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Water Treatment and Disinfection by Natural Solar Radiation in the Ferrous-Persulfate System

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Abstract. The simultaneous treatment and disinfection of natural water and municipal wastewater using solar-enhanced Fenton-like process was studied. Using herbicide atrazine and bacterium *Escherichia coli* as model pollutants, the kinetics of separate and simultaneous processes of destruction and inactivation in different aqueous matrices (deionized water – DW, lake water – LW and wastewater – WW) were studied in the ferrous-persulfate system, activated with natural solar radiation {Solar/Fe²⁺/S₂O₈²⁻}. It was found, that the presence of bacterial cells inhibited the rate of atrazine destruction in all water types, decreasing the pseudo-first-order rate constants by one order of magnitude. The accumulated solar doses (Q_{UVA}) for 90% atrazine removal from DW, NW and WW were 5.2, 5.7 and 9.2 kJ/L, respectively. By contrast, the presence of atrazine in NW and WW did not affect negatively on the *E. coli* inactivation rates. Inactivation of 95% cells was achieved (~1.5 log reduction) at doses Q_{UVA} of 4-6 kJ/L, that is comparable with the literature data on *E. coli* inactivation in other oxidation systems. The combined method of simultaneous destruction of micropollutants and inactivation of microbial pathogens was proposed by using natural solar radiation in the ferrous-persulfate system.

1. Introduction

Nowadays, contamination of aquatic ecosystems by organic micropollutants (pharmaceuticals and their metabolites, herbicides, personal care products) and pathogenic microorganisms is a global environmental problem. In Russia, the problem of uncontrolled growing presence of organic micropollutants in natural waters remains to be little investigated [1, 2]. They come to the aquatic ecosystems, mainly, as components of insufficiently treated industrial and municipal wastewater, which, in turn, may contain pathogenic microorganisms. Despite of the relatively low concentrations of organic micropollutants detected in water (1 ng/L–1 µg/L), a constant discharge and presence of their residual amounts are hazardous for living organisms, including humans, and cause chronic toxic effects (e.g., herbicide atrazine (ATZ) affects the endocrine system of amphibians, inducing their feminization).

It is known, that one of the most effective technologies of water treatment and disinfection are based on the advanced oxidation processes (AOPs), where an organic substance is oxidized by highly reactive oxygen species (ROS). In photo-induced AOPs, ROS are generated by irradiating an aqueous solution with UV light of various origin in the presence of environmentally-safe oxidants (H₂O₂, HSO₅⁻, S₂O₈²⁻) or catalysts (TiO₂, Fe²⁺ in Fenton-like systems).

In recent years, sulfate radical-based AOPs (SR-AOPs) have attracted an increasing attention as



effective solution to the water treatment [3, 4]. The SR-AOPs utilize sulfate radicals (mainly, sulfate anion radical – $\text{SO}_4^{\bullet-}$), which can be generated via activation of persulfate ($\text{S}_2\text{O}_8^{2-}$) or peroxymonosulfate with various methods, most commonly, with transition metals and UV radiation. In view of environmental safety and energy efficiency, the solar-induced AOPs are among of most promising in the world practice. Meanwhile, the solar-enhanced AOPs for simultaneous destruction of chemical pollutants and microbial inactivation have been little studied [5]. The principal feasibility of simultaneous treatment and disinfection of natural and municipal wastewater in the ferrous-persulfate system using xenon lamp as a solar simulator has been shown in our previous study [6]. The purpose of this study was to establish the kinetics and evaluate the energy-efficiency of simultaneous destruction of atrazine and inactivation of *Escherichia coli* in the ferrous-persulfate system, activated by natural solar radiation {Solar/ Fe^{2+} / $\text{S}_2\text{O}_8^{2-}$ }.

2. Materials and methods

2.1. Reagents

ATZ (99.1%, Sigma-Aldrich), iron (II) sulfate heptahydrate (Khimreaktivsnab, Irkutsk, Russia), potassium persulfate (Vektor, St. Petersburg, Russia) were used as received. HPLC-grade acetonitrile (ACN) was purchased from Cryochrom (Russia), and methanol (MeOH) and acetic acid from Khimreaktivsnab. Stock solutions of compounds were prepared in deionized water (18.2 m Ω cm) produced by a Simplicity[®]UV system from Millipore.

2.2. *E. coli* preparation

E. coli K-12, supplied by the State Research Institute of Genetics and Selection of Industrial Microorganisms ("Genetika", Moscow, Russia), was inoculated in 30 mL of nutrient broth (State Research Center for Applied Microbiology and Biotechnology, Obolensk, Russia) and grown aerobically in an incubator overnight at 37 °C and 180 rpm (Biosan ES-20, Latvia). The cells were then harvested in 15 mL conical tubes at 4000 rpm for 5 min (Centurion Scientific, UK), washed twice with phosphate-buffered saline, PBS (pH 7.4, Gibco[®] Life technologies, UK), and resuspended in PBS solution. This stock solution of *E. coli* contained 10⁹ CFU/mL. An aliquot of 0.5 mL suspended in the water samples to be irradiated gave an initial population of 10⁵ CFU/mL.

2.3. Water matrices

Lake water (LW) was sampled from Lake Baikal and wastewater (WW) after biological treatment was collected from the municipal wastewater treatment plant in Ulan-Ude, Russia. The samples were delivered and filtered the same day (0.45 mm RC, Vladisart, Russia) and stored at 4 °C until experiments were performed. Table 1 presents the general water quality data.

2.4. Treatment procedure

An aqueous matrix, contaminated with ATZ (4 mg/L) and/or *E. coli* (10⁵ CFU/mL) was irradiated by natural sunlight in the presence of $\text{S}_2\text{O}_8^{2-}$ (150 mg/L) and Fe^{2+} (5 mg/L) in a static photoreactor under magnetic stirring (IKA[®]Color Squid, 250 rpm). Initial concentrations of Fe^{2+} and $\text{S}_2\text{O}_8^{2-}$ were selected on the basis of effective molar ratios of oxidant and catalyst found previously by Khandarkhaeva et al. [7]. The incident solar irradiance was measured using radiometer TKA-PKM-06 ("TKA" Scientific Instruments, Russia). Experiments were performed in 2-5 replicates at pH 4.5. During each experiment, samples were taken after 0, 5, 15, 30, 45, 60 and 90 min irradiation, filtered after adjusting the pH to 8.0 and further analyzed for residual ATZ by HPLC.

The microbial inactivation was determined by comparing the average number of CFU after incubation of 100 μL of control (non-irradiated) and irradiated sample on an agar medium at 37 °C for 24 h in triplicates. The results are presented as plots of *E. coli* inactivation ($\text{Lg}(N/N_0)$) versus Q_{UVA} doses. The accumulated solar energy dose (Q_{UVA} , kJ/L) across UVA range (315-400 nm) per unit volume was calculated by Eq. (1) [8]:

$$Q_{\text{UVA}} = \sum_n \overline{UV} A_{n-1} \cdot \frac{A_t}{V_t} \cdot (t_n - t_{n-1}) \quad (1)$$

where t_n – irradiation time of sample n , $\overline{UV} A_{n-1}$ – the average UVA irradiance during time interval $(t_n - t_{n-1})$, A_t – area of irradiated surface (cm^2) and V_t – water volume (L).

Table 1. Hydrochemical characteristics of the selected waters.

Parameter	Lake water	Wastewater
pH	7.9	7.7
DOC, mg/L	1.5	14.4
Conductivity, $\mu\text{S}/\text{cm}$	110.7	1105
Ammonium, mg/L	<0.05	15.60±3.28
Total iron, mg/L	<0.007	0.14±0.03
Bicarbonate, mg/L	60.00±7.32	125.1±15.0
Carbonate, mg/L	<6.0	<6.0
Nitrate, mg/L	<0.1	199.6±25.9
Nitrite, mg/L	<0.1	21.04±2.74
Sulfate, mg/L	5.94±0.77	80.82±10.51
Chloride, mg/L	0.53±0.07	281.9±36.6
Phosphate, mg/L	<0.1	20.58±2.68
COD, mgO/L	3	34

2.5. Analytical methods

Water quality was analyzed using the standard methods listed in the environmental normative federal documents (Federal Center of Analysis and Assessment of Technogenic Exposure, Russia). ATZ was determined using an Agilent 1260 Infinity HPLC system with a UV detector equipped with a Zorbax SB-C18 column (4.6×150 mm). The ACN and 75 mM CH_3COOH (40:60) were used for ATZ elution. ATZ was detected at 220 nm and flow rate of 0.5 mL/min. pH was measured using a Metrohm 827 pH meter with a Primatrode NTC glass electrode (Metrohm, Switzerland). Dissolved organic carbon (DOC) was measured by TOC-L CSN (Shimadzu, Japan). The absorbance spectra of selected waters were taken using a Shimadzu UV-1800 spectrophotometer.

3. Results and discussion

Figure 1 shows the plots of ATZ destruction (C/C_0) and *E. coli* inactivation ($\text{Lg}(N/N_0)$) as a function of Q_{UVA} doses in the absence and in the presence of cells or ATZ in DW, LW and WW. In all cases, the presence of cells inhibited the rate of ATZ destruction, presumably, due to decrease of ROS effective concentrations consumed during oxidation of competing substrates – a bacterium and a chemical compound [9]. From linear plots $\text{Ln}(C/C_0)$ versus dose the pseudo-first order rate constants of ATZ destruction were calculated (Table 2).

Table 2. The rate constants (k) of ATZ degradation in the absence (–) and in the presence (+) of cells in $\{\text{Solar}/\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}\}$ system.

Water matrix	<i>E. coli</i>	$k \times 10^{-2}$ (cm^2/mJ)	R^2
DW	–	0.22	0.99
	+	0.04	0.95
NW	–	0.32	0.99
	+	0.04	0.96
WW	–	0.35	0.98
	+	0.02	0.94

The rates of ATZ destruction in the absence of *E. coli* were by one order higher than those found in presence of cells in all selected water types. In this case, the values of destruction constants in LW and WW were higher than in DW. This is probably due to higher ROS exposure in the presence of dissolved organic matter [10].

The presence of ATZ also had an inhibitory effect on *E. coli* inactivation in DW. Thus, the dose of about 2.5 and 6 kJ/L was required to reduce CFU by 2 logs (99%) in the absence and in the presence of micropollutant, respectively. There was no measurable difference between inactivation rates in LW and WW (Figure 1). In this case, the inactivation curves showed a tailing effect at a dose of about 4 kJ/L. This effect was probably associated with the absorption of photons by ATZ molecules and/or the light absorption and scattering by cells. The inactivation efficiency reached 0.5-log reduction (about 70%), then there was a rapid decrease by 1.5-logs (95%), regardless of ATZ presence in water. This is consistent with the results by Rodríguez-Chueca et al. [11], who achieved *E. coli* inactivation in WW using the photo-Fenton system {Solar/Fe²⁺/H₂O₂}, despite the complex composition of original matrix.

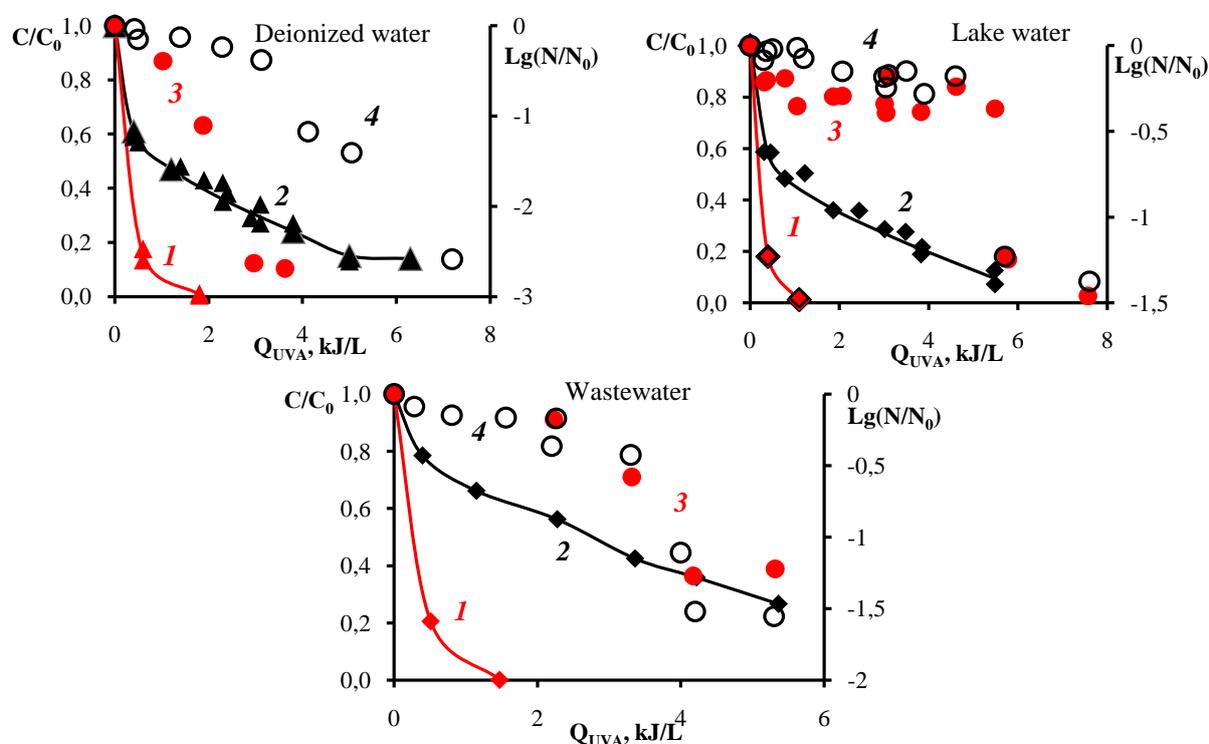


Figure 1. Destruction of atrazine and inactivation of *E. coli* in different water matrices in the absence and in the presence of cells/micropollutant in {Solar/Fe²⁺/S₂O₈²⁻} system. 1 – Atrazine, 2 – Atrazine + *E. coli*, 3 – *E. coli*, 4 – *E. coli* + Atrazine.

The accumulated solar energy doses Q_{UVA} required for 90% micropollutant destruction and 90% cells inactivation were further calculated. As can be seen from Table 3, the required Q_{UVA} doses for destructing ATZ in the absence of cells were by one order of magnitude lower than in the presence of bacteria, regardless of water type. Particularly, the highest dose of 9.2 kJ/L was needed for simultaneous treatment and disinfection of WW. Meanwhile, the doses Q_{UVA} for 90% *E. coli* inactivation (without ATZ) were up to one order of magnitude higher than those found for destructing ATZ (without cells). Unlike DW, the doses required for disinfection of LW and WW in the absence and in the presence of ATZ were similar within the same water type (Table 3).

Table 3. Q_{UVA} doses for destruction/inactivation of 90% atrazine/*E. coli* in the absence (–) and in the presence (+) of cells/micropollutant in {Solar/ $Fe^{2+}/S_2O_8^{2-}$ } system.

Substrate \ Matrix	DW	LW	WW
Atrazine	0.8	0.6	0.5
<i>E. coli</i>	2	6	4
Atrazine + <i>E. coli</i>	5.7	5.2	9.2
	4	6	4

The energy solar doses for simultaneous destruction of organic pollutant and inactivation of *E. coli* were not found in the literature. However, table 4 shows that the obtained Q_{UVA} values for simultaneous destruction and inactivation were comparable with those reported earlier for *E. coli* inactivation in other solar-based advanced oxidation processes.

Table 4. Literature data on the efficiency of solar-based advanced oxidation processes for *E. coli* inactivation in various aqueous matrices.

Water matrix	DOC ^a (mg/L)	System	N_0 (CFU/mL)	Result	Q_{UV} (kJ/L)	Reference
Natural water	0.8	{Solar/ TiO_2 }	10^4	Residual concentration <1 CFU/mL	12.5	[12]
		{Solar/ TiO_2 }	10^5	-/-	13.5-21	[13]
		{Solar/ TiO_2/Fe^{3+} }	10^4	-/-	11	
		{Solar/ H_2O_2/Fe^{3+} }	10^5	-/-	2.5, 7.5	
Distilled water	<0.5	{Solar/ TiO_2 }	10^4	3 log reduction	up to 5	[14]
Distilled water	-	{Solar/ TiO_2 }	10^6	3-5 log reduction	4-13	[15]
Synthetic wastewater	25 (DOC)	{Solar/ H_2O_2/Fe^{3+} }	10^6	6 log reduction (pH 5)	24–30 (pH 5) 2-20 (pH 3)	[11]
Real wastewater	17 (DOC)	{Solar/ H_2O_2/Fe^{3+} }	10^3	3 log reduction (pH 5)		
0.9% NaCl in distilled water	-	{Solar/ TiO_2 (P25, PC500, Ruana and Bi_2WO_6)}	10^6	100% inactivation	0,7 (P25)	[16]
					1.6 (PC500)	
					10 (Ruana) 7-12 (Bi_2WO_6)	

^a - dissolved organic carbon.

Regarding ATZ, the Q_{UV} values of 4.4 to 10.8 kJ/L for DW treatment were previously reported for {Solar/ TiO_2 } and {Solar/ H_2O_2/Fe^{2+} } systems, respectively [17]. It should be noted, that the obtained solar energy doses for ATZ destruction without *E. coli* in the ferrous-persulfate system were up to one order lower than those presented in Table 4.

4. Conclusions

The combined method of simultaneous destruction of micropollutants and inactivation of pathogenic microorganisms in the ferrous-persulfate system, activated with natural solar radiation, was proposed. We suppose that this method is energy-efficient for simultaneous water treatment and disinfection.

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