ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 1, pp. 321–332. © Pleiades Publishing, Ltd., 2015.
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Photodynamic Water Disinfection

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Received February 1, 2013

Abstract—The main features of photodynamic bacteria inactivation in aqueous media were determined. Pilot plant for producing portable water including photodynamic disinfection stage was designed, constructed and successfully tested on the Rublevsk water treatment station. The photodynamic water treatment under sunlight was applied for the remediation of surface water polluted by bacteria. Proflavine acetate, as disinfectant, is included into the State Registry by the Federal Service for Supervision of Consumer Rights Protection and Human Well-being and is recommended for disinfection of water reservoirs under emergency conditions.

DOI: 10.1134/S1070363215010466

INTRODUCTION

Widespread environmental pollution led to the deterioration of water quality of natural water sources by both the chemical and the microbiological parameters. Currently, the processes of chlorination and ozonation, as well as UV irradiation are used for water disinfection. At the same time, the development of new, environmentally friendly methods of disinfection of the water remains the urgent problem.

In 2002, the State Research Center NIOPIK with the support of Moscow Government initiated the development of a new water disinfection method based on the photodynamic effect.

It would seem that the goal may be achieved simply, i.e., by introducing a sensitizer into the water to cause formation of cytotoxic active oxygen forms under irradiation, because the efficiency of the photodynamic inactivation of microorganisms has been demonstrated by more than 100 years ago in Raab's study [1].

However, our first experiments with the use of Photosense (sulfonated aluminum phthalocyanine), a well-developed sensitizer for photodynamic therapy of cancer, failed. The development of a valid photodynamic method of water purification took many years of theoretical and experimental investigations of chemists, physicists, microbiologists and toxicologists.

The participants of the study were colleagues from the State Research Center "NIOPIK," Rublevsk water treatment station, Sysin Research Institute of Human Ecology and Environmental Hygiene, Lomonosov Moscow Institute of Fine Chemical Technology, Biocenter of the Lomonosov Moscow State University, Bach Institute of Biochemistry of the Russian Academy of Sciences, and those from other institutions. In our study, their participation is indicated in the corresponding sections of the text and in the references.

The Theoretical Background of the Photodynamic Water Disinfection

Figure 1 demonstrates a general mechanism of the photodynamic action of sensitizers [2]. The sensitizer molecule absorbs quantum of visible light to pass from the ground electronic state $^1S_0$ to the first singlet excited state $^1S_1$* and then relaxes into the ground state via the radiative (fluorescence F) or non-radiative internal conversion (IC) processes. The intersystem crossing (ISC) gives a relatively long-lived triplet excited state ^3S*, which can be deactivated via phosphorescence (P) and ISC, as well as via the interaction with other molecules by two main mechanisms (I and II).

According to the mechanism I, the sensitizer in the excited triplet state is involved into the transfer of the hydrogen atom (mechanism IA) or electron (mechanism IB) to form reactive radical ions of oxygen and substrate. The interaction of the sensitizer in the excited triplet state with molecular oxygen can result in the energy transfer to oxygen (mechanism II). In this case, reactive singlet oxygen $^1O_2$ is formed,

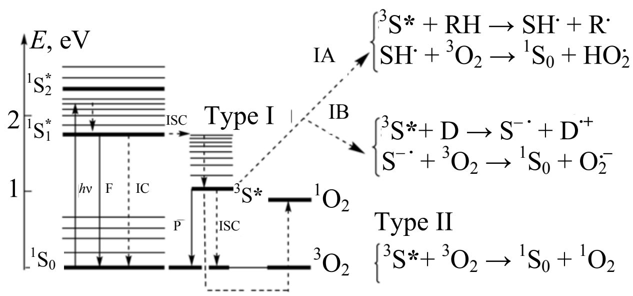


Fig. 1. The excitation and relaxation of the sensitizer S (Yablonski diagram). The generation of the active oxygen species with the excited sensitizer.

whereas the sensitizer passes into the ground state. The ground state of the oxygen molecule, $^3O_2$ triplet, is spin-forbidden and has low reactivity. The mechanism II, mediated by $^1O_2$, in the presence of oxygen is the basic mechanism of photodynamic action of the majority of sensitizers.

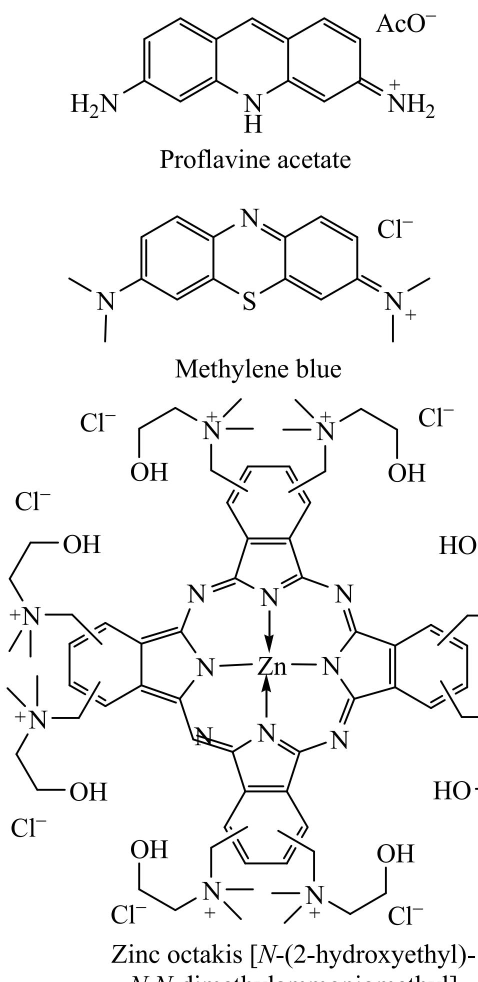


Fig. 2. The structure of the sensitizers.

Singlet oxygen is a rather strong oxidizing agent, substantially more reactive than triplet oxygen, it is able to oxidize important biochemical compounds, such as amino acids of proteins (methionine, histidine, tryptophan, etc.), nucleosides of nucleic acids, lipids, and polysaccharides leading to the loss of vital functions and cell death [3–6]. However, the lifetime of singlet oxygen in aqueous media is short (3.09±0.06 μs [7]), i.e., shorter by 1–2 orders of magnitude than in other solvents. Therefore, effective inactivation of microorganisms in water needs its affinity to a sensitizer. It was shown [8] that the sensitizers bind to bacteria by the electrostatic interaction [8]. The outer shell of most of bacteria at physiological pH values has a negative charge, which is mainly due to lipopolysaccharides constituting its outer layer [9]. It is therefore not only Gram-positive but also Gram-negative cells [10–13] are sensitized to visible light under the action of cationic dyes only, whereas anionic and neutral dyes do not possess this ability [12–15].

In this study, the cationic sensitizers, including the known dyes (methylene blue and proflavine), were used for photoinactivation of microorganisms. The structure of the sensitizers is given in Fig. 2. For photodynamic water disinfection the authors used proflavine acetate, a more water soluble compound than proflavine salts with inorganic anions, which was synthesized by the specially developed method. The study was performed at the laboratory of Prof. E.A. Lukyanets under the leadership of leading research worker V.I. Alekseeva.

Table 1. Indicators of photodynamic killing activity of photosensitizer $ZnPcChol_8$ (1.5×10^{-6} M) with respect to the museum strains of microorganisms. Data from the Sysin Research Institute of Human Ecology and Environmental Hygiene

Microorganism	Number of microorganisms		Photodisinfection efficiency, %
	before photodisinfection	after photodisinfection	
Escherichia coli 1257, CFU/100 mL	7.3×10^4	0	100
Enterococcus faecalis, CFU/100 mL	1.3×10^5	0	100
Enterococcus faecium, CFU/100 mL	3.0×10^4	0	100
Pseudomonas aeruginosa, CFU/100 mL	9.3×10^4	0	100
Salmonella enteritidis, CFU/100 mL	1.5×10^5	10	99.99
Salmonella infantis, CFU/100 mL	1.6×10^5	0	100
Spores of sulphite-reducing clostridia, CFU/20 mL	80	80	0

Within this study, large series of the cationic phthalocyanines was synthesized and their physico-chemical and photobactericidal properties were investigated [16–19]. A number of new compounds as sensitizers for photodynamic water disinfection were patented in the Russian Federation [20–23]. Of these, zinc octakis [*N*-(2-hydroxyethyl)-*N,N*-dimethylammoniomethyl] phthalocyanine was studied in detail. Due to the presence of eight positively charged branched substituents, a phthalocyanine $ZnPcChol_8$ does not form photochemically inactive aggregates in water and has high photodynamic activity against a wide range of pathogenic bacteria and viruses [24]. $ZnPcChol_8$ was also patented as a drug for anti-microbial photodynamic therapy [25] and is produced at the NIOPIK pilot plant under the brand name Holosens.

The plasma membrane is one of the main critical targets of cytotoxic destruction in cells of different nature [26, 27]. Its irreversible damage results in leakage of intracellular content, including ATP and K^+ ions, out of cells and causes inactivation of enzymes and transport systems [11]. For certain types of bacteria, the charge and morphology of the outer membrane can differ significantly. As a result, different types of the microorganisms exhibit different susceptibility to photodynamic inactivation. Table 1 presents data on the photoinactivation of a number of museum bacterial strains under the influence of $ZnPcChol_8$, a sensitizer of the cationic phthalocyanine series. The data are obtained at the Sysin Institute of Human Ecology and Environmental Hygiene under the leadership of leading research worker T.Z. Artemova. As seen, the photodynamic inactivation of *Escherichia coli* 1257, *Enterococcus faecalis*, *Enterococcus faecium*, *Pseu-domonas aeruginosa*, and *Salmonella infantis* is 100% and that *of Salmonella enteritidis,* 99.99%.

Sulfite-reducing clostridia spores are resistant to photodynamic treatment under these conditions. The most vulnerable of the tested strains are *Enterococcus* and *Enterococcus faecalis*. The spores have dense waxy shell that protects them from the photodynamic treatment. The dependence of efficiency of the bacterial photodecontamination on the morphology of the bacteria under the action of other sensitizers is similar [18, 19].

It was established that the photoinactivation efficiency depends on the incubation time of microorganisms in a solution of the sensitizer (see Fig. 3). For inactivation of coliform bacteria sensitized by proflavine and $ZnPcChol_8$, the incubation time is 5–10 min, whereas in the case of methylene blue, it is 0.5–1.0 h.

Also, the photoinactivation efficiency is largely affected by the quality of the treated water, namely, by the level of bacterial contamination and presence of dissolved organic substances and suspended particles. The studies showed that in the presence of 0.002 g/L methylene blue and 0.001 g/L acridine yellow as sensitizers the concentration of microorganisms is decreased by 2–3 orders of magnitude, which is sufficient for water photodisinfection of a majority of water sources. However, in highly contaminated water, such as sewage water (CFU ≈ 30000–75000), the residual concentration of living microorganisms may

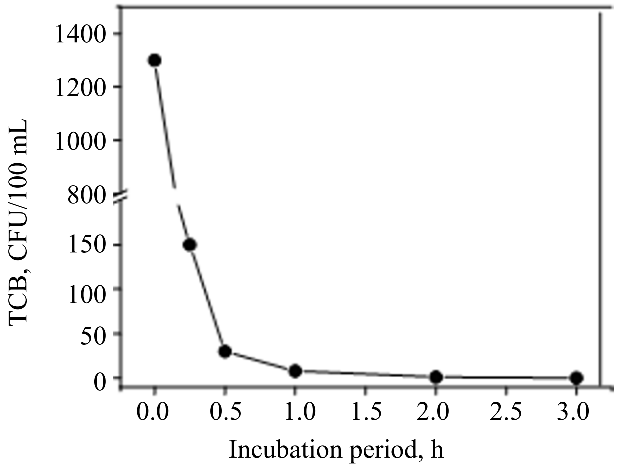


Fig. 3. The photoinactivation of total coliform bacteria (TCB) in the presence of methylene blue vs. the incubation period. The sensitizer concentration 5×10^{-6} M; irradiation time 0.5 h; CFU/100 mL is the number of forming colonies germs in 100 mL of the liquid (colony-forming units).

be present. In this case, complete disinfection is attained with increased sensitizer concentration and process time.

We studied how the water quality parameters, including turbidity, content of organic substances (permanganate oxidability), and color, affect the photoinactivation efficiency in the presence of 2 mg/L methylene blue and 3 mg/L $ZnPcChol_8$ as cationic sensitizers. Experiments were carried out on water of the Moskva River in the flood period (March-April 2006). The efficiency of photodynamic inactivation of total microorganisms and coliform bacteria depends strongly on the degree of water pollution. Turbid water contains a significant amount of solid and colloidal microparticles, which scatter light and thus reduce the depth of its penetration into the treated water. Figure 4 demonstrates the negative effect of turbidity on the photoinactivation of total microorganisms and coliform bacteria. The effect of water color on the photoinactivation is the same (see Fig. 5). The color of the river water, the Moskva river in particular, is mainly determined by the presence of humic and fulvic acids. These polymers in water are charged negatively and sorb positively charged sensitizers, which show the most efficiency for photoinactivation of microorganisms, as was shown above. The photodynamic treatment of water with a turbidity of up to 5–6 mg/L and color index to ~40 deg is reasonably efficient.

The Method of Producing Drinking Water by Photodynamic Disinfection

The photodynamic disinfection method [19] for production of drinking water from surface water sources includes four stages of water purification (see Fig. 6). In the first step, the water is clarified by coagulation and filtration through sand. This stage is used in all water supply systems without exception. At this stage, water quality is improved by all (chemical and bacteriological) indicators to a level suitable for photodynamic disinfection, which is the second stage of the process. In the third stage, chemical contaminants, dye, and products formed in its photodestruction are removed from the water by sorption onto activated carbon. Similar step is included

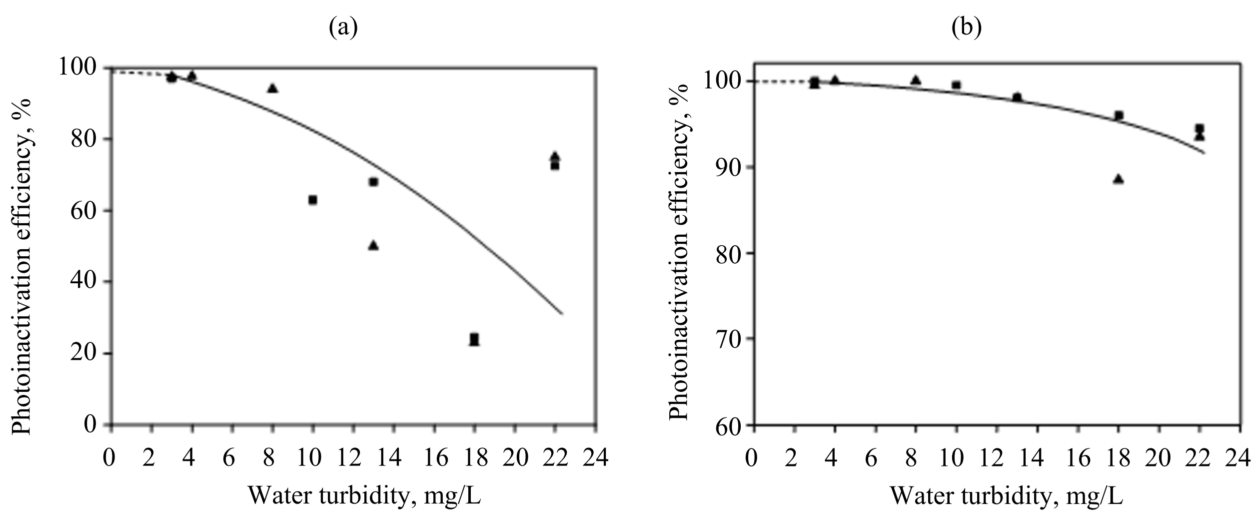


Fig. 4. The influence of water turbidity on the efficiency of photodynamic inactivation of (a) total microorganisms and (b) total coliforms with (■) methylene blue and (▲) zinc phthalocyanine.

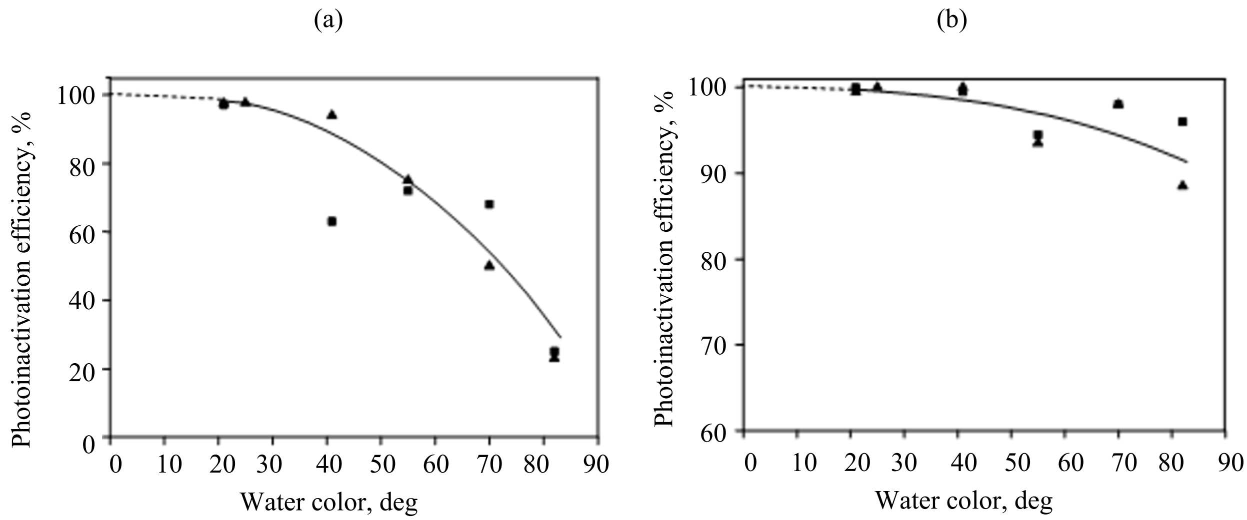


Fig. 5. Influence of water color on the efficiency of photodynamic inactivation of (a) total microorganisms and (b) coliform bacteria with (■) methylene blue and (▲) zinc phthalocyanine $ZnPcChol_8$.

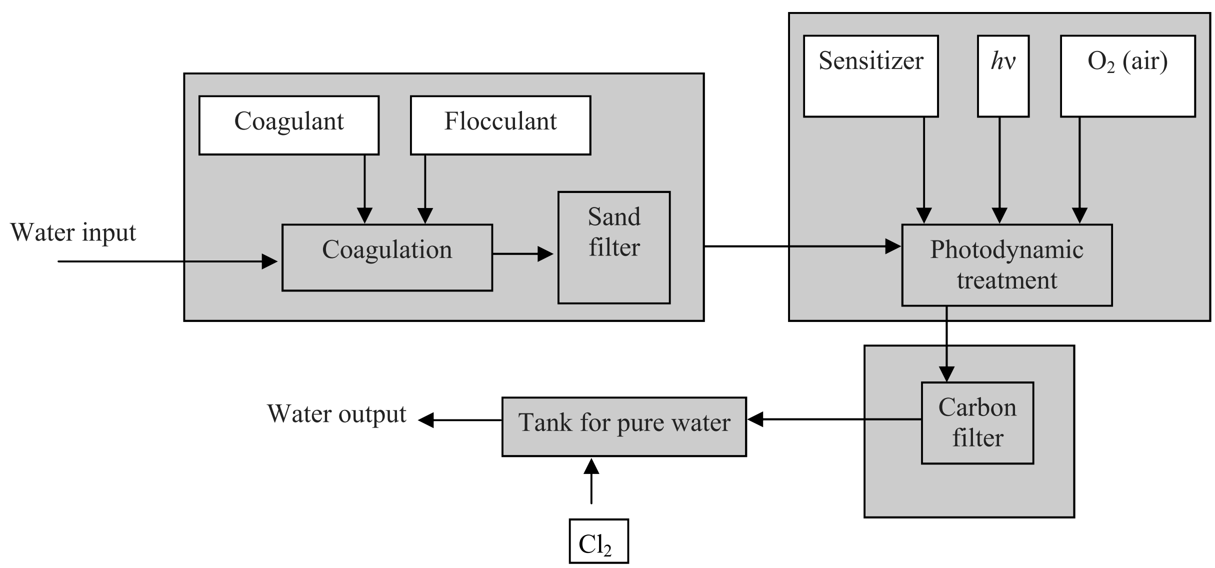


Fig. 6. The technological stages of drinking water production by the photodynamic disinfection method.

into the ozone sorption, a method recognized worldwide for drinking water disinfection. The secondary disinfection (fourth stage) is carried out in tank for pure water with low doses of chlorine, the only disinfectant having prolonged action and ensuring the safe delivery of water through a supply system to the consumer. Chlorination of drinking water in the final stage of the purification is provided in all water-treatment methods.

In photodynamic water treatment, both artificial light sources and natural sunlight may be applied. The drinking water installations developed by us are based on the same technological scheme (Fig. 6) and use both types of the irradiation sources differing by the designs of the irradiation blocks.

Based on the performed tests and taking into account the energy consumption at various combinations of sensitizer and irradiation source suitable for it, we used blue luminescent lamps as irradiation source and 0.7 mg/L of proflavine acetate for the photodynamic treatment of water [28]. The preliminary estimate of the energy consumption for the implementation of this process gives the value ~2 kW h m^{-3} of water.

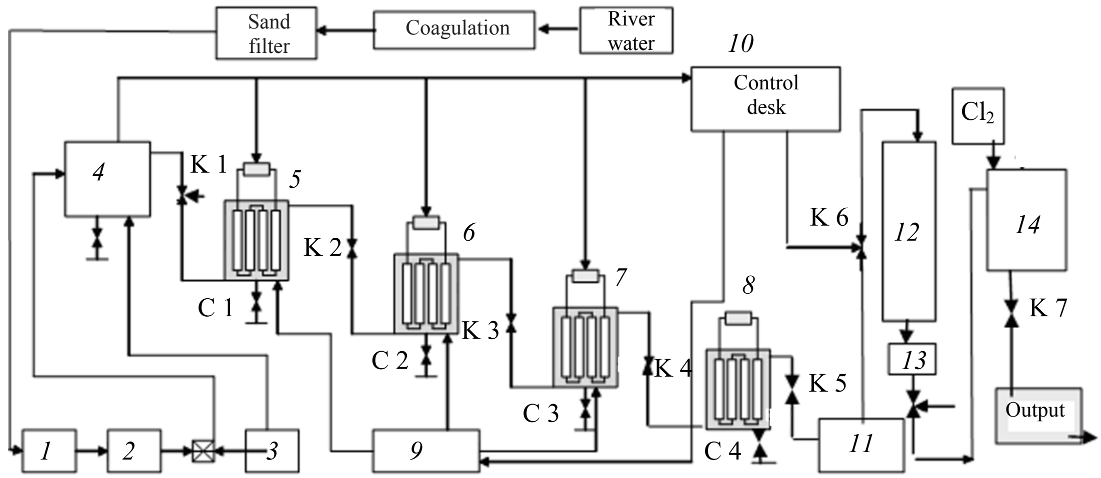


Fig. 7. The scheme of the installation for drinking water production using photodynamic disinfection and artificial light sources. (*1*) buffer capacity for the input pump; (*2*) input pump of the filtrate; (*3*) batcher of sensitizer concentrated solution; (*4*) mixing chamber; (*5, 6, 7, 8*) irradiation chambers; (*9*) compressor; (*10*) management system; (*11*) pump; (*12*) carbon filter; (*13*) rotameter; (*14*) tank for clean water; (K 1–K 7) taps for sampling; (C 1–C 4) emergency drain cocks.

The drinking water installation with the productivity 200 L/h using the photodynamic disinfection was constructed and tested on the Rublevsk water treatment station with the participation of E.N. Gorina and other colleagues in collaboration with the researches from the Faculty of Physics, Moscow State University, under the leadership of U. Yusupaliev. The scheme of the installation is shown in Fig. 7 and the bacteriological and chemical indicators of water quality through the stages of the technological line of this installation in the course of the tests on 13.02.08 are given in Table 2.

In the stage of contact coagulation with a complex coagulant-flocculant Instaflok, all quality parameters of the clarified water were significantly improved, with sulfite-reducing clostridia removed completely.

The following photodynamic treatment was performed in four tanks equipped with fluorescent lamps submerged into them (light dose 1.36 kJ/L of water). The air oxygen in the irradiation blocks was bubbled under pressure through the water. With the passing water flow through the tanks, the concentration of the photosensitizer decreases owing to photodegradation under irradiation and at the output from the fourth tank, the proflavine in the water is practically absent. As seen from Table 2, the disinfection of water by photodynamic method is complete, ensuring destructtion of all kinds of bacteria and coliphages.

Adsorption of proflavine onto the MAU AN-K3 bactericidal carbon prepared on the basis of anthracite is the third stage. This sorbent was specially developed at the Lomonosov Moscow Institute of Fine Chemical Technology (Profs. O.N. Temkin and Hoang Kim Bong). The MAU AN-K3 activated carbon has the uniform pore size distribution (pore radius ~10 Å) and high adsorption capacity: its dynamic adsorption capacity for proflavine and methylene blue is about 0.5 g/g of carbon. The carbon was modified with 0.1% of silver nitrate to prevent bacterial overgrowth in the course of the work. The method of the production of AN-K3 carbon by the single-stage activation of anthracite [29], the method of its following recovery [30], and the modification method for the preparation of MAU AN-K3 carbon with antibacterial properties [31] are protected by the Russian Federation Patents.

Adsorption purification of water on MAU AN-K3 activated carbon allows complete removal of residual proflavine acetate and products formed in its photodestruction and improves water quality (including turbidity, color, and permanganate oxidability).

The chemical and bacteriological quality of water at the output of the installation meets the requirements for drinking water. The time of continuous working of the installation during the test was 10 days.

The drinking water installation was developed and tested using the sunlight for photodynamic disinfection. As was noted above, the stages of water purification for both installations are the same (clarification by coagulation, photodynamic disinfection, adsorption on activated carbon, and chlorination

Table 2. Bacteriological and chemical indicators of water quality through the stages of the technological scheme with use of photodynamic disinfection (tests on 13.02.08)[a]

Indicator	Water				
	Input	After clarification	After photodynamic disinfection	After sorption on carbon filter	After chlorination at the output
Turbidity, mg/L	2.0	0.342	–	0.117	0.113
Color, deg.	20	14	–	1.000	2.000
pH	7.76	7.53	–	7.800	7.860
Permanganate oxidability, mg/L	3.5	3.36	–	0.960	0.880
TMN, CFU/1 mL	120	20	Not found	Not found	Not found
TCB, CFU/100 mL	1000	40	Not found	Not found	Not found
TtCB, CFU/100 mL	1000	40	Not found	Not found	Not found
Clostridia, CFU/20 mL	13	Not found	Not found	Not found	Not found
Coliphages, PFU/100 mL	150	9.3	Not found	Not found	Not found

[a] (TMN) total microbial number, (TCB and TtCB) total coliform and thermotolerant coliform bacteria, respectively, (CFU) colony-forming units, and (PFU) plaque-forming units.

at the outlet of the installation), whereas their irradiation units are different (see Fig. 8).

In terms of the development of the photodynamic method for drinking water production, the toxicity of the sensitizers and products of their photodestruction was extensively studied [32–35]. It was found that endoperoxide is the primary product formed by phototransformation of proflavine acetate in water [36, 37] (see Scheme 1).

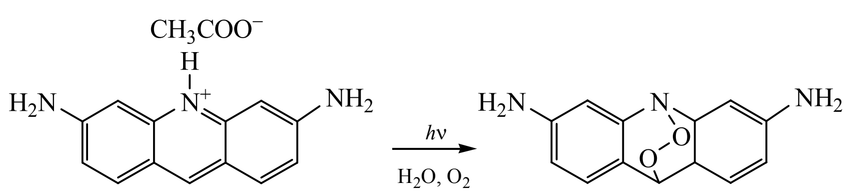
Profs. O.O. Sinitsyna and Z.I. Zholdakova of the Sysin Research Institute of Human Ecology and Environmental Health scientifically proved that maximum permissible concentrations of proflavine acetate and its endoperoxide in household and recreational waters are at the level of 0.002 and 0.04 mg/L, respectively. A method for the determination of the above compounds in water at the quantitative level was developed and water quality at the outlet of the installation was monitored in accordance with the hygiene requirements.

Disinfection of Water in Open Water Reservoirs

In accordance with the Sanitary Rules and Regulations, household and recreational water reservoirs should not be contaminated with pathogenic microorganisms. Meanwhile, recreational water reservoirs in the urban environment are contaminated owing to surface runoff of rainwater and meltwater. Because chlorine disinfection is unacceptable owing to severe toxicity to aquatic biota, the search for of reasonably efficient and ecologically friendly methods is urgent for reducing bacterial contamination of water reservoirs.

For the first time, the photodynamic method was used by us, as a development of studies on drinking water disinfection, to improve bacteriological indica-

Scheme 1. Formation of proflavine endoperoxide by photooxidation of proflavine acetate in water.



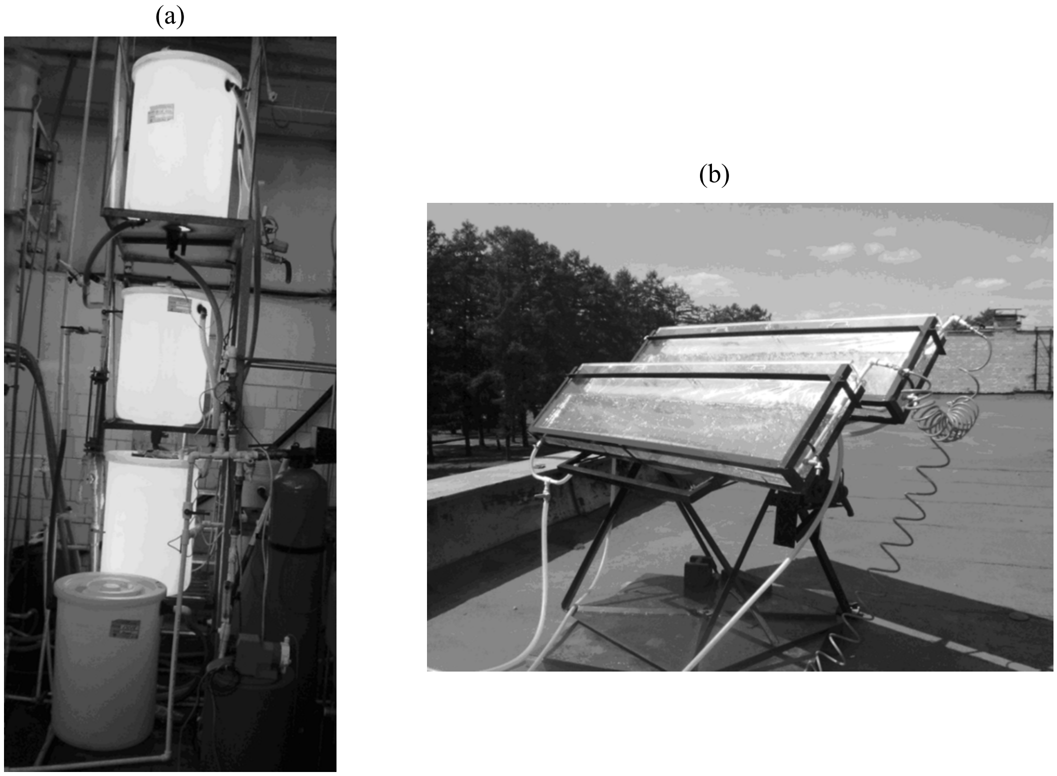


Fig. 8. The irradiation units using (a) artificial light sources and (b) sunlight for water disinfection by photodynamic method.

tors of water quality in natural water bodies under the action of sunlight, with no detrimental effect exerted on their flora and fauna.

In the first stage of these studies, the effect exerted by methylene blue and proflavine acetate, as sensisizers, on the processes of natural purification of water reservoirs and their hydrobiological and hydrochemical characteristics and on the organoleptic properties of water were determined under laboratory conditions. The studies were performed by researches with the Lomonosov Moscow State University (Hydrobiology Department) under the leadership of Prof. O.F. Filenko, who obtained data on the toxicity of methylene blue and proflavine acetate to aquatic organisms belonging to different biological groups within the scheme of ecological and fishery valuation (Table 3). These data suggest that the MPC, at which the basic characteristics of water remain unchanged, is 0.01 mg/L (class-4 hazard) for proflavine and 0.001 mg/L (class-3 hazard) for methylene blue.

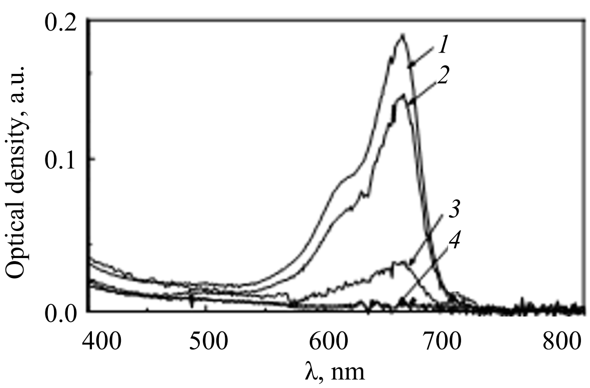


Fig. 9. The electronic absorption spectra of samples of the pond water treated with methylene blue at a dose of 0.2 g/m^2 of the water area. Spectra (*1, 2, 3*), and (*4*) were recorded in 2 h, 4 h, 1 day, and 3 days after the sensitizer was introduced.

Full-scale experiments on water disinfection using methylene blue were carried out on two ponds (area 4000 and 6000 m^2, average depth about 2 m) in Moscow in 2004 and 2005. The sensitizer, as aqueous solution, was spread on the surface of water bodies at the doses of 0.5 and 0.2 g/m^2 of the water area. The concentration of the sensitizer, assuming its uniform distribution, in the top layer of the water (thickness 1 m) was 0.5 and 0.2 mg/L, respectively. Figure 9 demonstrates electronic absorption spectra of samples of the pond water treated with methylene blue at a dose of 0.2 g/m^2 of the water area. As seen from these spectra, trace amounts of the sensitizer in water are still present

Table 3. The threshold concentrations of methylene blue and proflavine acetate relative to different test objects of water reservoir

Test object	Threshold concentration, mg/L	
	methylene blue	proflavine acetate
Dissolved oxygen	> 0.5	> 0.5
Hydrogen ions	> 0.5	>0.5
BOD_5	0.01	0.05
Nitrification		
First phase	0.001	0.01
Second phase	0.005	0.05
Ammonium nitrogen	0.01	0.1
Saprophytes (growth dynamics)	0.01	0.1
Sanitary regime of the reservoir as a whole	0.001	0.01
Alga *Scenedesmus quadricauda*	0.001	0.1
Alga *Synechocystis sp*	0.57	16.89
Alga *Chlorella pyrenoidosa*	2.5	5
Crustaceans *Daphnia magna*	0.003	0.01
Fish *Brachydanio rerio*	3	0.3

after a day and then decrease to undetermined value (lesser than MPC).

Results of the tests under conditions of a natural reservoir showed that methylene blue is the significant antimicrobial agent, especially for sanitary-indicative groups of microorganisms, exerting photobactericidal effect during the first two days and bacteriostatic effect, up to 5 days. Thus, after 2 hours of exposure to methylene blue and sunlight the concentration of coliform bacteria in the pond water decreased from 2400 to <50 CFU/100 mL.

The hydrobiological study showed that the photodynamic treatment with methylene blue at a dose of 0.2 mg/L has no adverse effect on the state of phytoplankton and zooplankton. The treatment of the pond water at higher dose of the reagent (0.5 mg/L) decreases the number of plankton to a permissible value in the first 5 days after introduction of the reagent. After 2 weeks, the number of plankton in the pond recovered. The reagent exerted no effect on the life of fish, macrophytes, and submerged coastal aquatic vegetation.

The experiment on photodynamic water treatment using acetate proflavine was performed on ponds of the All-Russian Research Institute of Freshwater Fish Farming in 2009. Two hatchery ponds were studied (water surface area 400 m^2 and depth 2.5 m each); 100 thousands of carp larvae were introduced into the each pond before introducing a reagent.

Preliminary laboratory tests were performed at the Lomonosov Moscow State University (Hydrobiology Department) under the leadership of Prof. S.E. Plekhanov. It was shown that the photodynamic treatment of pond waters by proflavine (0.5–1.0 mg/L) suppresses bacterial growth by several orders of magnitude. Under these conditions, the state of aquatic organisms at higher level of organization (plankton communities) is practically unchanged. In view of these data, it was established that for the decontamination of water reservoirs with a depth of 1.5–2 m it is reasonable to use 0.5 g/m^2 of proflavine acetate. At this dose and under the conditions that the photodisinfectant is distributed in the upper layer of water to a depth of 1 m its concentration is 0.5 mg/L. This concentration of chemically unstable proflavine, though exceeds

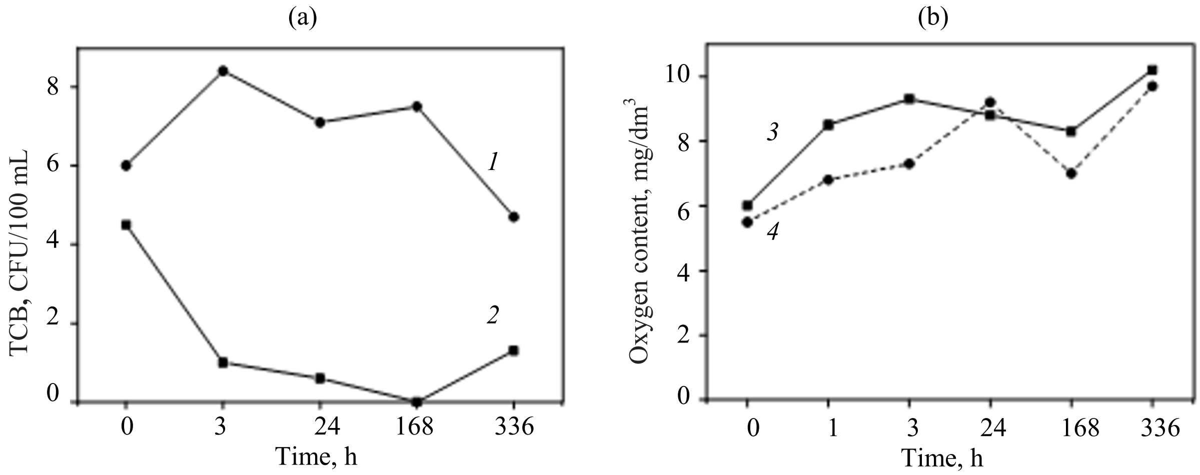


Fig. 10. Dynamics of the number (a) of coliform bacteria in (*1*) reference and (*2*) test ponds and (b) the content of dissolved oxygen in water of (*3*) reference and (*4*) test ponds after proflavine acetate was introduced.

permissible value for aquatic organisms, decreases to a less than MPC during daylight.

Pond water was treated with proflavine at a dose of 0.5 g/m^2 of the water area under experimental conditions. To do this, an aqueous solution of proflavine was sprayed homogeneously on the surface of the pond.

No longer than after 2 h of introduction, proflavine in the pond water was not determined. Consequently, the photodynamic effect exerted by the above dose of proflavine acetate and sunlight irradiation on the natural water reservoir does not exceed two hours. Nevertheless a bacteriostatic effect is retained up to two weeks (Fig. 10).

The experiment showed that the photodynamic treatment with proflavine has no significant effect on the content of dissolved oxygen, permanganate oxidability, and processes of biochemical oxygen consumption in water. The hydrochemical parameters of purified water meet the requirements of SanPiN2.1.5.980-00 (Sanitary Rules and Regulations) parameters for recreational water. The fact that the drug has no adverse effect on the abundance and biomass of phyto- and zooplankton, as well as on the primary production and destruction of organic substances by phytoplankton, and the data on the chemical and biological analysis show that proflavine does not adversely affects the processes of natural self-purification of natural water reservoirs. It was found that the effect on the total saprophyte microorganisms is slight, with the level of microorganisms in the sanitary-indicative group decreased considerably.

Results of the experiments on the photodynamic treatment of ponds with the sensitizers (methylene blue and proflavine) show that the effective dose of the latter sensitizer reduces to a less than MPC value for a shorter time (within 1–2 h). Therefore, proflavine acetate was recommended for disinfection of water reservoirs under emergency conditions.

CONCLUSIONS

The photodynamic method of drinking water disinfection does not use high-toxicity molecular chlorine and other hazardous chlorinating agents in the main stage of water disinfection. Alongside with a number of advantages, the photodynamic method needs a quite expensive sensitizer, which is a significant drawback. Currently, a group of the authors of this method has achieved significant results [38–43] on the development of heterogeneous sensitizers, which, in principle, can solve the problem of multiple use of expensive materials. The use of sunlight in photodynamic disinfection is economically more profitable and promising in comparison with artificial insolation and makes process suitable to field conditions.

The photodynamic disinfection using proflavine is the promising method to reduce bacterial contamination of water reservoirs. Proflavine as disinfectant is included into the State Registry by the Federal Service for Supervision of Consumer Rights Protection and Human Well-being and is recommended for disinfection of water reservoirs under emergency conditions.

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