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To cite this article: M S Khandarkhaeva *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **272** 022080

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# Photochemical Degradation of Micropollutants in Aqueous Media

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**Abstract.** Natural sunlight was employed to enhance degradation of micropollutants in a Fenton-like oxidative system involving persulfate as the oxidant and ferrous iron (Fe(II)) as the catalyst  $\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}/\text{Solar}$ . Experiments were carried out in a bench-scale compound parabolic collector (CPC) and a batch photoreactor. The micropollutants tested were *p*-chlorophenol, atrazine, and triclosan. The reaction rates and degree of micropollutant degradation increased in the order:  $\{\text{Solar}\} < \{\text{S}_2\text{O}_8^{2-}/\text{Solar}\} < \{\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}\} \ll \{\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}/\text{Solar}\}$ . It was proven that photocatalytic oxidation activated by solar radiation leads not only to complete degradation of micropollutants, but also to substantial drops in levels of total organic carbon in the solution (i.e. leads to mineralization). Based on the results, a method of deep degradation of toxic organic pollutants based on the solar photo-Fenton process  $\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}/\text{Solar}$  was suggested.

## 1. Introduction

In recent years, a lot of research is done on the advanced oxidation processes (AOPs) that can be driven by solar radiation [1-9]. The AOPs are based on radical chain oxidation of organic contaminants by *in situ* generated reactive oxygen species. The oxidative processes have been shown to be promising in water/wastewater treatment [10].

Recently, the use of persulfate as an oxidant in AOPs has drawn a lot of attention [11-14]. Persulfate is a strong non-selective oxidant effective within a wide range of pH. Besides, the activated persulfate yields sulfate anion radical that is even a stronger oxidant than persulfate itself. Persulfate can be activated by reactions with transition ion metals ( $\text{Fe}^{2+}$ ,  $\text{Cu}^+$ , etc.), as well as by exposure to UV, ultrasound, high temperature, etc. Among the reactive oxygen species derived from peroxo- compounds (oxygen peroxide and persulfate), hydroxyl and sulfate anion radicals are the two strongest oxidants (Table 1) [11, 15, 16].

Iron compounds are commonly used to activate persulfate and can be regarded as environmentally friendly catalysts as redox reactions of iron are widespread in natural ecosystems. The oxidation reactions involving ferrous ion and persulfate  $\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}$  are often called "Fenton-like" due to similarities in the mechanism with the original Fenton reaction  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ . In such reactions, concentration of  $\text{Fe}^{2+}$  decreases over time leading to lower reaction rates, even though the oxidant might be present in the solution. One of the ways to regenerate  $\text{Fe}^{2+}$  is to reduce  $\text{Fe}^{3+}$  by subjecting the reaction medium to UV [17]. The use of



natural sunlight to enhance efficiency of Fenton-like reactions could be more attractive than the use of electricity powered UV light from an energy-efficiency as well as environmental perspective [18].

**Table 1.** Standard electrode potentials of some oxidizing species.

Oxidant	E <sup>0</sup> (V)
Hydroxyl radical	2.8
Sulfate anion radical	2.5-3.1
Atomic oxygen	2.42
Ozone	2.06
Persulfate	2.01
Hydrogen peroxide	1.78
Hypochlorite	1.49
Chlorine dioxide	1.27
Oxygen	1.23

The aim of the study was to assess the feasibility of using natural sunlight to enhance Fenton-like oxidative system based on persulfate and ferrous ion  $\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}/\text{Solar}$ . The solar-enhanced Fenton-like oxidative system was used to oxidize three micropollutants - *p*-chlorophenol, atrazine and triclosan.

## 2. Materials and Methods

The model compounds used in the experiments were *p*-chlorophenol (99%, Merck), atrazine (98%, Sigma Aldrich); triclosan (99.8 %, Irgasan Sigma Aldrich). In degradation experiments, potassium peroxodisulfate and iron sulfate (II) were used. Methanol and *tert*-butyl alcohol were used as scavengers of free radicals. All stock solutions were prepared using deionized water (Simplicity<sup>®</sup>UV, Millipore). pH was adjusted using 1% solutions of  $\text{H}_2\text{SO}_4$  and NaOH.

Concentrations of models compounds were monitored by HPCL (chromatograph Agilent 1260 Infinity with a diode-array UV detector and Zorbax SB-C18 column). The extent of mineralization of the target compounds was assessed by changes in total organic carbon (TOC) content measured using Shimadzu TOC-L CSN.

Field experiments were conducted during summer of 2017 in Ulan-Ude city, Russia (51°48'47.747''N 107°7'19.536''E). The intensity of solar radiation was measured using radiometers "TKA-PKM" ("TKA Scientific instruments").

A bench-scale photoreactor unit was built for experiments on degradation of micropollutants using solar radiation (Figure 1).



**Figure 1.** A bench-scale photoreactor unit used in the study

In the unit, solar radiation is collected (concentrated) by parabolic reflector surface and directed onto the photoreactor made of quartz tubes connected in a sequence. The aqueous test solutions were pumped through the quartz tubes at a flow rate of 1 L/min. The total volume of the treated solution was 1 L.

### 3. Results and discussion

The model compound *p*-chlorophenol was subjected to different treatments, including exposure to sunlight only Solar, dark Fenton-like process  $\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}$ , combined persulfate and sunlight exposure  $\text{S}_2\text{O}_8^{2-}/\text{Solar}$ , and a combination of a Fenton-like process and sunlight exposure  $\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}/\text{Solar}$  (Table 2).

**Table 2.** Initial reaction rates, rate constants, half-lives and extent of *p*-chlorophenol degradation as a result of oxidative treatments.  $[p\text{-CP}]_0 = 156 \mu\text{M}$ ,  $[\text{Fe}^{2+}]_0 = 89 \mu\text{M}$ ,  $[\text{S}_2\text{O}_8^{2-}]:[p\text{-CP}] = 5:1$ ,  $\text{pH} = 5.4 \pm 0.2$

Oxidative treatment	$W_0$ , ( $\mu\text{M min}^{-1}$ )	Degradation* (%)	$K$ ( $\text{min}^{-1}$ )	$\tau_{1/2}$ (min)
<b>Solar</b>	0.20	3	0.001	693
<b><math>\text{S}_2\text{O}_8^{2-}/\text{Solar}</math></b>	0.48	8	0.002	330
<b><math>\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}</math></b>	1.76	23	0.013	54
<b><math>\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}/\text{Solar}</math></b>	6.95	90	0.094	7.36

\* – after 20 min of treatment

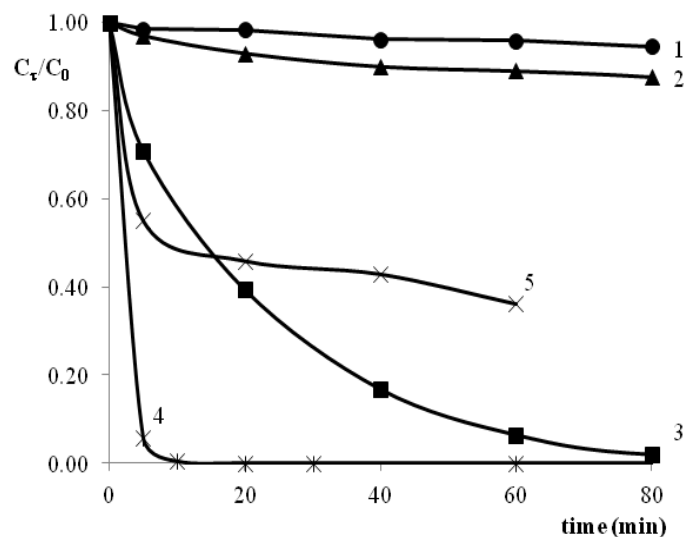
Virtually no oxidation of *p*-chlorophenol was observed in the processes without the catalyst  $\text{Fe}^{2+}$ . When  $\text{Fe}^{2+}$  was present but there was no sunlight exposure (i.e. dark reaction), the reaction rate of *p*-chlorophenol degradation increased at the beginning but then leveled off and did not increase further. When a Fenton-like process and sunlight exposure  $\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}/\text{Solar}$  were applied, the rate of *p*-chlorophenol degradation was 3.5 times higher than during the Fenton-like process alone, i.e. without sunlight exposure  $\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}$  (Table 2). The reaction rate constant  $k$  and half-life  $\tau_{1/2}$  of *p*-chlorophenol calculated for the solar-enhanced reaction were  $0.094 \text{ min}^{-1}$  and 7.36 min, respectively. Furthermore, the content of total organic carbon (TOC) in the solution had fallen to about 60% of its original level, the extent of mineralization thus being about 40%.

Direct photolysis of atrazine under sunlight is apparently a slow process (Figure 2).

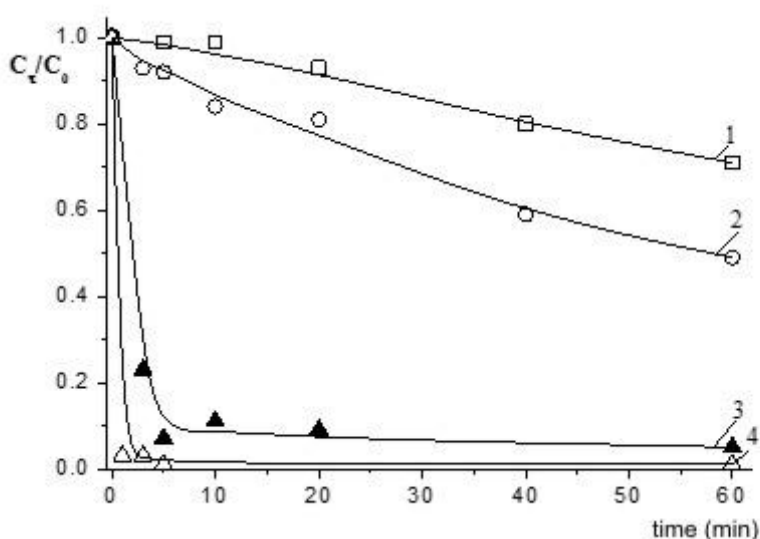
About 12% of atrazine was degraded after 60 min of treatment. Additional sunlight exposure resulted in an additive effect and atrazine degradation rate reached 20% after 60 min of treatment. As with the previous model compound, the best results were obtained when atrazine was treated with  $\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}/\text{Solar}$  system.

Triclosan was found to adsorb onto inner surfaces of the compound parabolic collector (presumably onto the PVC fittings connecting quartz tubes). Therefore experiments on triclosan oxidation were carried out in a batch reactor. The results are shown in Figure 3.

Exposure to sunlight only resulted in degradation of 50 % of triclosan after 1 hour of exposure. The addition of the oxidant had not significant impact on the oxidation process (curves 1, 2 in Figure 3). When treated with  $\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}$  (i.e. dark Fenton-like process), oxidation of 90% of triclosan was achieved after 5 min of treatment. However, further treatment did not lead to further oxidation. The main product of triclosan degradation identified at this stage using HPLC was 2,4-dichlorophenol. During the solar-enhanced Fenton-like process  $\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}/\text{Solar}$ , triclosan degradation rate was higher and 100% degradation was achieved. The main products of triclosan breakdown were aliphatic acids.



**Figure 2.** Kinetic curves of atrazine degradation during treatment with the following: 1- $\text{S}_2\text{O}_8^{2-}$ ; 2-Solar; 3-  $\text{S}_2\text{O}_8^{2-}$ /Solar; 4-  $\text{Fe}^{2+}$ /  $\text{S}_2\text{O}_8^{2-}$ /Solar; 5 –  $\text{Fe}^{2+}$ /  $\text{S}_2\text{O}_8^{2-}$ .  $[\text{ATZ}]_0=18.5 \mu\text{M}$ ;  $[\text{S}_2\text{O}_8^{2-}]=0.78 \text{ mM}$ ;  $[\text{Fe}^{2+}]=89 \mu\text{M}$ .



**Figure 3.** Kinetic curves of triclosan degradation during treatment with the following: 1- {Solar}; 2 -  $\{\text{S}_2\text{O}_8^{2-}/\text{Solar}\}$ ; 3 –  $\{\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}\}$ ; 4 –  $\{\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}/\text{Solar}\}$ .  $[\text{TCS}]_0=13.8 \mu\text{M}$ ;  $\text{Fe}^{2+}=89 \mu\text{M}$ ;  $[\text{S}_2\text{O}_8^{2-}]:[\text{TCS}]=42.1:1$ ;  $\text{pH}=5.8$

For all the tested micropollutants the degradation reaction rates and extent of degradation increased in the order: {Solar} <  $\{\text{S}_2\text{O}_8^{2-}/\text{Solar}\}$  <  $\{\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}\}$  <<  $\{\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}/\text{Solar}\}$ . The extent of oxidative degradation was very low in treatments without the catalyst. In treatments involving the catalyst but without sunlight exposure (i.e. dark reaction), the reaction rates decreased over time. The decline in the

degradation rate is due to consumption of  $\text{Fe}^{2+}$ , which catalyzes radical formation from  $\text{S}_2\text{O}_8^{2-}$ , along the process and its slow regeneration (reactions 1 and 2)



In order to assess the roles of  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  radicals during treatments with  $\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}/\text{Solar}$ , the radical scavengers methanol and *tert*-butyl alcohol were used. The inhibition of radical chain reactions is widely used to ascertain the involvement of free radicals in oxidation processes [19]. Based on the reaction rates of different radicals with a radical scavenger, it is possible to evaluate the radical's contribution to an oxidation process. For example, the rate constant of the reaction between methanol and  $\text{SO}_4^{\cdot-}$  radical is  $1.6 \div 7.7 \times 10^7 \text{ L} \cdot \text{mol}^{-1} \text{ s}^{-1}$ , while the rate constant of the reaction between methanol and  $\cdot\text{OH}$  radical is about 5 times higher –  $1.2 \div 2.8 \times 10^8 \text{ L} \cdot \text{mol}^{-1} \text{ s}^{-1}$ . For *tert*-butyl alcohol, the rate constants for its reactions with  $\cdot\text{OH}$  and  $\text{SO}_4^{\cdot-}$  are  $3.8 \div 7.6 \times 10^8 \text{ L} \cdot \text{mol}^{-1} \text{ s}^{-1}$  and  $4.0 \div 9.1 \times 10^5 \text{ L} \cdot \text{mol}^{-1} \text{ s}^{-1}$ , respectively [20]. It is obvious that methanol would react with both  $\cdot\text{OH}$  and  $\text{SO}_4^{\cdot-}$ , while *tert*-butyl alcohol would react predominantly with  $\cdot\text{OH}$ . In our experiments, the addition of methanol led to significantly lower atrazine degradation rates. After 60 min of treatment, the degradation extent of atrazine was 35 % in the presence of methanol and 56 % in the presence of *tert*-butyl alcohol. The results indicate that both  $\cdot\text{OH}$  and  $\text{SO}_4^{\cdot-}$  are involved in the oxidative system  $\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}/\text{Solar}$ , with  $\text{SO}_4^{\cdot-}$  being more dominant. The results agree well with the literature data on peroxodisulfate-involved oxidation of carbamazepine [21], erythromycin [22] and ciprofloxacin [23, 24].

#### 4. Conclusions

The use of solar radiation in combination with the Fenton-like oxidative system  $\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}/\text{Solar}$  greatly enhances the efficiency of the oxidative system. The reaction rates and degree of micropollutant degradation increases in the order:  $\{\text{Solar}\} < \{\text{Solar}/\text{S}_2\text{O}_8^{2-}\} < \{\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}\} \ll \{\text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}/\text{Solar}\}$ . The combination of solar radiation and the Fenton-like process holds promise as an environmentally-friendly way to supplement conventional treatment methods. The oxidative processes warrant further research, particularly on the application of the approach for treatment of complex matrices like real wastewater and technical and economic feasibility of scaling up.

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### Acknowledgements

This work was conducted under the Program of Basic Research of SB RAS № 007-00207-18-00.