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Use of Ultrasound and Ultraviolet Radiation in Hybrid Methods for Water Disinfection

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Abstract—Hybrid photochemical methods are considered for water disinfection in which treatment with ultraviolet (UV) and ultrasonic (US) radiations are combined (US/UV) and applied consecutively or simultaneously; the use of catalysts is also included. The literature survey shows that inactivation of pathogenic microorganisms in aquatic media by high-frequency US (>100 kHz) has not been studied adequately, whereas only low-frequency (<100 kHz) US and low-pressure mercury vapor lamps (254 nm) were used in hybrid US/UV methods. Irradiation with high-frequency US generates reactive oxygen species (primarily hydroxyl radicals) in greater proportions, and a synergistic effect is observed when UV irradiation is included in treatment. Therefore, the use of high-frequency US and mercury-free UV sources in hybrid oxidizing systems, including those based on Fenton-like processes, is promising for intensifying disinfection processes and improving their effectiveness.

Keywords: ultrasound, ultraviolet radiation, microorganisms, inactivation, water disinfection

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INTRODUCTION

Biogenic pollution of aquatic ecosystems remains a global ecological problem and poses a threat to human health. According to WHO estimates, as of March 2018, at least 2 billion people consumed water with fecal contamination, while acute intestinal infections cause 502000 deaths yearly [1]. Domestic waters and industrial waste waters that were not purified adequately are typical sources of pathogenic microflora. Contamination of surface and ground waters with such effluents results in lack of quality drinking water. To reduce the level of biogenic pollution of aquatic systems, including drinking water sources, we must develop modern, sustainable methods for disinfection of natural and waste waters and use technologies based on these methods.

It is known that a variety of methods are used for water disinfection, with chlorination, ozonation, and ultraviolet (UV) light and ultrasonic (US) irradiation being the most common. The two latter methods, i.e., photolysis and sonolysis, represent reagent-free methods and are the most promising from sustainability considerations. For historical reasons, a low-frequency range with generation frequencies below 100 kHz was studied well and found technological application; it is currently commonly used for different purposes, including disinfection. A great body of literature has been accumulated by now on the use of low-frequency US radiation (mainly 20–45 kHz) and UV radiation from low- and medium-pressure mercury vapor lamps for inactivation of pathogenic microorganisms in water (as independent methods). Meanwhile, the use of the UV method is limited because of its low efficiency when microorganisms or suspended solids are present in water in high concentrations. The reasons are the absorption and scattering of radiation, the reduction in the effective radiation dose, and a possibility for photoreactivation of cells to occur. As is known, upon exposure to US, the phenomenon of acoustic cavitation—generation of microbubbles (hot spots)—takes place. When collapsing in water, the latter generate hydrogen peroxide and reactive oxygen spices (ROS), such as $OH^\bullet$, $HO_2^\bullet$ and $O^\bullet$ radicals [2–4], which are capable of deactivating enzymes and causing damage to the plasma membrane, DNA, and liposomes [5, 6]. In addition, the effect of cavitation results in mechanical destruction of the cell by causing lysis and disintegration [7, 8]. With the US frequency being one key factor affecting hot spot and ROS generation, the maximum $OH^\bullet$ radical concentrations were earlier observed at high frequencies of 585 and 1040 kHz [2]. US frequencies optimal for producing efficient acoustic cavitation fall in the range of 200–600 kHz [4], in which a large number of hot spots and radicals are generated. Irradiation with low-frequency US (<100 kHz) generates fewer bubbles, and they are smaller, which reduces the ROS yield [4]. It is thought that the bactericidal effect is achieved due to physical destruction of cells by collapsing cavitation bubbles, whereas the effect of high-frequency US (>100 kHz

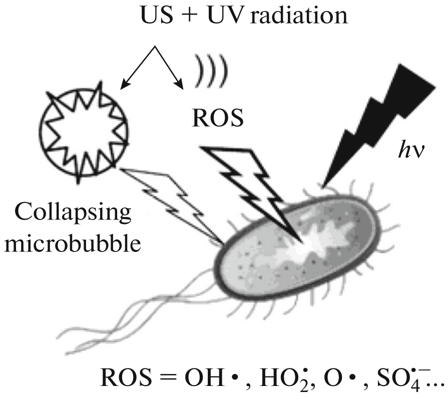

Fig. 1. Key pathways for inactivation of a cell by US and UV radiation.

and the MHz range) brings about inactivation primarily through oxidation reactions involving the generated radicals [8–10] (Fig. 1). Therefore, the use of high-frequency US is promising for ROS generation and, thus, intensification of inactivation processes.

DISINFECTION OF WATER WITH HIGH-FREQUENCY ULTRASOUND

Our literature survey showed that processes of microorganism inactivation in water by high-frequency US has barely been studied, and there are only a few published works on the subject (Table 1). Taking *E. coli* and *S. mutans* as examples, it was shown that high-frequency US displays better bactericidal activity than low-frequency US [11, 12]. The degrees of inactivation of *E. aerogenes* in deionized water by high- and low-frequency US were comparable [8]; however, the same authors showed in another study [9] that irradiation with US with a frequency of 850 kHz led to inactivation of >99% of bacteria and *A. pullulans* fungi. The authors proposed a sonochemical inactivation mechanism involving generation of free radicals and H_2O_2. For inactivation of cyanobacteria, a frequency of 580 kHz proved to be more effective than 1146 kHz [10]. These studies demonstrated the efficiency of high-frequency US in inactivation of microorganisms in aquatic environments; however, in isolated instances, mostly deagglomeration of cells was observed [13, 14], while low-frequency US was more effective in inactivating mycobacteria [15]. Thus, lack of literature data dictates the necessity to carry out more advanced studies of processes that take place during water disinfection by high-frequency US, including the use of hybrid methods.

HYBRID US/UV METHOD

Hybrid methods are among other methods for water purification and disinfection that has recently been developed in order to achieve more intensive oxidation processes and reduce processing duration (energy consumption). These include a sono-photochemical method based on US in combination with UV irradiation that was implemented in two designs: US → UV (consecutive treatment) and US + UV (simultaneous treatment). A summary of research in this area is presented in Table 2.

The first laboratory studies, which were conducted by T. Blume (Germany), showed that US pretreatment breaks down coarse particles and improves the efficiency of water disinfection [16]. This result was confirmed in later studies by other research groups that established the presence of a synergistic effect in consecutive US → UV treatment [17–21]. And this method was also implemented in a pilot unit for disinfection of effluents with poor light transparency [18]. It was remarked that US treatment also suppresses biofouling, including that of UV lamps, and diminishes photoreactivation of cells [22, 23]. The US → UV method was also shown to be effective against eukaryotic organisms (infusoria, nematodes, and crustaceans) in recirculating aquaculture systems [24].

In Russia, a method based on simultaneous exposure to US and UV was implemented in the "Lazur'" technology in which water is irradiated with low-frequency US and low-pressure mercury vapor lamps in modular units [25]. The author concluded that a synergistic effect took place, but this is at variance with the conclusion in review [26]. Nevertheless, the presence of a synergistic effect was also established in disinfection of domestic effluents carried out using a US + UV method in both laboratory scale and pilot flow-through sono-photo reactors [27, 28]. In contrast to UV radiation, simultaneous action of US and UV was found to be more effective in inactivation of sea zooplankton in ship's ballast water [29]. Thus, the hybrid method in its two variants (US → UV and US + UV) affords higher rates of inactivation of target microorganisms and is more energy-efficient in both model and real aqueous solutions, while providing a synergistic effect (Table 2).

As for disinfection of other liquid media, different consecutive combinations of US and UV did not produce a synergistic effect in the inactivation of *A. acidoterrestris* spores in apple juice [30]. Nevertheless, in disinfecting fruit juices, simultaneous treatment (US + UV) was more energy-efficient than the consecutive version (US → UV) [31] and US and UV treatments applied separately to inactivate *Z. bailii* in apple juice [32] and *E. coli* and coliform bacteria in milk [33].

In all studies concerning inactivation of microorganisms by the hybrid US/UV method, low-frequency US with generation frequencies of a few tens of kHz was used along with a low-pressure mercury vapor lamp (254 nm) as a source of UV light. Meanwhile, the use of mercury is being phased down on the global scale in accord with Minamata convention on mercury (2013), which was signed by Russia on September 24,

Table 1. Summary of literature data on inactivation of microorganisms in water by high-frequency US

Microorganism, initial concentration	US frequency, kHz	Aqueous matrix	Outcome	References
Enterobacter aerogenes (10^8 CFU/mL)	20 and 850	Deionized water, skim milk	At 850 kHz, the number of cells reduced by three orders of magnitude for 60 min (at 20 kHz, by 3.6 orders of magnitude); inactivation in milk was not observed	[8]
Enterobacter aerogenes, *Bacillus subtilis*, *Staphylococcus epidermidis*, *Aureobasidium pullulans* (10^8 CFU/mL)	850	0.9% physiological solution	Inactivation >99%	[9]
Microcystis aeruginosa (10^6 CFU/mL)	20, 580, and 1146	Not provided	20 and 580 kHz were effective in inactivation; cell deagglomeration at 1146 kHz.	[10]
Escherichia coli (10^6 CFU/mL)	20, 205, 358, 618, and 1017	Distilled water	Maximum inactivation rate at 205 kHz (~4 orders of magnitude for 60 min)	[11]
Escherichia coli IAM 12058, *Streptococcus mutans* JCM 5175 (10^8 CFU/mL)	20 and 500	0.9% physiological solution	Inactivation effectiveness higher at 500 kHz than at 20 kHz	[12]
Bacillus subtilis	20, 38 512, and 850	–	Deagglomeration of cells at 512 and 850 kHz	[13]
Escherichia coli, Klebsiella pneumonia (10^5 CFU/mL)	20, 40, and 580	Phosphate buffer solution	Deagglomeration of cells at 580 kHz, a decrease by 2–3 orders of magnitude at 20 and 40 kHz	[14]
Mycobacterium sp. strain 6PY1 (2.15×10^{-3}–1.4×10^{-2} mg protein/L)	20, 612	Mineral salt medium	Irradiation at 20 kHz is more effective (inactivation by 93%) than at 612 kHz (inactivation by 35.5%)	[15]

2014, among another 118 countries [34]. In the past years, in view of the Minamata convention, sustainability, and some other advantages, mercury-free UV sources, e.g., exciplex lamps (excilamps) [35] and light-emitting diodes (LEDs) [36, 37], have been considered to replace commonly used mercury lamps in water purification and water treatment technologies. In water disinfection, the best results were achieved using a KrCl excilamp (222 nm) [38, 39].

The development of nitride-based semiconductors led to the production of LEDs emitting in the germicidal range of 200–280 nm (UVC). The new generation of UV LEDs is attractive due to their long service life and low energy consumption, which thus surpasses deuterium, xenon, and mercury gas-discharge lamps [40]. With the above in mind, from our perspective, the use of *high-frequency* US in combination with UV irradiation (e.g., from excilamps and LEDs) in hybrid methods is promising. For instance, simultaneous exposure to high-frequency US (582, 862, or 1142 kHz) and visible light irradiation furnished a more effective inactivation of the MS2 bacteriophage in a phosphate physiological solution [41]. Earlier, we successfully used high-frequency US (1.7 MHz) in combination with UV irradiation from an excilamp for disinfection of surfaces [42]. To the best of our knowledge, no other studies of microorganism inactivation by high-frequency US and light radiation have been performed yet.

Table 2. Summary of literature data on inactivation of microorganisms in water by hybrid US/UV methods

Microorganism, initial concentration	US frequency, kHz	Aqueous matrix	Outcome	References
Consecutive US → UV treatment				
Total coliform bacteria (4.8 × 10^5 CFU/100 mL), *E. coli* (4.6 × 10^4 CFU/100 mL) and fecal streptococci (5.6 × 10^3 CFU/100 mL)	20	Domestic waste water after decontamination	Higher inactivation effectiveness (energy efficiency) with US → UV treatment	[16]
Total coliform bacteria	20	Same	Increase in the inactivation rate, diminution of the plateau effect on inactivation curves, breaking down of coarse particles (>60 μm)	[17]
Total coliform bacteria (2.7 × 10^5 CFU/100 mL), *E. coli* (1.4 × 10^4 CFU/100 mL)	39	Same	Synergistic effect for US → UV treatment	[18]
E. coli (2.6 × 10^6–3.2 × 10^7 CFU/L)	20, 28, 40, 83	Same	Synergistic effect for US → UV treatment	[19]
E. coli (10^5 CFU/mL)	20	0.9% physiological solution	Synergistic effect for US → UV treatment, no synergy for UV → US treatment	[20]
E. coli (5 × 10^8 CFU/mL)	40	Distilled water	Synergistic effect for US → UV treatment in the presence of Ag^+, the number of cells reduced by eight orders of magnitude	[21]
Total coliform bacteria (10^3–10^4 CFU/mL)	80	Domestic waste water	Inactivation of 100% of cells and no photoreactivation after US → UV treatment	[22]
E. coli (10^8 CFU/mL)	33	Deionized water, aqueous kaolin suspension, domestic waste water after purification	With US pretreatment, disinfection is more effective and photoreactivation of cells is diminished	[23]
Simultaneous US + UV treatment				
E. coli, MS2 bacteriophage, *B. subtilis* spores, *Giardia muris* cysts, and polio viruses	<100	For the presented curves, inactivation was not specified	Synergistic effect for simultaneous action of US and UV; effective doses of UV radiation are 100–150 mJ/cm^2	[25]
Fecal coliform bacteria (3.67 × 10^5– 9.48 × 10^7 CFU/L)	28	Domestic waste water after purification	US + UV treatment in a flow-through sono-photo reactor brings about the highest reduction in the cell number: 4.24 orders of magnitude at an energy consumption of 0.219 kW h/m^3. Synergistic effect	[27]
Fecal coliform bacteria (3.7 × 10^5 CFU/L), *E. coli* (2.2 × 10^5 ± 7.8 × 10^4 CFU/L) and fecal streptococci (1.0 × 10^5 ± 3.3 × 10^4 CFU/L)	28	Same	High inactivation effectiveness after US + UV treatment in a pilot flow-through sono-photo reactor. In 87% cases, the number of coliform bacteria was <100 CFU/L	[28]

HYBRID US/UV METHODS USING OXIDIZERS AND CATALYSTS

Hybrid sono-photochemical processes using ecologically friendly oxidizers and/or catalysts is one of the most interesting research directions in the area of water purification and disinfection. Peroxo and peroxy sulfo compounds, such as H_2O_2, HSO_5^-, $S_2O_8^{2-}$, are used as oxidizers, and TiO_2, (nano)composites based on it, and transition metals—most often these are iron(II) ions in Fenton systems (Fe^{2+}/H_2O_2) and Fenton-like systems (e.g., $Fe^{2+}/S_2O_8^{2-}$)—are used as catalysts. Oxidizing systems containing peroxymono- and peroxydisulfates are of particular interest. In these systems, sulfate radical anions $SO_4^{\bullet-}$ are generated along with $OH\bullet$. The former are characterized by a comparable redox potential (2.5–3.1 V) and fairly long life time (30–40 μs) [43]. We note that hybrid sono-photochemical processes of destruction of organic pollutants in the presence of oxidizers and/or catalysts (primarily, sono-photocatalysis) have been studied fairly well [4, 44], whereas there was hardly any research concerning microbial inactivation in this area.

By the present time, a study [45] has been published concerning inactivation of *E. coli* (10^6 CFU/mL) in waste water by using high-frequency US (275 kHz) in combination with a photo-Fenton system based on simulated solar radiation (a $US/h\nu/Fe^{2+}/H_2O_2$ system). A synergistic effect with a synergy index of 1.57 was established to take place between US and the Fenton reaction (Fe^{2+}/H_2O_2, no irradiation), whereas it was lower for the $US/h\nu/Fe^{2+}/H_2O_2$ system; however, a complete disinfection of effluents was achieved only with the latter system for a treatment duration of 4 h. US pretreatment was shown to improve inactivation effectiveness in the photo-Fenton system by making up for dark reactions and suppressing reactivation of cells [45]. We note that a considerable synergistic effect was also registered in pilot reactors for the same hybrid system (i.e., $US/h\nu/Fe^{2+}/H_2O_2$) applied to removal of organic pollutants from water using high-frequency US (400 kHz) [46]. That being so, such hybrid methods, including those based on photo-Fenton and Fenton-like processes, can be highly effective in disinfection as well.

CONCLUSIONS

The potential for using high-frequency US with generation frequencies beyond 100 kHz in disinfection of natural and waste waters has not been explored adequately. Nonetheless, since irradiation of water with high-frequency US produces more ROS, there is a potential in using it in combination with UV irradiation (e.g., from UV LEDs). With low-frequency US as an example, it was proven that hybrid US/UV treatment of aquatic media is accompanied by a synergistic effect, while the disinfection effectiveness is enhanced. In our opinion, hybrid sono-photochemical methods using oxidizers and catalysts are of great interest from both scientific and technological perspectives in view of their application for intensifying microbial inactivation and improving their energy efficiency. Microbial inactivation processes have not been studied in such oxidizing systems and call for further research.

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