Comparison of UV Fluences (365 nm) for Water Treatment by Photo-Fenton-Like Process

G. Matafonova(✉), S. Popova, I. Tsenter, N. Garkusheva, and V. Batoev

Baikal Institute of Nature Management SB RAS, 6 Sakhyanovoy St, Ulan-Ude 670047, Russia
ngal@binm.ru

Abstract. The integration of water treatment and disinfection processes is beneficial for reducing energy requirements. The photo-Fenton-like process using UVA light-emitting diode (365 nm) and peroxydisulfate (PDS) was investigated in terms of light fluence (dose) requirements for concurrent degradation of 20 μM emerging organic contaminant (bisphenol A) and inactivation of 10^5 CFU/mL bacteria (*E. coli* and *E. faecalis*) in aqueous solution. The photo-Fenton-like oxidation system {UVA/PDS/Fe^{2+}} was the most efficient for degrading bisphenol A without co-existing bacteria and inactivation of *E. faecalis* in the absence of bisphenol A. The highest UV fluences of up to 5.7 J/cm^2 were obtained for 90% degradation of bisphenol A in the presence of bacteria. These fluences concurrently inactivated 100% co-existing bacterial cells due to their lower fluence requirements for total inactivation (up to 2.1 J/cm^2). The lowest fluences were needed for total inactivation of *E. coli* regardless of the presence of bisphenol A (~1 J/cm^2). The obtained fluences are comparable with the literature values for separate degradation or inactivation by other photo-induced advanced oxidation processes at 365 nm. Results show the feasibility and energy-efficiency of the integrated processes for efficient elimination of both chemical and biological contaminants from water.

Keywords: Photo-Fenton-like process · UV LED · Persulfate · Water treatment · Degradation · Inactivation

1 Introduction

Pollution of aquatic ecosystems with emerging organic contaminants and pathogenic microflora is of a global environmental concern. To date, advanced oxidation processes (AOPs) are regarded as one of the most efficient means of removing them from wastewater effluents and reducing their level in water bodies. Specifically, the homogenous photo-Fenton-like processes have attracted a significant research attention for water treatment and disinfection. Peroxydisulfate ($S_2O_8^{2-}$, PDS) and ferrous (Fe^{2+}) ions are efficient and environmentally friendly reagents for producing hydroxyl radicals (•OH) and sulfate radical anions (SO_4•$^-$) in water through Fenton-like reactions (1–5):

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4 \bullet^- + SO_4^{2-} \quad (1)$$

A. A. Radionov et al. (eds.), *Proceedings of the 5th International Conference on Construction, Architecture and Technosphere Safety*, Lecture Notes in Civil Engineering 168,
https://doi.org/10.1007/978-3-030-91145-4_44

$$SO_4\bullet^- + H_2O \rightarrow \bullet OH + HSO_4^- \quad (2)$$

$$SO_4^{2-} + \bullet OH \rightarrow SO_4\bullet^- + OH^- \quad (3)$$

$$Fe^{3+} + S_2O_8^{2-} \rightarrow Fe^{2+} + 2SO_4\bullet^- \quad (4)$$

$$Fe^{2+} + SO_4\bullet^- \rightarrow Fe^{3+} + SO_4^{2-} \quad (5)$$

Ultraviolet (UV) light is employed for activating peroxydisulfate and enhancing the production of $SO_4\bullet^-$ (6):

$$S_2O_8^{2-} \xrightarrow{UV} 2SO_4\bullet^- \quad (6)$$

The radicals can be used for concurrent water treatment and disinfection due to their dual ability of degrading organic contaminants and inactivating microbial cells. The integration of degradation and inactivation processes is beneficial for reducing the total energy consumption. Over the last few years, there has been a growing research interest in concurrent removal of organic contaminants and pathogenic microorganisms from water and wastewater by different AOPs. Most works focused on the solar-assisted photo-Fenton processes using hydrogen peroxide [1–5]. Regarding photo-Fenton-like processes, recent research showed that the addition of Fe^{2+}, PDS or peroxymonosulfate significantly enhanced the solar degradation of organic contaminants and inactivation of microorganisms in drinking water under mild conditions [6, 7]. It should be pointed out that the target organic pollutants and microorganisms were not treated in a mixture in the above investigations. However, under optimized operating conditions, the photo-Fenton-like treatment with low-pressure mercury lamp (254 nm) provided the concurrent removal of bacteria and organic contaminants from urban wastewater [8].

Meanwhile, switching to energy-efficient and mercury-free light sources, such as UVA/visible light-emitting diodes (LED), is crucial to saving energy and supporting the Minamata Convention on Mercury (2013). To date, UVA diodes (315–400nm) have become rather cost-effective and have a relatively high wall-plug-efficiency [9]. Recently, it was found that the photo-Fenton process with UVA LED was efficient for elimination of propranolol and bacteria from agricultural effluents [10]. However, the photo-Fenton-like systems using PDS towards concurrent degradation and inactivation remain less investigated. Moreover, the energy requirements in terms of light fluences (doses) have been rarely reported in the related literature.

This study aimed at calculating and comparing the UV fluences for degradation of endocrine disrupting compound bisphenol A (BPA) and inactivation of bacteria *Escherichia coli* and *Enterococcus faecalis* in the photo-Fenton-like system {UVA/PDS/Fe^{2+}} using UVA LED (365 nm).

2 Materials and Methods

Bisphenol A (99%, Sigma-Aldrich), potassium peroxydisulfate (Vekton, Russia), iron (II) sulfate and sulfuric acid (Khimreaktivsnab, Russia) were used as received. All

stock and working solutions were prepared in MilliQ-water (Simplicity®UV system, Millipore). The solvents acetic acid and acetonitrile for HPLC were supplied by Khimreaktivsnab and Cryochrom (Russia), respectively.

The stock suspensions of *E. coli* K-12 and *E. faecalis* B 4053 strains (SRIGSIM, Russia) were prepared from the overnight cultures after centrifugation, double washing out and resuspension in phosphate buffered saline (Gibco® Life technologies, UK). The overnight cultures were grown by aerobic incubation in nutrient broth (SRCAMB, Russia) and tryptic soy broth (Merck), respectively.

Experiments were conducted in a thermostabilized glass photoreactor under magnetic stirring. A UVA LED array (Yonton, 100 W, China) was positioned above the open reactor and also thermostated by a circulating water. The LED emission spectrum with a maximum at 365 nm is shown in Fig. 1.

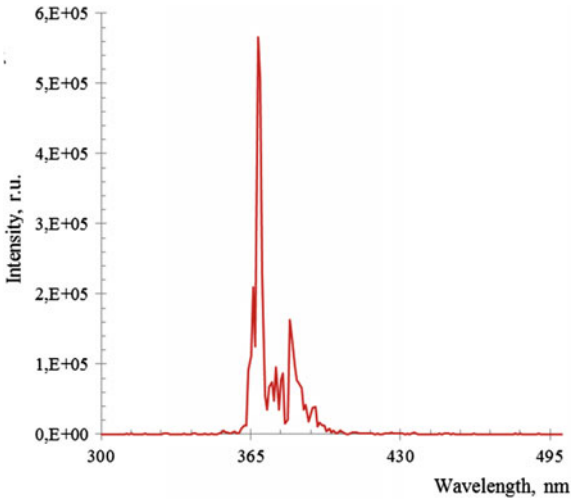

Fig. 1 Emission spectrum of UVA LED (365 nm)

The incident irradiance (at the surface of the sample), measured with a polychromatic ferrioxalate actinometry [11–14], was 2.46 mW/cm^2 over the 300–400 nm range. The model aqueous solution, contaminated with 20 μM BPA and/or 10^5 CFU/mL *E. coli* (*E. faecalis*), was irradiated by UVA LED in the photo-Fenton-like system at pH 5.0 in the presence of PDS and Fe^{2+} ions. Control experiments were performed under sole UVA irradiation, UVA/PDS and PDS/Fe^{2+} (dark) treatments. To monitor the degradation and inactivation kinetics, the samples were taken at selected times and analyzed by HPLC (BPA) and plating technique (bacteria) for residual concentrations and counts of survived cells, respectively. The BPA analysis details were described previously [15].

The absorbance spectra for fluence calculations were measured using a Shimadzu UV-1800 spectrophotometer. The fluences were calculated as the product of the average irradiance throughout the water volume (mW/cm^2) and the corresponding treatment times (s). In turn, the calculation of average irradiance accounted for the water absorbance and the relative emission spectrum of the LED across the UVA spectrum [16].

3 Results and Discussion

Initially, the efficient Fe^{2+} dosage was selected in the photo-Fenton-like system {UVA/PDS/Fe^{2+}} by varying the molar ratios at a fixed PDS concentration of 84.5 mg/L (312.5 μM) [17]. The obtained plots of BPA degradation showed that the measurable kinetics was observed at the lowest tested Fe^{2+} concentration of 1 mg/L (17.4 μM) (Fig. 2). Therefore, a molar ratio of 18:1 (312.5 μM PDS: 17.4 μM Fe^{2+}) was used in further experiments.

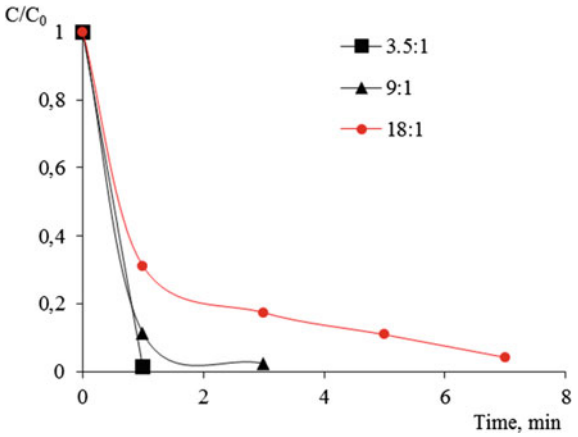

Fig. 2 The plots of bisphenol A degradation by photo-Fenton-like process at different molar ratios of PDS and Fe^{2+}. $[BPA]_0 = 20$ μM, $[PDS]_{fixed} = 312.5$ μM, $[Fe^{2+}]_{variable} = 17.4$ μM (18:1), 34.7 μM (9:1), 89.3 μM (3.5:1), pH = 5.0

Further on, degradation experiments were conducted in the oxidation systems, namely, {UVA} (direct photolysis), {PDS/Fe^{2+}} (dark Fenton-like), {UVA/PDS} and {UVA/PDS/Fe^{2+}}, and the obtained plots are shown in Fig. 3. BPA with two absorption spectrum peaks at 225 and 276 nm was not photolyzed by sole UVA irradiation. Addition of peroxydisulfate lead to generation of $SO_4^{\bullet-}$ and complete BPA degradation in 30 min ($k_{BPA,\ SO4^{\bullet-}} = 1.37 \times 10^9$ [18]). The highest degradation rate was observed in the UVA/PDS/Fe^{2+} system, which was 3.7 times higher than that found in the UVA/PDS system. Dark treatment (PDS/Fe^{2+}) resulted in removing approximately 30% by the Fenton-like reaction.

The experiments on BPA degradation in the presence of bacteria were conducted in the most efficient UVA/PDS/Fe^{2+} system. The pseudo-first-order fluence-based rate constants, which were obtained from the corresponding fluence-based linear plots (not shown), are given in Table 1. Evidently, the degradation rates significantly decreased after adding bacteria. This is consistent with the literature data on inhibition effect of co-existing microorganisms on the degradation of organic contaminants at relatively high initial concentrations at mg/L level [19–23]. These organic substrates are competed with each other for •OH and $SO_4^{\bullet-}$, thereby decreasing the radical levels and exposures.

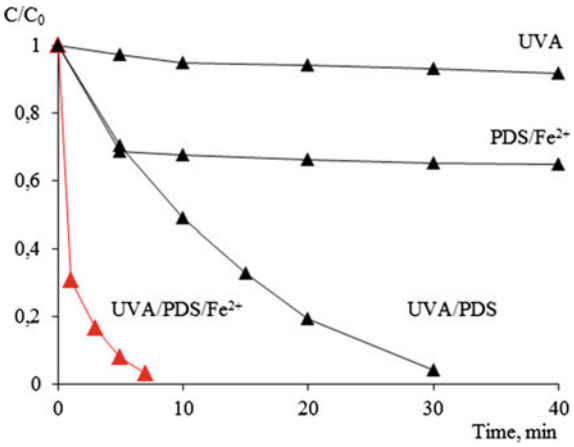

Fig. 3 The plots of bisphenol A degradation in different oxidation systems without co-existing bacteria. $[BPA]_0 = 20$ μM, $[PDS]:[Fe^{2+}] = 18:1$, pH = 5.0

Table 1 The fluence-based rate constants (k) of bisphenol A degradation by photo-Fenton-like process. $[BPA]_0 = 20$ μM, $[Bacteria]_0 = 10^5$ CFU/mL, pH = 5.0

System	$k \times 10^{-2}$ (cm^2/mJ)	R^2
UVA/PDS/Fe^{2+}	0.27	0.99
UVA/PDS/Fe^{2+} + *E. coli*	0.05	0.98
UVA/PDS/Fe^{2+} + *E. faecalis*	0.04	0.95

Additionally, the sorption of compound molecules onto bacterial cells also contributes to the inhibition. This was supported by control experiment (BPA + bacteria), which showed 8–12% BPA decay in 20 min stirring without any exposure.

The UV fluences required for 90% degradation were determined from the corresponding fluence-based constants. As shown in Fig. 4, the fluences for BPA removal in the presence of *E. coli* or *E. faecalis* are expectedly higher than those obtained without bacteria, increasing to 5.7 J/cm^2.

Mostly, the obtained UV fluences were within the range of the previously reported values for degrading organic contaminants by UV_{365}-induced AOPs. Specifically, the fluences for degrading BPA (along with other emerging contaminants) by LED/NO_2^- and crotamiton by UVA/Fe^{III}-NTA/Oxone were 3.66 [24] and 3.9 J/cm^2 [25], respectively. LED/Chlorine treatment required 1.9 J/cm^2 for removing 96% acetaminophen [26]. Other literature fluences, which were estimated by multiplying the given irradiance by irradiation time, reached 9.4 J/cm^2 for degrading acetamiprid by LED/Fenton [27] and varied in the range of 30.6–122.4 (60–240 min) for decomposing *p*-hydroxybenzoic acid by LED/TiO_2 process [28]. Another estimated fluence of 2.36 J/cm^2 (0.15 kJ) was also reported for photocatalytic elimination of sulfamethoxazole, oxytetracyline and 17-α-Ethynylestradiol [29].

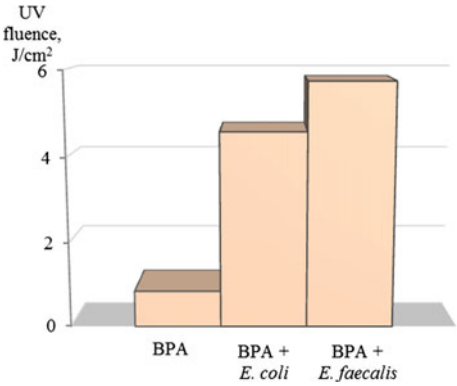

Fig. 4 The UV fluences required for 90% degradation of bisphenol A with and without co-existing bacteria by photo-Fenton-like process. $[BPA]_0 = 20$ μM, $[Bacteria]_0 = 10^5$ CFU/mL, pH = 5.0

Unlike degradation, the plots of *E. coli* and *E. faecalis* inactivation did not follow the pseudo-first-order kinetics and some exhibited the lag time, during which no measurable inactivation was observed. Comparing the inactivation rates by sole UVA, UVA/PDS, PDS/Fe^{2+} and target UVA/PDS/Fe^{2+} processes, the latter was the fastest for total inactivation of *E. faecalis* (10 min). Its efficiency for *E. coli* was similar to the UVA/PDS treatment, achieving the total inactivation in 7 min by both processes. This suggests the predominant contribution of high-intensity UV radiation to inactivation of gram-negative *E. coli*, which is more sensitive to UV light than gram-positive *E. faecalis*. Indeed, *E. coli* was inactivated faster than *E. faecalis* under sole UVA irradiation (10 versus 20 min). Dark treatment (PDS/Fe^{2+}) did not cause a measurable inactivation of both species.

When BPA was present in the solution, the inactivation rates also decreased that support the statement of competition for radicals between co-existing chemical compounds and microorganisms (Fig. 5). Notably, the inhibition effect of BPA was more pronounced during *E. faecalis* inactivation.

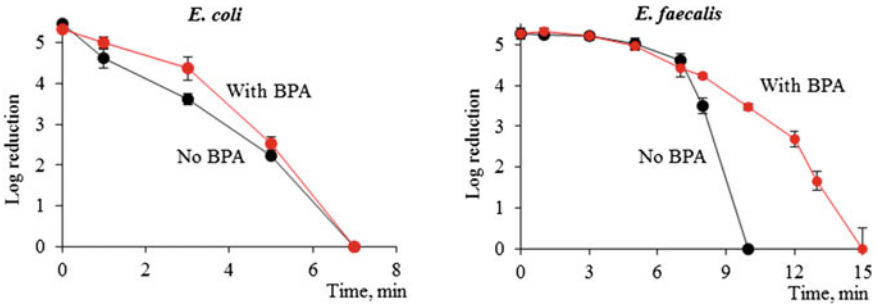

Fig. 5 The plots of *E. coli* and *E. faecalis* inactivation with and without co-existing bisphenol A by photo-Fenton-like process. $[BPA]_0 = 20$ μM, $[Bacteria]_0 = 10^5$ CFU/mL, [PDS]:[Fe^{2+}] = 18:1, pH = 5.0

The UV fluences required for total (100%) bacterial inactivation are depicted in Fig. 6.

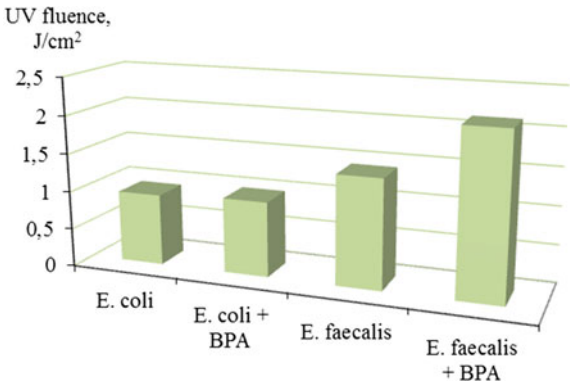

Fig. 6 The UV fluences required for 100% inactivation of *E. coli* and *E. faecalis* with and without bisphenol A by photo-Fenton-like process. $[BPA]_0 = 20$ μM, $[Bacteria]_0 = 10^5$ CFU/mL, pH = 5.0

Overall, the UV fluences for *E. faecalis* were higher and reached 2.1 J/cm^2. The concurrent presence of organic contaminant prolonged the total inactivation and increased the final fluence by ~30%. Since BPA did not cause the significant inhibition of *E. coli* inactivation, the corresponding fluence was the same regardless of co-existing contaminant (~1 J/cm^2, 7 min). The obtained fluences are substantially lower that those reported in the literature with UVA LED alone. However, only a few studies reported the UV fluences at 365 nm for microbial inactivation by photo-based AOPs. Specifically, the fluences of 0.688–0.870 and 0.105 J/cm^2 were needed to attain 3-log [30] and 0.4-log reductions of *E. coli* by UVA/TiO_2 treatment [31]. The reported values are comparable with the obtained fluences for *E. coli*. Overall, the UV fluences for total inactivation of *E. coli* and *E. faecalis* are considerably lower than those found for BPA degradation.

4 Conclusions

The homogenous photo-Fenton-like process using UVA LED and peroxydisulfate is efficient towards the concurrent degradation of BPA and inactivation of *E. coli* and *E. faecalis* in model aqueous solution. Although the degradation rates substantially decreased in the presence of bacteria, the required fluences (doses) are comparable with the previously reported values for degradation of organic contaminants by other UV_{365}-based advanced oxidation processes without any co-existing microorganisms. The UV fluences required for degradation of 90% BPA in the presence of bacterial cells provide their concurrent inactivation. In this regard, degradation and inactivation in a single treatment step appear to be a promising energy-effective process for further up-scaling.

Acknowledgements. The authors thank Dr. Sara Beck for methodological help and fruitful discussions. This research was conducted within the frame of the Basic Research Program of Baikal

Institute of Nature Management SB RAS (Project No. 0273-2021-0006) using the equipment of CCU BINM SB RAS (Ulan-Ude, Russia).

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