiO_2 doped with iron.

It is known that photodegradation of chlorinated hydrocarbons in the water under the action of ultraviolet irradiation is slow. This process proceeds efficiently in the presence of titanium dioxide and platinumized titanium dioxide.

Doped with iron and platinum, TiO_2 has a higher photocatalytic activity than pure PC (Figure 4). In the investigated processes, which are hydroxyl radicals, photogenerated by photoinduced transfer of electron between the ion-modifier element and a water molecule or a hydroxyl ion play an important role [14].

Introduction of cerium ions in the columns of the titanium dioxide in the interlayer space of montmorillonite increases photocatalytic activity of TiO_2 -crosslinked decomposition of dichloromethane and 1,2-dichloroethane chlorinated methane and ethane [24]. As a result of photodegradation of these pollutants CO_2 , HCl, and lower carboxylic acids are formed.

Introduction of cerium ions in the columns of titania in the preparation of TiO_2 -fixed montmorillonite increases its

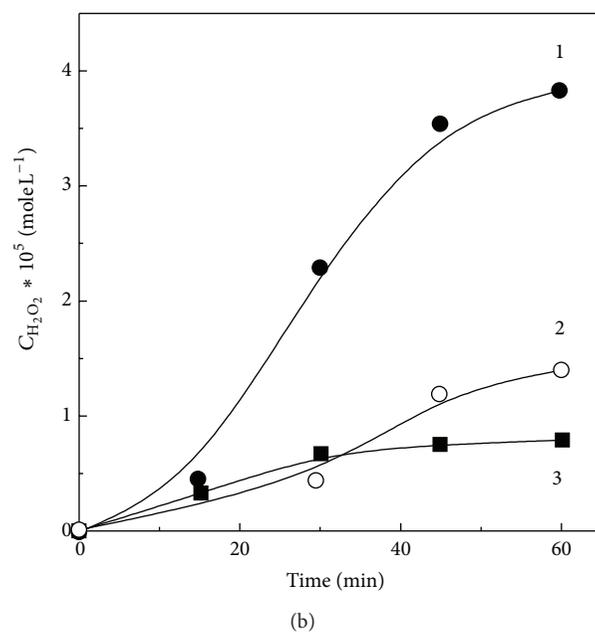
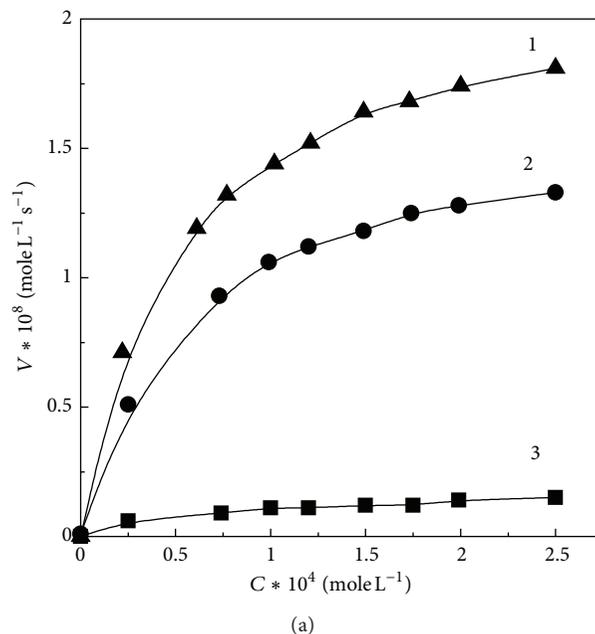


FIGURE 5: The dependence of the initial velocity (V) of DCPA photocatalytic oxidation by atmospheric oxygen on initial concentration of the DCPA (C) in the aqueous suspensions Fe_2O_3 (0,5 wt.%)— TiO_2 (1), TiO_2 (2), and Fe_2O_3 (3) a composite system based on in water (pH 4.5) (a); photo generation of H_2O_2 in aqueous suspension Fe_2O_3 (1 wt%)— TiO_2 , ($1 \text{ g } \mu\text{M}^{-3}$) in an oxygen atmosphere under UV light (high-pressure mercury UV lamp SVD-120, 380–400 nm) at pH: 1–6.0; 2–3.0; 3–9.0 (b).

photocatalytic activity, which allows intensifying photodestruction of dichloroethane in water and dichloromethane.

Composite based on the system Fe_2O_3 - TiO_2 has increased process ability as compared to the initial TiO_2 (Figure 5(a)). In this case, there is a symbiotic relationship between sorption and photocatalytic properties of PC. These

photocatalytic processes also involve generation of hydrogen peroxide by oxidation of water holes (Figure 5(b)).

4. Conclusions

The results of these studies and the literature data indicate a high efficiency of photocatalytic methods in the oxidative degradation of organic pollutants in aquatic environments. The paper discusses the basic laws of the oxidative degradation of organic compounds of different classes with the use of homogeneous and heterogeneous photocatalytic systems with a view of their complete mineralization.

The comparative evaluation of different methods of chemical modification of semiconductor catalysts in terms of improving the efficiency of their use in industrial water treatment schemes and ways to improve the efficiency of oxidative destructive process by establishing composite photocatalytic materials are submitted.

References

- [1] V. V. Goncharuk, *Environmental Aspects of Modern Technologies Protect the Aquatic Environment*, Naukova Dumka, Kiev, Ukraine, 2005.
- [2] V. V. Goncharuk, N. M. Soboleva, and A. A. Nosonovich, "Physico-chemical aspects of soil contamination with heavy metals and hydrosphere," *Khimiya V Interesakh Ustoichivogo Razvitiya*, vol. 11, no. 6, pp. 795–809, 2003.
- [3] N. M. Soboleva, M. N. Saprykina, V. N. Kosinova, A. A. Nosonovich, and V. V. Goncharuk, "Inactivation of *Candida albicans* in the photo-fenton system," *Journal of Water Chemistry and Technology*, vol. 34, pp. 96–102, 2012.
- [4] V. V. Goncharuk, V. F. Vakulenko, T. N. Sitnichenko, O. Yu. Shvadchina, and A. N. Sova6, "Photocatalytic destruction of fulvic acids by ozone and oxygen," *Journal of Water Chemistry and Technology*, vol. 35, pp. 62–70, 2013.
- [5] E. G. Solozhenko, N. M. Soboleva, and V. V. Goncharuk, "Using of H_2O_2 - Fe^{2+} (Fe^{3+}) catalytic system in wastewater treatment," *Journal of Water Chemistry and Technology*, vol. 26, no. 3, pp. 1–16, 2004.
- [6] E. G. Solozhenko, N. M. Soboleva, and V. V. Goncharuk, "Decolourization of azodye solutions by Fenton's oxidation," *Water Research*, vol. 29, no. 9, pp. 2206–2210, 1995.
- [7] I. V. Stolyarova, I. B. Kovban', R. V. Prihod'ko, A. O. Kushko, M. V. Sychev, and V. V. Goncharuk, "Relationship between the catalytic behavior of FeZSM-5 zeolites in oxidative degradation of dyes and the nature of their active centers," *Russian Journal of Applied Chemistry*, vol. 80, no. 5, pp. 746–753, 2007.
- [8] M. Dükkançi, G. Gündüz, S. Yilmaz, and R. V. Prihod'ko, "Heterogeneous Fenton-like degradation of Rhodamine 6G in water using CuFeZSM-5 zeolite catalyst prepared by hydrothermal synthesis," *Journal of Hazardous Materials*, vol. 181, no. 1–3, pp. 343–350, 2010.
- [9] R. Prihod'ko, I. Stolyarova, G. Gündüz et al., "Fe-exchanged zeolites as materials for catalytic wet peroxide oxidation. Degradation of Rodamine G dye," *Applied Catalysis B*, vol. 104, no. 1–2, pp. 201–210, 2011.
- [10] C. H. M. Hofman-Caris, D. J. H. Harmsen, and E. F. Beerendonk, "Degradation of priority compounds by UV and UVoxidation," *Advanced Oxidation Processes*, TECHNIAU, 2003.
- [11] I. Arslan and I. A. Balcioglu, "Degradation of commercial reactive dyestuffs by heterogenous and homogenous advanced oxidation processes: a comparative study," *Dyes and Pigments*, vol. 43, no. 2, pp. 95–108, 1999.
- [12] A. A. Nosonovich, N. M. Soboleva, and V. V. Goncharuk, "Generation of hydrogen peroxide in oxidative degradation process of the organic compounds," *Journal of Water Chemistry and Technology*, vol. 33, no. 5, pp. 465–476, 2011.
- [13] V. V. Goncharuk, N. M. Soboleva, and A. A. Nosonovich, "Photooxidative destruction of organic compounds by hydrogen peroxide in water," *Journal of Water Chemistry and Technology*, vol. 33, no. 5, pp. 456–476, 2010.
- [14] A. A. Nosonovich, N. M. Soboleva, and V. V. Goncharuk, "Photodestructive oxidation of cetylpyridinium bromide in water," *Khimiya i Tekhnologiya Vody*, vol. 17, no. 5, pp. 451–456, 1995.
- [15] V. V. Goncharuk, "Photooxidation degradation of the organic compounds in water," *Khimiya V Interesakh Ustoichivogo Razvitiya*, vol. 4, no. 5, pp. 345–355, 1997.
- [16] J.-M. Herrmann, "Heterogeneous photocatalysis: state of the art and present applications," in *Topics in Catalysis*, vol. 34, pp. 149–465, 2005.
- [17] N. M. Soboleva, A. A. Nosovich, and V. V. Goncharuk, "The heterogenic photocatalysis in water treatment processes," *Journal of Water Chemistry and Technology*, vol. 29, no. 2, pp. 72–89, 2007.
- [18] U. I. Gaya and A. H. Abdullah, "Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamentals, progress and problems," *Journal of Photochemistry and Photobiology C*, vol. 9, no. 1, pp. 1–12, 2008.
- [19] A. L. Stroyuk, A. I. Kryukov, S. Y. Kuchmii, and V. D. Pokhodenko, "Quantum size effects in semiconductor photocatalysis," *Theoretical and Experimental Chemistry*, vol. 41, no. 4, pp. 207–228, 2005.
- [20] N. Serpone and A. V. Emeline, "Suggested terms and definitions in photocatalysis and radiocatalysis," *International Journal of Photoenergy*, vol. 4, no. 3, pp. 93–131, 2002.
- [21] A. Mitsionis, T. Vaimakis, C. Trapalis, N. Todorova, D. Bahnemann, and R. Dillert, "Hydroxyapatite/titanium dioxide nanocomposites for controlled photocatalytic NO oxidation," *Applied Catalysis B*, vol. 106, no. 3–4, pp. 398–404, 2011.
- [22] J. Peller, O. Wiest, and P. V. Kamat, "Synergy of combining sonolysis and photocatalysis in the degradation and mineralization of chlorinated aromatic compounds," *Environmental Science and Technology*, vol. 37, no. 9, pp. 1926–1932, 2003.
- [23] E. Selli, C. L. Bianchi, C. Pirola, G. Cappelletti, and V. Ragaini, "Efficiency of 1,4-dichlorobenzene degradation in water under photolysis, photocatalysis on TiO_2 and sonolysis," *Journal of Hazardous Materials*, vol. 153, no. 3, pp. 1136–1141, 2008.
- [24] M. Giah, S. Habibi, S. Toutounchi, and M. Khavei, "Photocatalytic degradation of anionic surfactant using zinc oxide nanoparticles," *Russian Journal of Physical Chemistry A*, vol. 86, no. 4, pp. 689–693, 2012.

Research Article

Fenton-Like Oxidation of Malachite Green Solutions: Kinetic and Thermodynamic Study

Saeedeh Hashemian

Chemistry Department, Islamic Azad University, Yazd Branch, P. O. Box 89195/155, Yazd, Iran

Correspondence should be addressed to Saeedeh Hashemian; sa_hashemian@yahoo.com

Received 25 May 2013; Revised 19 June 2013; Accepted 25 June 2013

Academic Editor: Oleksandr A. Loboda

Copyright © 2013 Saeedeh Hashemian. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Oxidation by Fenton-like ($\text{Fe}^{3+}/\text{H}_2\text{O}_2$) reactions is proven to be an economically feasible process for destruction of a variety of hazardous pollutants in wastewater. In this study, the degradation and mineralization of malachite green dye are reported using Fenton-like reaction. The effects of different parameters like pH of the solution, the initial concentrations of Fe^{3+} , H_2O_2 , and dye, temperature, and added electrolytes (Cl^- and SO_4^{2-}) on the oxidation of the dye were investigated. Optimized condition was determined. The efficiency of 95.5% degradation of MAG after 15 minutes of reaction at pH 3 was obtained. TOC removal indicates partial and insignificant mineralization of malachite green dye. The results of experiments showed that degradation of malachite green dye in Fenton-like oxidation process can be described with a pseudo-second-order kinetic model. The thermodynamic constants of the Fenton oxidation process were evaluated. The results implied that the oxidation process was feasible, spontaneous, and endothermic. The results will be useful for designing the treatment systems of various dye-containing wastewaters.

1. Introduction

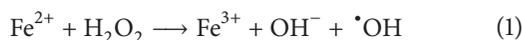
Dyes in wastewater are of particular environmental concern since they not only give an undesirable color to the waters but also in some cases are harmful compounds and can originate dangerous by-products through oxidation, hydrolysis, or other chemical reactions taking place in the waste phase. Environmental research has paid special attention to dye compounds because of the extensive environmental contamination arising from dyeing operations. Various attempts have been made for the removal of dyes from water and wastewater. There are several methods applicable for the reclamation of dyeing wastewaters [1, 2]. Commonly applied treatment methods for color removal from dye-contaminated effluents consist of various processes involving biological, physical and chemical decolorization methods. The biological treatment is not a complete solution to the problem due to biological resistance of some dyes [3]. The traditional treatment techniques were applied in wastewaters, such as ozonation [4], membrane [5], oxidation [6, 7], photochemical [8], and adsorption [9–13]. Various Fenton processes were used for oxidation of dyes. Homogenous Fenton reaction ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) is one of the most important processes to

generate hydroxyl radicals $\cdot\text{OH}$ [14–16]. These processes are involved in the generation of highly reactive radicals (especially hydroxyl radicals) in enough quantity to affect water purification, and their use is justified by the low organic content of the wastewaters to be treated. They have low reaction temperatures and thus require the presence of very active oxidation agents. In particular, the oxidation using Fenton's reagent has proved to be a promising and attractive treatment method for the effective destruction of a large number of hazardous and organic pollutants [17–21].

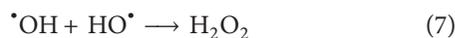
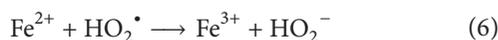
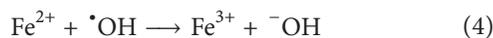
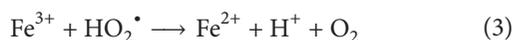
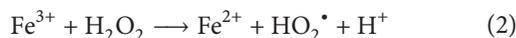
The Fenton process completely destroys contaminants and breaks them down into harmless compounds, such as carbon dioxide, water, and inorganic salts. However, its applications are limited due to the generation of excessive amounts of ferric hydroxide sludge that requires additional separation process and disposal [22].

Malachite green is classified in the dyestuff industry as a triarylmethane dye. Malachite green (MAG) is usually used as a dye for materials such as silk, leather, and paper. Removal of malachite green by different methods such as oxidation [23], catalytic oxidation [24], electrooxidation [25], and adsorption by agro-industry waste [26], peel [27], and solid agricultural waste [28, 29] was studied.

Fenton's reagent is a mixture of ferrous ion and hydrogen peroxide generating hydroxyl radical ($\cdot\text{OH}$) in situ according to the following equation:



Fe(III) can catalyze the decomposition of H_2O_2 . The reaction of H_2O_2 with Fe^{3+} (the so-called Fenton's-like reagent) goes through the formation of hydroperoxyl radical $\text{HO}_2\cdot$ [30]:



The specific objectives of this study are the investigation of removal efficiencies of malachite green (MAG) by Fenton-like process. Important variables such as oxidation time, effect of pH, dosages of H_2O_2 , and ferrous ions were examined. The kinetics and thermodynamic of process also were determined.

2. Experimental

2.1. Material and Methods. The basic dye, MAG, has molecular formula $\text{C}_{23}\text{H}_{25}\text{ClN}_2$ and molar mass 364.911 g/mol with λ_{max} 620 nm and was used as received without further purification to prepare simulated wastewater. 5.0×10^{-3} stock solution of MAG was prepared, and working solutions are prepared by the dilution. Experimental solutions of the desired concentration were obtained by successive dilutions. The chemical structure of malachite green (4-[(4-dimethylaminophenyl)phenyl-methyl]-N,N-dimethylaniline) is shown in Figure 1.

All the reagents used in the experiments were in analytical grade (Merck) and were used without further purification. All the experiments were conducted at room temperature. The dye oxidation was achieved by Fenton-like reagent which was composed of a mixture of $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ and H_2O_2 (30%). The necessary quantities of Fe^{3+} and H_2O_2 were added simultaneously in the dye solution. All experiments were conducted in a 500 mL thermostated batch glass reactor equipped with the magnetic stirrer. The kinetics of oxidation was followed by taking samples at regular time interval.

The residual concentration of the MAG in the solution at different times of sampling was determined. The residual concentration of the dye was deduced from the calibration curves which were produced at wavelength corresponding to the maximum of absorbance (620 nm) on an UV-visible spectrophotometer apparatus (Shimadzu 160 A). The cells used were in quartz 1 cm thick. The discoloration efficiency

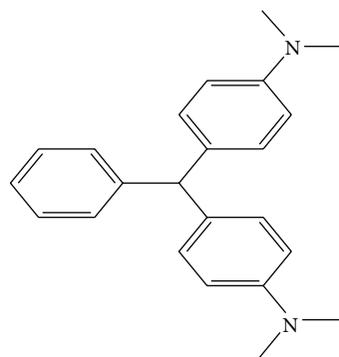


FIGURE 1: Chemical structure of malachite green (MAG).

of the dye (X) with respect to its initial concentration is calculated as

$$\%X = ([\text{MAG}]_0 - [\text{MAG}] / [\text{MAG}]_0) \times 100, \quad (8)$$

where $[\text{MAG}]_0$ and $[\text{MAG}]$ are the initial and appropriate concentrations of dye at any reaction time t , respectively.

3. Results and Discussion

3.1. Effect of pH on Decolorization. pH has a major effect on the efficiency of MAG treatment. The oxidation was done for 120 min under controlled pH condition with constant dose of Fe^{3+} (1.0×10^{-4} M) and H_2O_2 (5×10^{-2} M). The effect of pH on the removal of malachite green using 50 mg L^{-1} of dye was studied. The oxidation of MAG as a function of pH is shown in Figure 2. It is evident that change in the pH of the solution to Fenton-like value of 3 leads to increases in the extent of MAG oxidation. It is apparent from that extent of decolorization decreases with increase in pH, and at pH 3.0 almost >95% color removal was observed. Therefore, the results demonstrate that the pH value for the most effective oxidation of MAG is approximately 3. The decrease in oxidation rate at pH > 3 could be explained by the formation of $\text{Fe}(\text{OH})_3$, which has lower catalytic activity in the decomposition of H_2O_2 [30]. The low activity detected for high pH has been reported, and the results closely agreed with those in the literature [19, 30–32].

3.2. Effect of Fe^{3+} Ferrous Dosage. The concentration of Fe^{3+} is one of the critical parameters in Fenton processes. In the present study, the influence of different iron concentrations ($\text{Fe}^{3+} = 1.0 \times 10^{-6}$ – 1.0×10^{-3} M) expressed as MAG removal is illustrated in Figure 3. The concentration of hydrogen peroxide is fixed as 0.05 M, and MAG concentration is 3.0×10^{-5} M. It can be seen from results that MAG degradation increased with increasing Fe^{3+} concentrations. This is due to the fact that Fe^{3+} plays a very important role in the decompositions of H_2O_2 to generate the $\cdot\text{OH}$ in the Fenton process. The lower degradation capacity of Fe^{3+} at small concentration is probably due to the lowest $\cdot\text{OH}$ radicals producing a variable for oxidation [16, 19], for higher concentration of Fe^{3+} oxidation of dye will decrease. This can be explained by

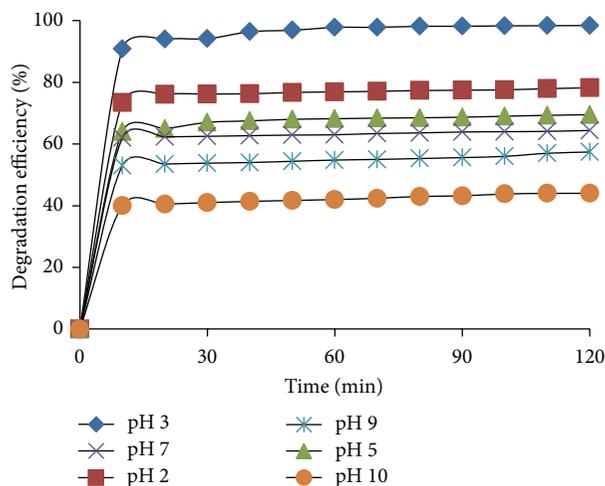


FIGURE 2: Effect of pH on the discoloration efficiency for Fenton-like oxidation process, ($[\text{Fe}^{3+}] = 1.0 \times 10^{-4} \text{ M}$, $[\text{H}_2\text{O}_2] = 5.0 \times 10^{-2} \text{ M}$, $[\text{MAG}] = 3.0 \times 10^{-5} \text{ M}$).

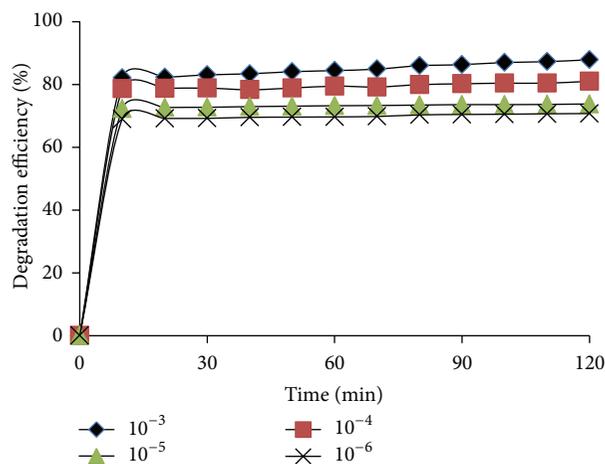


FIGURE 3: Effect of Fe^{3+} concentration on the discoloration efficiency for Fenton-like oxidation process, ($[\text{H}_2\text{O}_2] = 5.0 \times 10^{-2}$, $[\text{MAG}] = 3.0 \times 10^{-5} \text{ M}$).

the fact that, when the concentrations of Fe^{3+} are high, can react with the HO_2^\bullet and finally reduce consumed the very reactive $^\bullet\text{OH}$ radical according to (3).

3.3. Effect of H_2O_2 Concentration. H_2O_2 plays the role of an oxidizing agent in this process. The selection of an optimal H_2O_2 concentration for the decolorization of MAG is important from practical point of view due to the cost of H_2O_2 [33].

Oxidation of dyes by Fenton and Fenton-like process is carried out by $^\bullet\text{OH}$ radicals that are directly produced from the reaction between H_2O_2 , Fe^{2+} , and Fe^{3+} . To determine the concentration of H_2O_2 giving the maximum MAG discoloration efficiency, experiments were conducted, and results obtained are represented in Figure 4. The discoloration efficiency according to time for different concentrations of

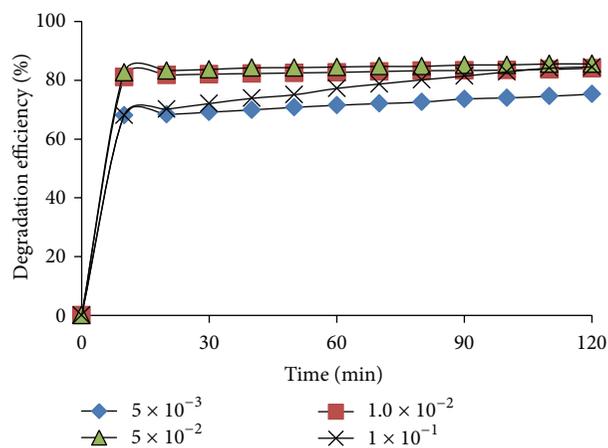


FIGURE 4: Effect of H_2O_2 concentration on the discoloration efficiency for Fenton-like oxidation process ($[\text{MAG}] = 3.0 \times 10^{-5} \text{ M}$, $[\text{Fe}^{3+}] = 1.0 \times 10^{-4}$).

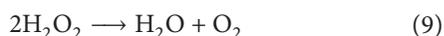
H_2O_2 shows that the dye degradation yield increases with increasing concentration of H_2O_2 . For the oxidation process, the addition of H_2O_2 from 5.0×10^{-3} – $1.0 \times 10^{-1} \text{ M}$ increases the decolorization from 68 to 95% at 10 min. The increase in the decolorization is due to the increase in hydroxyl radical concentration by addition of H_2O_2 [17]. However at higher H_2O_2 concentration, efficiency of dye removal showed no significant efficiency, which is due to recombination of hydroxyl radicals, and scavenging the OH radicals will occur, which can be expressed by (2), (5), and (6).

3.4. Effect of Relation $[\text{Fe}^{3+}]/[\text{H}_2\text{O}_2]$. The main process variables affecting the rate of a Fenton-like reaction are the molar concentrations of the oxidant (H_2O_2) and catalyst (Fe^{3+}), particularly the $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ molar ratio. Therefore, color removal as a function of the initial molar ratio of $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ was investigated. The different ratios of $[\text{Fe}^{3+}]/[\text{H}_2\text{O}_2]$ 1–400 are reported from the literature. The experimental results showed that the optimum $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ molar ratio for the removal of MAG was 1:50 [19, 34]. The reaction of Fe^{3+} with H_2O_2 leads to the formation of Fe^{2+} ions, which can further react with H_2O_2 to produce OH radical. Therefore, a low Fe^{3+} concentration decreases MAG degradation. MAG removal actually ceased when the $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ molar ratio increased from 1:50 to 1:500 for 1 mM Fe^{3+} , indicating that H_2O_2 was overdosed when its concentration rose tenfold. In the presence of 50 mM of H_2O_2 , the ionic liquid is probably eliminated solely by the reaction with $^\bullet\text{OH}$, but at 500 mM; as it is expected, most of the H_2O_2 dosage applied was consumed in the first stage of the fast reaction. The oxidation of ionic liquids was done not only by reaction with $^\bullet\text{OH}$ radicals but also by other radical species generated in vigorous $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ reactions such as FeO^{3+} [35] and $\text{Fe}^{3+}\text{HO}_2^{2+}$ [30] which then decrease.

3.5. Effect of Dye Concentration. The efficiency of the Fenton-like process as a function of initial concentration of dye was

evaluated. Figure 5 shows the changes of MAG concentration with the reaction time. The results indicated that decolorization efficiency increased when the initial dye concentration increased. Concentration plays a very important role in reactions according to the collision theory of chemical reactions. Two reactants were in a closed container. All the molecules contained within are colliding constantly. By increasing the concentration of one or more reactants, the frequency of collisions between reactant molecules is increased, and the frequency of effective collisions that causes a reaction to occur will also be high. The lifetime of hydroxyl radicals is very short (only a few nanoseconds), and they can only react where they are formed; therefore, as increasing the quantity of dye molecules per volume unit logically enhances the probability of collision between organic matter and oxidizing species, leading to an increase in the decolorization efficiency [36].

3.6. Effect of Temperature. The influence of reaction temperature on the decolorization efficiency of MAG was investigated by varying temperature from 20°C to 70°C. Temperature is critical to the reaction rate, product yield, and distribution. The result is illustrated in Figure 6. It can be seen that raising the temperature has a positive impact on the decolorization of MAG. The decolorization efficiency within 10 min reaction increased from 78% to 95% as the different temperatures. This is due to the fact that higher temperature increased the reaction rate between hydrogen peroxide and the catalyst, thus increasing the rate of generation of oxidizing species such as $\cdot\text{OH}$ radical or high-valence iron species [34]. In addition, a higher temperature can provide more energy for the reactant molecules to overcome reaction activation energy [37]. Although the decolorization efficiency for $T = 30^\circ\text{C}$ is lower than those obtained at $T = 40^\circ\text{C}$, the values of dyes removal achieved at 30°C might be considered satisfactory. At higher temperature, the efficiency of MAG oxidation decreases. This phenomenon may be due to the decomposition of H_2O_2 at the relatively high temperatures (9). This is consistent with results found in the literature [38]:



3.7. Mineralization Study. The complete mineralization of 1 mol MAG dye molecule implies the formation of the equivalent amount (23 moles) of CO_2 at the end of the treatment. However, the depletion in TOC (shown in Figure 7) clearly indicates that the reaction does not go to completion. Extent of mineralization of the dye by Fenton-like process can be evaluated by measuring Total Organic Carbon (TOC). To determine the change in the TOC of reaction medium, initial TOC (pure dye solution) and the TOC of a sample at different intervals during the reaction were measured. TOC reduction was determined as follows:

$$\text{TOC}_{\text{removal}} = \frac{1 - \text{TOC}_t}{\text{TOC}_0} \times 100, \quad (10)$$

where TOC_t and TOC_0 (mg L^{-1}) are values at time (t) and at time (0), respectively. 70% TOC reduction is achieved for MAG dye in 30 min. In fact, after 30 min of reaction,

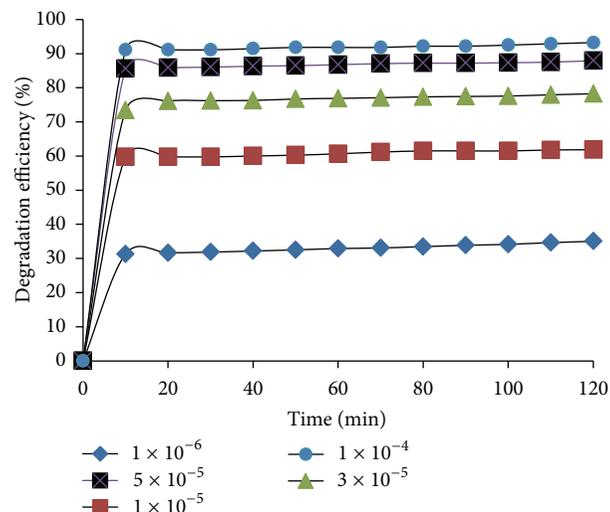


FIGURE 5: Effect of MAG concentration on the discoloration efficiency for Fenton-like oxidation process.

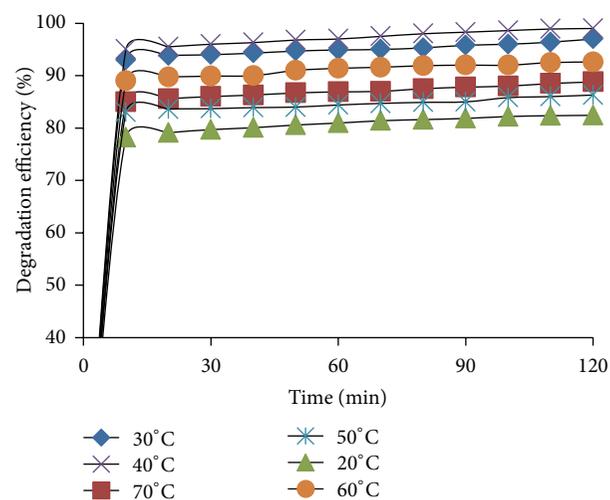


FIGURE 6: Effect of temperature on the discoloration efficiency for Fenton-like oxidation process.

about 70% of the initial organic carbon had been transformed into CO_2 , which implied the existence of other organic compounds in the solution and the partial mineralization of dyes [39, 40].

3.8. Effect of Cl^- and SO_4^{2-} on Fenton Effectiveness. Cl^- and SO_4^{2-} are common coexisting anions with dyes in wastewater; therefore, the effect of Cl^- and SO_4^{2-} ions on MAG removal by Fenton-like process was investigated. It was found that the presence of Cl^- at the concentration range of $0\text{--}0.1 \text{ mol L}^{-1}$ did not have a significant effect on removing MAG. The effect of SO_4^{2-} on the removal of MAG was significant at the concentration range of $0\text{--}0.1 \text{ mol L}^{-1}$. The removal of MAG decreased at a concentration of 0.02 mol L^{-1}

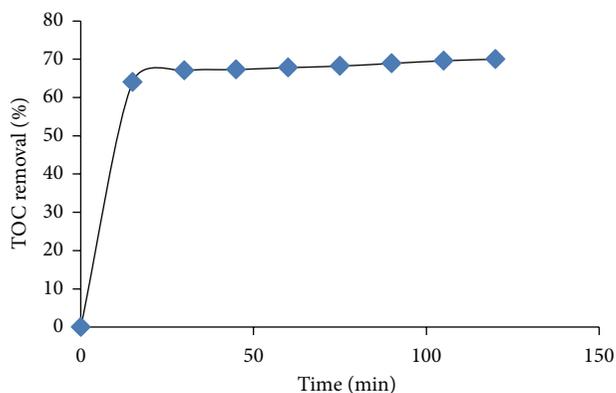


FIGURE 7: TOC removal for MAG dye by Fenton-like oxidation process.

of SO_4^{2-} . The removal of MAG decreased to 45% for concentration of 0.02 mol L^{-1} of SO_4^{2-} .

3.9. Kinetic of Fenton Reaction. The general elementary rate law for reaction of a target organic compound (MAG) can be written as follows:

$$\frac{-dC_{\text{MAG}}}{dt} = k_{\text{HO}}k_{\text{OH}}k_{\text{RH}} + \sum K_{\text{oxi}}C_{\text{oxi}}C_{\text{RH}}, \quad (11)$$

where oxi represents oxidants other than $\cdot\text{OH}$ that may be present, such as ferryl, hydroxyl radical which is usually regarded as the sole or most important reactive species. Then

$$\frac{-dC_{\text{MAG}}}{dt} = k_{\text{HO}}k_{\text{OH}}k_{\text{MAG}}. \quad (12)$$

And, by integration, the rate law of first-order reaction can be written as follows:

$$\ln C_{\text{MAG}} = \ln C_{(\text{MAG})0} - k_{\text{app}}t, \quad (13)$$

where C_{MAG} and $C_{(\text{MAG})0}$ are initial concentration of MAG and concentration of MAG at any time. A plot of $\ln C_{\text{MAG}}$ versus time generated a straight line with a negative slope. The slope of this line corresponds to the apparent rate constant value for the degradation of the organic target compound. In our case, we follow the rate of decolorization of the MAG dye. Consequently, (13) was converted to

$$\frac{\ln C_{\text{MAG}}}{\ln C_{(\text{MAG})0}} = -k_{\text{app}}t. \quad (14)$$

Figure 8 shows the plot of first-order Fenton reaction. Rate law of the second-order reaction can be written as follows:

$$\frac{1}{[C_{\text{MAG}}]} - \frac{1}{[C_{(\text{MAG})0}]} = kt. \quad (15)$$

The plot of $1/[C]$ against k shows the rate constant of second-order Fenton reaction (Figure 9). The results from R^2 of Figures 8 and 9 show that the kinetic of Fenton-like reaction for degradation of MAG was second-order reaction [41].

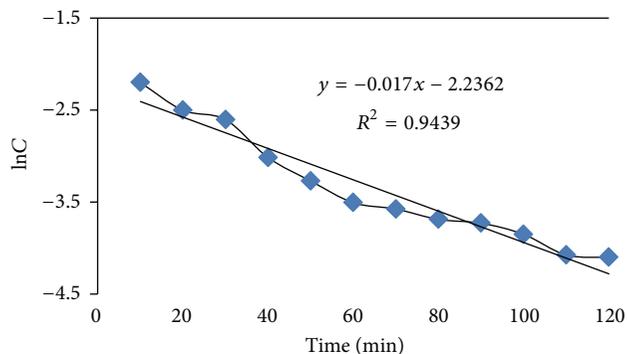


FIGURE 8: Pseudo-first-order model for Fenton-like oxidation of MAG.

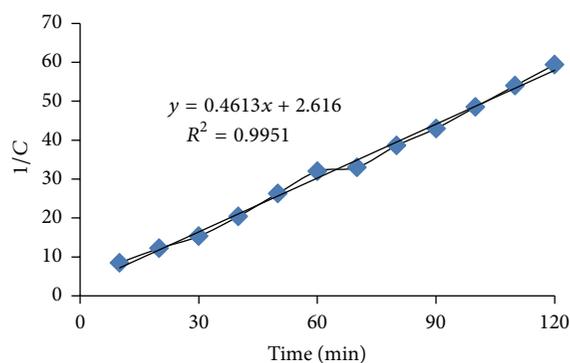


FIGURE 9: Pseudo-second-order model for Fenton-like oxidation of MAG.

3.10. Thermodynamic of Fenton Reaction. Thermodynamic parameters including Gibbs free energy ΔG° , standard enthalpy ΔH° , and standard entropy ΔS° are the parameters to better understand the temperature effect on degradation of dye which was studied. Gibbs free energy ΔG° by using equilibrium constant K_C is calculated:

$$\Delta G^\circ = -RT \ln K_C. \quad (16)$$

K_C value is calculated from the following formula:

$$K_C = \frac{C_{\text{Ae}}}{C_{\text{Se}}}. \quad (17)$$

C_{Ae} is amount of degradation dye at equilibrium and C_{Se} equilibrium concentration of dye at the solution.

Standard enthalpy ΔH° and standard entropy ΔS° are as van't Hoff equation:

$$\ln K_C = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}. \quad (18)$$

In this equation R is the gas constant equal to the public ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). The amounts of degradation dye at equilibrium at different temperatures $25\text{--}55^\circ\text{C}$ have been examined to obtain thermodynamic parameters for Fenton-like reaction of MAG. ΔH° and ΔS° were calculated as the slope and intercept of van't Hoff plots of $\ln K_C$ versus

TABLE 1: Thermodynamic parameters for Fenton oxidation of MAG ([MAG] = 3.0×10^{-5} M, $[\text{Fe}^{3+}] = 1.0 \times 10^{-4}$ M, $[\text{H}_2\text{O}_2] = 5.0 \times 10^{-2}$ M).

ΔS° ($\text{J mol}^{-1}\text{k}^{-1}$)	ΔH° (J mol^{-1})	ΔG° (KJ mol^{-1})	K_C	T (K)	
43.2823	9.610	-3.255	3.80	293	Fenton like oxidation
		-3.408	3.870	303	
		-4.213	4.80	323	
		-5.680	7.33	333	

$1/T$. The results of thermodynamic parameters are given in Table 1. As observed in Table 1, negative value of ΔG° at different temperatures shows the oxidation process to be spontaneous. The ΔH° positive value indicates that the uptake is endothermic [42].

4. Conclusion

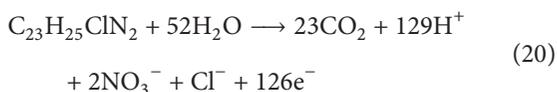
The results of Fenton-like oxidation process of MAG showed the following.

- (1) The optimal parameters for Fenton-like process are

$$[\text{MAG}] = 3 \times 10^{-5} \text{ M}, \quad [\text{Fe}^{3+}] = 1.0 \times 10^{-3} \text{ M}, \quad (19)$$

$$[\text{H}_2\text{O}_2] = 5 \times 10^{-2} \text{ M}, \quad \text{pH} = 3.$$

- (2) Fenton-like process not only completes decolorization of MAG dye (95%) but also mineralizes it (70%).
- (3) The oxidation process of MAG follows pseudo-second-order kinetic model.
- (4) The negative values of ΔG° and positive value of ΔH° obtained indicated that the MAG dye oxidation by Fenton reaction processes is spontaneous and endothermic.
- (5) The overall equation of MAG degradation and production of carbon dioxide and nitrate ion is as follows:



References

- [1] A. Wang, J. Qu, J. Ru, H. Liu, and J. Ge, "Mineralization of an azo dye Acid Red 14 by electro-Fenton's reagent using an activated carbon fiber cathode," *Dyes and Pigments*, vol. 65, no. 3, pp. 227–233, 2005.
- [2] J. Pierce, "Colour in textile effluents—the origins of the problem," *Journal of the Society of Dyers & Colourists*, vol. 110, no. 4, pp. 131–133, 1994.
- [3] C. Galindo, P. Jacques, and A. Kalt, "Photochemical and photocatalytic degradation of an indigoid dye: a case study of acid blue 74 (AB74)," *Journal of Photochemistry and Photobiology A*, vol. 141, no. 1, pp. 47–56, 2001.
- [4] M. Muthukumar and N. Selvakumar, "Studies on the effect of inorganic salts on decolouration of acid dye effluents by ozonation," *Dyes and Pigments*, vol. 62, no. 3, pp. 221–228, 2004.
- [5] R. Sabry, A. Hafez, M. Khedr, and A. El-Hassanin, "Removal of lead by an emulsion liquid membrane. Part I," *Desalination*, vol. 212, no. 1–3, pp. 165–175, 2007.
- [6] P. K. Malik and S. K. Saha, "Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst," *Separation and Purification Technology*, vol. 31, no. 3, pp. 241–250, 2003.
- [7] E. E. Ebrahiem, M. N. Al-Maghrabi, and A. R. Mobarki, "Removal of organic pollutants from industrial wastewater by applying photo-Fenton oxidation technology," *Arabian Journal of Chemistry*. In press.
- [8] I. Fatimah, S. Wang, and D. Wulandari, "ZnO/montmorillonite for photocatalytic and photochemical degradation of methylene blue," *Applied Clay Science*, vol. 53, no. 4, pp. 553–560, 2011.
- [9] S. Hashemian, "MnFe₂O₄/bentonite nano composite as a novel magnetic material for adsorption of acid red 138," *African Journal of Biotechnology*, vol. 9, no. 50, pp. 8667–8671, 2010.
- [10] S. Hashemian, "Removal of acid red 151 from water by adsorption onto nano-composite MnFe₂O₄/kaolin," *Main Group Chemistry*, vol. 10, no. 2, pp. 105–114, 2011.
- [11] S. Hashemian, "Study of adsorption of acid dye from aqueous solutions using bentonite," *Main Group Chemistry*, vol. 6, pp. 97–107, 2007.
- [12] S. Hashemian and M. Salimi, "Nano composite a potential low cost adsorbent for removal of cyanine acid," *Chemical Engineering Journal*, vol. 188, pp. 57–63, 2012.
- [13] S. Hashemian and M. Mirshamsi, "Kinetic and thermodynamic of adsorption of 2-picoline by sawdust from aqueous solution," *Journal of Industrial and Engineering Chemistry*, vol. 1, pp. 2010–2015, 2012.
- [14] A. R. Khataee, V. Vatanpour, and A. R. Amani Ghadim, "Decolorization of C.I. Acid Blue 9 solution by UV/Nano-TiO₂, Fenton, Fenton-like, electro-Fenton and electrocoagulation processes: a comparative study," *Journal of Hazardous Materials*, vol. 161, no. 2–3, pp. 1225–1233, 2009.
- [15] J. Ma, W. Song, C. Chen, W. Ma, J. Zhao, and Y. Tang, "Fenton degradation of organic compounds promoted by dyes under visible irradiation," *Environmental Science and Technology*, vol. 39, no. 15, pp. 5810–5815, 2005.
- [16] F. Chen, W. Ma, J. He, and J. Zhao, "Fenton degradation of malachite green catalyzed by aromatic additives," *Journal of Physical Chemistry A*, vol. 106, no. 41, pp. 9485–9490, 2002.
- [17] M. S. Lucas and J. A. Peres, "Decolorization of the azo dye reactive black 5 by Fenton and Photo-Fenton oxidation," *Dyes and Pigments*, vol. 71, no. 3, pp. 236–244, 2006.
- [18] W.-P. Ting, M.-C. Lu, and Y.-H. Huang, "Kinetics of 2,6-dimethylaniline degradation by electro-Fenton process," *Journal of Hazardous Materials*, vol. 161, no. 2–3, pp. 1484–1490, 2009.
- [19] H.-J. Fan, S.-T. Huang, W.-H. Chung, J.-L. Jan, W.-Y. Lin, and C.-C. Chen, "Degradation pathways of crystal violet by Fenton and Fenton-like systems: condition optimization and intermediate separation and identification," *Journal of Hazardous Materials*, vol. 171, no. 1–3, pp. 1032–1044, 2009.
- [20] E. Neyens and J. Baeyens, "A review of classic Fenton's peroxidation as an advanced oxidation technique," *Journal of Hazardous Materials*, vol. 98, no. 1–3, pp. 33–50, 2003.
- [21] C. Bouasla, M. E.-H. Samar, and F. Ismail, "Degradation of methyl violet 6B dye by the Fenton process," *Desalination*, vol. 254, no. 1–3, pp. 35–41, 2010.
- [22] N. Masomboon, C. Ratanatamskul, and M.-C. Lu, "Kinetics of 2,6-dimethylaniline oxidation by various Fenton processes," *Journal of Hazardous Materials*, vol. 192, no. 1, pp. 347–353, 2011.

- [23] M. H. Baek, C. O. Ijagbemi, and D. S. Kim, "Spectroscopic studies on the oxidative decomposition of malachite green using ozone," *Water Science and Technology*, vol. 62, no. 6, pp. 1304–1311, 2010.
- [24] H. Zheng, H. Zhang, X. Sun, P. Zhang, T. Tshukudu, and G. Zhu, "The catalytic oxidation of malachite green by the microwave-Fenton processes," *Dyes Pigments*, vol. 62, no. 1, pp. 1–10, 2004.
- [25] P. A. Soloman, C. A. Basha, M. Velan, and N. Balasubramanian, "Electro oxidation of malachite green and modeling using ANN," *Chemical and Biochemical Engineering Quarterly*, vol. 24, no. 4, pp. 445–452, 2010.
- [26] V. K. Garg, R. Kumar, and R. Gupta, "Removal of malachite green dye from aqueous solution by adsorption using agro-industry waste: a case study of Prosopis cineraria," *Dyes and Pigments*, vol. 62, no. 1, pp. 1–10, 2004.
- [27] T. Santhi and S. Manonmani, "Malachite green removal from aqueous solution by the peel of *Cucumis sativa* fruit," *Clean—Soil, Air, Water*, vol. 39, no. 2, pp. 162–170, 2011.
- [28] S. P. S. Syed, "Study of the removal of malachite green from aqueous solution by using solid agricultural waste," *Research Journal of Chemical Sciences*, vol. 881, no. 1, pp. 88–104, 2011.
- [29] G. H. Sonawanea and V. S. Shrivastava, "Kinetics of decolourization of malachite green from aqueous medium by maize cob (*Zea mays*): an agricultural solid waste," *Desalination*, vol. 250, pp. 94–105, 2009.
- [30] B. Ensing, F. Buda, and E. J. Baerends, "Fenton-like chemistry in water: oxidation catalysis by Fe(III) and H₂O₂," *Journal of Physical Chemistry A*, vol. 107, no. 30, pp. 5722–5731, 2003.
- [31] M. Neamtu, A. Yediler, I. Siminiceanu, and A. Kettrup, "Oxidation of commercial reactive azo dye aqueous solutions by the photo-Fenton and Fenton-like processes," *Journal of Photochemistry and Photobiology A*, vol. 161, no. 1, pp. 87–93, 2003.
- [32] M. Pérez, F. Torrades, X. Domènech, and J. Peral, "Fenton and photo-Fenton oxidation of textile effluents," *Water Research*, vol. 36, no. 11, pp. 2703–2710, 2002.
- [33] J.-H. Sun, S.-P. Sun, G.-L. Wang, and L.-P. Qiao, "Degradation of azo dye Amido black 10B in aqueous solution by Fenton oxidation process," *Dyes and Pigments*, vol. 74, no. 3, pp. 647–652, 2007.
- [34] D. R. de Souza, E. T. F. Mendonça Duarte, G. de Souza Girardi et al., "Study of kinetic parameters related to the degradation of an industrial effluent using Fenton-like reactions," *Journal of Photochemistry and Photobiology A*, vol. 179, no. 3, pp. 269–275, 2006.
- [35] M. L. Kremer, "Complex versus "Free Radical" mechanism for the catalytic decomposition of H₂O₂ by Fe³⁺," *International Journal of Chemical Kinetics*, vol. 17, pp. 1299–1314, 1985.
- [36] H. Hassan and B. H. Hameed, "Fenton-like oxidation of acid red 1 solutions using heterogeneous catalyst based on ball clay," *International Journal of Environmental Science*, vol. 2, no. 3, pp. 1–5, 2011.
- [37] H.-Y. Xu, M. Prasad, and Y. Liu, "Schorl: a novel catalyst in mineral-catalyzed Fenton-like system for dyeing wastewater discoloration," *Journal of Hazardous Materials*, vol. 165, no. 1–3, pp. 1186–1192, 2009.
- [38] G. R. Mahdavinia and R. Zhalebaghy, "Removal kinetic of cationic dye using poly (sodium acrylate)-carrageenan/Nanmontmorillonite nanocomposite superabsorbents," *Journal of Materials and Environmental Science*, vol. 3, no. 5, pp. 895–906, 2012.
- [39] S. Hashemian, M. Tabatabaee, and M. Gafari, "Fenton oxidation of methyl violet in aqueous solution," *Journal of Chemistry*, vol. 2013, Article ID 509097, 6 pages, 2013.
- [40] J. J. Pignatello, E. Oliveros, and A. MacKay, "Advanced oxidation processes for organic contaminant destruction based on the fenton reaction and related chemistry," *Critical Reviews in Environmental Science and Technology*, vol. 36, no. 1, pp. 1–84, 2006.
- [41] G. E. A. Mahmoud and L. F. M. Ismail, "Factors affecting the kinetic parameters related to the degradation of direct yellow 50 by Fenton and Photo-Fenton Processes," *Journal of Basic and Applied Chemistry*, vol. 1, no. 8, pp. 70–79, 2011.
- [42] L. Núñez, J. A. García-Hortal, and F. Torrades, "Study of kinetic parameters related to the decolourization and mineralization of reactive dyes from textile dyeing using Fenton and photo-Fenton processes," *Dyes and Pigments*, vol. 75, no. 3, pp. 647–652, 2007.