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Oxidative degradation of diclofenac by thermally activated persulfate: implication for ISCO

Jiabin Chen[1] · **Yajie Qian**[2] · **Hongmei Liu**[2] · **Tianyin Huang**[1]

Abstract Diclofenac (DCF), one of the typically recalcitrant pharmaceuticals, has been frequently detected in groundwater in recent years. This work investigated the performance of DCF degradation by thermally activated persulfate (PS) to further understand its application in in situ chemical oxidation (ISCO) for DCF-contaminated groundwater. The effects of various factors, including activation temperature, solution pH, PS/DCF ratio, and common constitutes, e.g., HCO_3^-, Cl^- and humic acid, and the toxicity of transformation products were evaluated. The results indicated that the oxidation of DCF was well-fitted with a pseudo-first-order kinetic model, and the rate constants increased with the elevated temperatures. The rate constants from 50–70 °C were further fitted to the Arrhenius equation, yielding an activation energy of 157.63 kJ·mol^{-1}. In addition, the oxidation of DCF was highly pH-dependent, with the rate constants rapidly decreased from pH 5 to 7, then slightly increased at the alkaline pH. The presence of a low dosage of Cl^- (0–10 mM) promoted the degradation of DCF, whereas high Cl^- addition (>10 mM) inhibited DCF degradation. HCO_3^- exhibited a negligible effect on DCF removal, while natural organic matters, e.g., humic acids, lightly inhibited DCF degradation. The rapid degradation of DCF was also confirmed in the real groundwater sample, which might be attributed to the pH drop during the reaction. Moreover, the radical quenching experiments revealed that sulfate radicals ($SO_4^{\cdot-}$) was the dominant reactive species for DCF oxidation. Finally, the acute toxicity of the DCF solution, as tested with a bioluminescent assay, was gradually decreased during the reaction, indicating that a thermally activated PS oxidation was a promising alternative approach for DCF-contaminated groundwater remediation.

Introduction

In recent decades, the occurrence of pharmaceutically active compounds (PhACs) in the environment has attracted a worldwide concern due to their continuous discharge and potential toxic effect on aquatic organisms and human health (Daughton and Ternes 1999). Diclofenac (DCF, sodium 2-[2-(2,6-dichloroanilino)phenyl]acetate) is one of the most frequently administered non-steroidal anti-inflammatory drugs (NSAIDs), with global consumption estimated at 940 tons per year (Zhang et al. 2008). DCF was resistant to biodegradation in the activated sludge process, which was the most commonly used process in wastewater treatment plants (WWTPs). Hence, a substantial amount of DCF escaped from these WWTPs, and has subsequently entered into the receiving water environment (Chen et al. 2014). DCF has been detected in sewage effluent, surface water, groundwater, and

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✉ Jiabin Chen
chenjiabincn@163.com

✉ Tianyin Huang
huangtianyin111@163.com

1 School of Environmental Science and Engineering, Suzhou University of Science and Technology, Suzhou 215001, People's Republic of China

2 College of Environmental Science and Engineering, Tongji University, Shanghai 200092, People's Republic of China

drinking water at concentrations ranging from ng/L to µg/L, and identified as one of the priority pharmaceuticals in the water environment (Chen et al. 2014; Sui et al. 2012). In Europe, DCF was also frequently detected in groundwater at concentrations ranging from 2 to 380 ng/L (Grundwasser et al. 1998; Heberer 2002; Rabiet et al. 2006), which might be indirectly exposed to humans when groundwater was taken as a drinking water source. Although DCF at environmental concentrations could not induce lethal effects on organisms, chronic toxicity was still possible. For example, DCF caused cytological changes of brown trout, and damaged the renal function of rainbow trout (Chen et al. 2012). Therefore, it is imperative to explore the methods of removing DCF from groundwater.

In situ chemical oxidation (ISCO) has become a promising technology for the remediation of contaminated groundwater. ISCO is always conducted by injecting oxidants, e.g., ozone, hydrogen peroxide, permanganate, and persulfate (PS), to the contaminated zone (Seol et al. 2003). Among the various ISCO processes, activated PS is the newest and least understood technology, receiving increasing attentions (Tsitonaki et al. 2010). Besides its strong redox potential (E^0=2.01 V), PS is highly soluble, moderately stable in the subsurface environment, and potentially transported from the injection point to the contaminated zone in the field sites (Liu et al. 2012). Although PS is a strong oxidant, it is usually activated by heat (Mora et al. 2011), UV (Wang and Liang 2014), base (Furman et al. 2010), and transition metal ions (Han et al. 2014; Liu et al. 2014), to form sulfate radicals ($SO_4^{\cdot-}$, E^0=2.6 V), which is highly reactive to most of the contaminants with second-order kinetic rate constants ranging from 10^7 to 10^{10} M^{-1} s^{-1} (Neta et al. 1988). Mahdi Ahmed et al. (2012) investigated the reactivity of DCF with $SO_4^{\cdot-}$ generated by Co(II) activated peroxymonosulfate (PMS), mainly focusing on the transformation kinetics and pathways of DCF during the reaction. Deng et al. (2013b) studied the degradation of DCF by $SO_4^{\cdot-}$ generated from PMS activated by $CoFe_2O_4$ magnetic nanoparticles, aiming at evaluating the performance of the magnetic nanomaterials on activation of PMS. Although the previous studies demonstrated a high reactivity of $SO_4^{\cdot-}$ towards DCF, research gaps still exist and need to be further explored. For example, $SO_4^{\cdot-}$ were generated from the activated PMS in the previous studies, instead of activated PS. In fact, PS is more practical and widely used in ISCO. Moreover, the effect of background ions in groundwater should be evaluated, due to their possible interference on the reactivity of $SO_4^{\cdot-}$ towards contaminant (Liang et al. 2006). Finally, toxicity assessment needs to be conducted to evaluate the toxicity of transformation products.

Thermally activated PS was reported to be a prominent alternative for degradation of recalcitrant contaminants, such as azo dye (Yang et al. 2010), TCE (Liang et al. 2003), PCB (Yukselen-Aksoy et al. 2010), perfluorooctanoic acid (Hori

et al. 2008; Lee et al. 2012) and so on. The temperature and reaction rates were found to obey the Arrhenius equation; thus, the degree of impact on the oxidation rate for each target contaminant depended on thermodynamic properties unique to each contaminant (Tsitonaki et al. 2010). Thermally activated PS process was significantly affected by the properties of the aqueous matrix. For example, the matrix pH could influence the distribution and concentration of radical species, thus affecting the contaminant degradation (Liang and Su 2009). The background ions, e.g., Cl^- and HCO_3^- could compete with target contaminants for a reaction with radicals. Therefore, the influence of the aqueous matrix should also be considered when applying thermally activated PS in practice (Gu et al. 2011). In this work, we investigated the oxidative degradation of DCF by thermally activated PS, aiming at providing an insight into the feasibility of thermally activated PS for the remediation of DCF-contaminated groundwater. Firstly, kinetic parameters and the activation energy of DCF degradation were determined. Furthermore, factors affecting the efficiency of DCF oxidation, including temperature, pH, background anions, and natural organic matters (NOM) were also evaluated. Finally, the toxicity of the DCF solution after treatment with thermally activated PS was evaluated by a bioluminescent assay with *Vibrio qinghaiensis sp.–Q67*, which was based on the reduction of luminescent bacteria after contact with contaminants. Such a bioluminescent assay was suitable for toxicity assessment in a freshwater environment, e.g., groundwater.

Materials and methods

Chemicals

DCF sodium salt and PS were obtained from Sigma-Aldrich at the highest purity. Acetonitrile, methanol, acetic acid, tert-butyl alcohol (TBA) were obtained from Sigma-Aldrich at a high performance liquid chromatography (HPLC) grade. Analytical grades of sodium dihydrogen phosphate (NaH_2PO_4), disodium hydrogen phosphate (Na_2HPO_4), sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), sodium chloride (NaCl), sodium bicarbonate ($NaHCO_3$), potassium iodide (KI), and humic acid (HA) were purchased from Sinopharm Chemical Reagent Co. Ltd., (China). All reagents were used as received without further purification. Deionized (DI) water was produced from a Millipore Milli-Q Ultrapure Gradient A10 purification system. Stock solutions of DCF were prepared in DI water at 1 g/L and stored at 5 °C before use and renewed weekly. Working solutions of DCF were prepared daily by appropriate dilution of the stock solutions.

Experimental procedures

Batch experiments were conducted in 100 ml amber glass serum bottles incubated in water baths with the temperatures controlled at 50, 55, 60, 65 and 70 °C. The solution pH was kept constant by 10 mM phosphate buffer, and adjusted to the designated pH by NaOH or H_2SO_4. The effect of phosphate species on $SO_4^{\cdot-}$-induced degradation was negligible because of their much slower reaction rate than target contaminants with $SO_4^{\cdot-}$ (Ghauch et al. 2012). Noting that the detection limit of DCF was higher than its environmental concentration, a relatively high initial concentration (0.047 mM) of DCF was employed in the degradation batch experiments to explore its degradation trend and kinetics. Typically, a designated volume of DCF working solution and phosphate buffer were added into the serum bottles and completely mixed by magnetic stirring. The PS was added immediately to initiate the reactions. The sample aliquots were taken at the predetermined time, immediately quenched by methanol, and then filtered through 0.22 μm syringe filters, finally stored in 2 ml amber vials at 5 °C before analysis. Control experiments without PS were also conducted, and a negligible decomposition of DCF was observed at different temperatures. All the experiments were conducted in duplicate or more.

Analysis methods

The concentration of DCF was determined on a high performance liquid chromatography (HPLC, 1200, Agilent Technology, USA) with a Zorbax RX-C18 column (4.6× 250 mm, 5 μm), and a UV detector at 280 nm. The mobile phase was composed of a 40/60 (v/v) mixture of acetic acid water (0.4 %) and acetonitrile. The analysis were performed at a flow rate of 1 ml.min^{-1} and sample inject volume was 20 μL. Calibration curve was linear between the concentration range of 1.6–63 μM (R^2=0.9996). The limits of detection and quantification of DCF were 0.1 and 0.31 μM, respectively. The precision of the method was indicated by a relative standard deviation (RSD, n=6) of 4.15 %.

PS was determined by a spectrophotometric method proposed by Liang et al. (2008). Briefly, the aliquots of the filtered sample without quenching were added into the solution containing KI and $NaHCO_3$, and the yellow color resulting from the reaction of the remaining PS and iodide in the presence of $NaHCO_3$ could be monitored at λ_{max}=352 nm on a UV/Vis spectrophotometer (Beckman DU520). The absorbance of the solution measured at 352 nm was calibrated to PS concentration according to the established calibration line.

Toxicity assessment

The toxicity of DCF solution (0.047 mM) degraded by thermally activated PS (0.47 mM, 60 °C) was assessed by a bioluminescent assay with *Vibrio qinghaiensis sp.–Q67* (Zhang et al. 2015). Briefly, 1.9 ml samples were collected with 0.1 ml osmotic pressure regulator solution (3 % NaCl) and then were mixed with 50 μl photobacteria. The bioluminescence of bacteria was measured by a drinking water safety detector (BHP9514, Hamatsu Photonics Co. Ltd., China) after 15 min of exposure. Luminescence inhibition percentage (Eq. 1) was used to express the toxic effect of DCF and its degradation products (L=luminescence) (Wang et al. 2015). All samples were conducted in triplicates.

$$\text{Inhibition rate} = \left(L_{\text{blank}} - L_{\text{sample}}\right)/L_{\text{blank}} \times 100\% \qquad (1)$$

Results and discussion

Effect of temperatures

Figure 1a presented the oxidative degradation of DCF by thermally activated PS at various temperatures. DCF was quite stable, and a negligible loss of DCF was observed in the absence of PS at 70 °C in the control test. In contrast, a temperature-dependent degradation of DCF was observed in the presence of PS, and higher temperature was favorable for DCF degradation. About 90 % DCF removal was achieved at 70, 65 and 60 °C over 2, 4 and 10 h, respectively. However, only 60 and 30 % removal of DCF was observed after 10 h at 55 and 50 °C, respectively. This observation was typical for the thermally activated PS oxidation, during which more reactive radicals, e.g., $SO_4^{\cdot-}$, were generated for the oxidation of target chemicals at higher temperatures (Ghauch et al. 2012). The decomposition of PS was also monitored during the reaction (Figure S1). The result indicated that more PS has disappeared at higher temperatures. For example, the decomposition of PS increased from 3 to 60 % over 10 h as the temperatures increased from 50 to 70 °C. Therefore, more PS was activated at higher temperatures to generate more $SO_4^{\cdot-}$, resulting in the higher removal efficiency of DCF.

In the previous studies, contaminant oxidation by the thermally activated PS was postulated to follow pseudo-first-order reaction kinetics (Huang et al. 2005; Liang et al. 2003). In this work, oxidation of DCF was also well-fitted to the pseudo-first-order kinetics model, and the corresponding rate constants were calculated to be 0.0321, 0.0924, 0.2316, 0.5087, and 0.9767 h^{-1} for 50, 55, 60, 65, and 70 °C, respectively. Arrhenius equation was used to fit the above rate constants, and the plot of ln$k$ vs $1/T$ was demonstrated in Fig. 1b. The degradation of DCF over the range of 50–70 °C showed an excellent fit with an Arrhenius behavior (R^2=0.9924), and the activation energy (E_a) was determined to be 157.63 kJ·mol^{-1}, which was comparable to 166.7±0.8 kJ·mol^{-1} from research about the degradation of diuron (Tan et al. 2012) and 163.86 kJ·mol^{-1} for TCA from Liang's research (Liang et al. 2003).
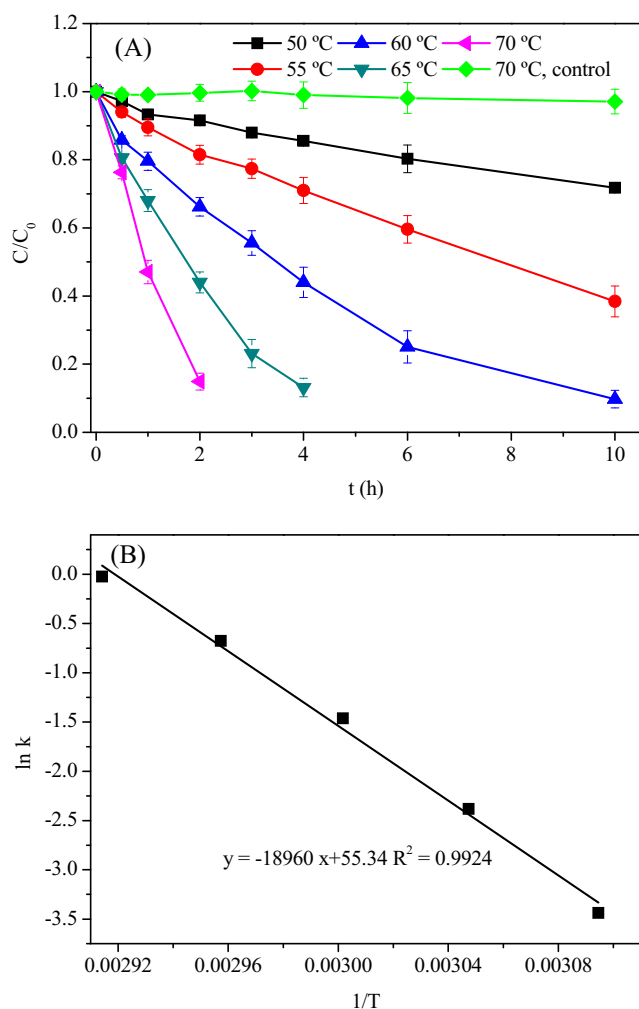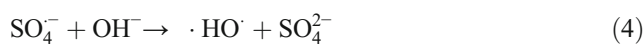
Fig. 1 (a) Degradation of DCF at different temperatures. (b) Arrhenius plot for DCF degradation with the observed degradation rate constants derived from (a) Experimental conditions: $[DCF]_0 = 0.047$ mM, $[PS]_0 = 0.47$ mM, and pH=7. Control was conducted at 70 °C without PS. The *error bars* represent the standard deviation of three replicate samples

Effect of pH

In order to investigate the effect of pH on DCF degradation by the thermally activated PS, the phosphate buffer was used to control pH, due to the low reactivity of phosphate species with $SO_4^{\cdot-}$ (Ghauch and Tuqan 2012; Liang et al. 2007). The degradation trend of DCF at different pH levels and the corresponding rate constants were shown in Fig. 2. The results indicated that the degradation of DCF was pH-dependent. Acidic pH levels were favorable for DCF degradation, and the rate constant at pH 5 was much higher than those at other higher pH levels. As pH increased to pH 7, the degradation rate decreased to the minimal value, but slightly increased in the basic pH levels. Under acidic pH levels, PS could be also activated by protons, i.e., acid-catalysis (Eqs. 2–3); thus, more $SO_4^{\cdot-}$ were generated to react with DCF. At the basic conditions, the generated $SO_4^{\cdot-}$ radicals could react with OH^- to

generate HO· (Eq. 4), which had a higher redox potential than $SO_4^{\cdot-}$. Acidic conditions favorable for contaminant degradation was also reported in the degradation of TCA (Gu et al. 2011) and methyl tert-butyl ether (MTBE) (Huang et al. 2002) by thermally activated PS oxidation. However, neutral pH was propitious to TCE oxidation at various temperatures (Liang et al. 2007). Similarly, the degradation of ibuprofen was faster in the neutral or basic pH levels than the acidic conditions (Ghauch et al. 2012). Therefore, the solution pH could differently affect the contaminant degradation by the activated PS and different characteristics of pollutants and mechanisms of oxidation might lead to different results (Gu et al. 2011).

$$S_2O_8^{2-} + H^+ \rightarrow HS_2O_8^- \tag{2}$$

$$HS_2O_8^- \rightarrow SO_4^{\cdot-} + HSO_4^- \tag{3}$$

$$SO_4^{\cdot-} + OH^- \rightarrow \ \cdot HO^\cdot + SO_4^{2-} \tag{4}$$

Effect of initial concentration

The concentration of PS or contaminant was an important factor affecting the oxidation process; thus, the effect of initial dosage of PS or DCF was evaluated at 60 °C and pH 7. By fixing DCF at 0.047 mM but varying the PS/DCF ratio from 1 to 20, the effect of the initial PS concentration on DCF degradation was evaluated and shown in Fig. 3a. The result indicated that the degradation of DCF increased with the increasing concentration of PS. All of te DCF was oxidized at 4 h with PS/DCF molar ratio of 20, while there were still 90, 40, and 10 % of DCF remaining at 10 h with PS/DCF of 1, 5, 10, respectively. Moreover, degradation of DCF could be well-fitted to the pseudo-first order kinetic model at different PS/DCF ratios, and the corresponding rate constants were shown in Fig. 3b. The rate constant was linearly increased with the increasing dosage of PS. A high concentration of PS might lead to the release of excessive $SO_4^{\cdot-}$, thus acting as scavengers (Eqs. 5–6) and affecting the contaminant degradation (Lee et al. 2012). This phenomenon was not observed in this study, which might be attributed to the relatively low concentration of PS used in this work. The proportion of rate constants with the initial PS concentration was also observed in the degradation of MTBE (Huang et al. 2002), chloramphenicol (Nie et al. 2014), and carbamazepine (Deng et al. 2013a) by the activated PS.

$$S_2O_8^{2-} + SO_4^{\cdot-} \rightarrow HS_2O_8^- + SO_4^{2-} \tag{5}$$

$$SO_4^{\cdot-} + SO_4^{\cdot-} \rightarrow S_2O_8^{2-} \tag{6}$$

At a fixed PS dosage of 0.47 mM, the effect of the initial DCF dosage on its degradation was evaluated at DCF/PS from 0.01 to 1(Fig. 3c). A higher initial DCF induced the slower

Fig. 2 pH effect on the degradation of diclofenac by thermally activated PS oxidation. The *insert* represents rate constants at different pH levels. Experimental conditions: $[DCF]_0$=0.047 mM, $[PS]_0$= 0.47 mM, and temperature= 60 °C. The *error bars* represent the standard deviation of three replicate samples
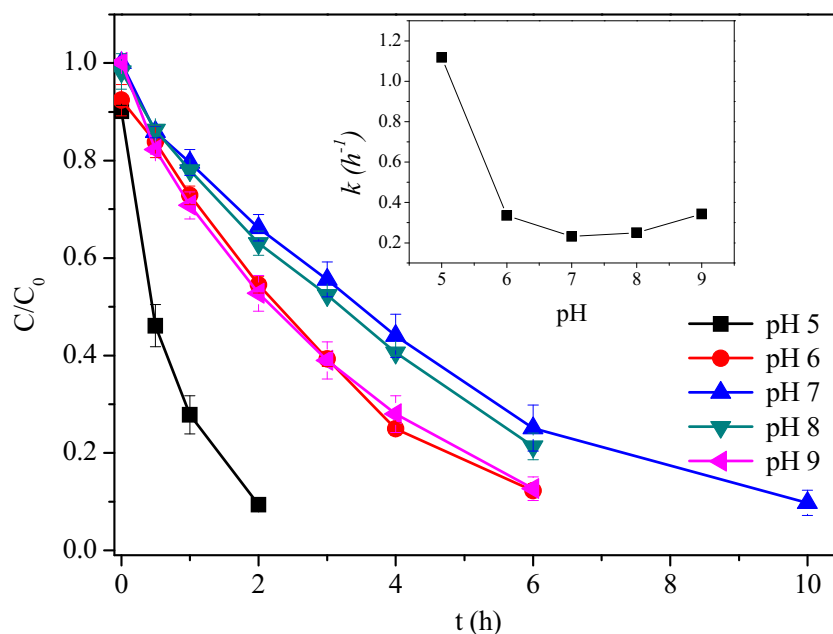
DCF degradation, and all the reactions exhibited pseudo-first-order kinetics pattern. The rate constants were slightly decreased when DCF/PS ratio increased from 0.01 to 0.1(Fig. 3d), indicating that the generated $SO_4^{\cdot -}$ was sufficient
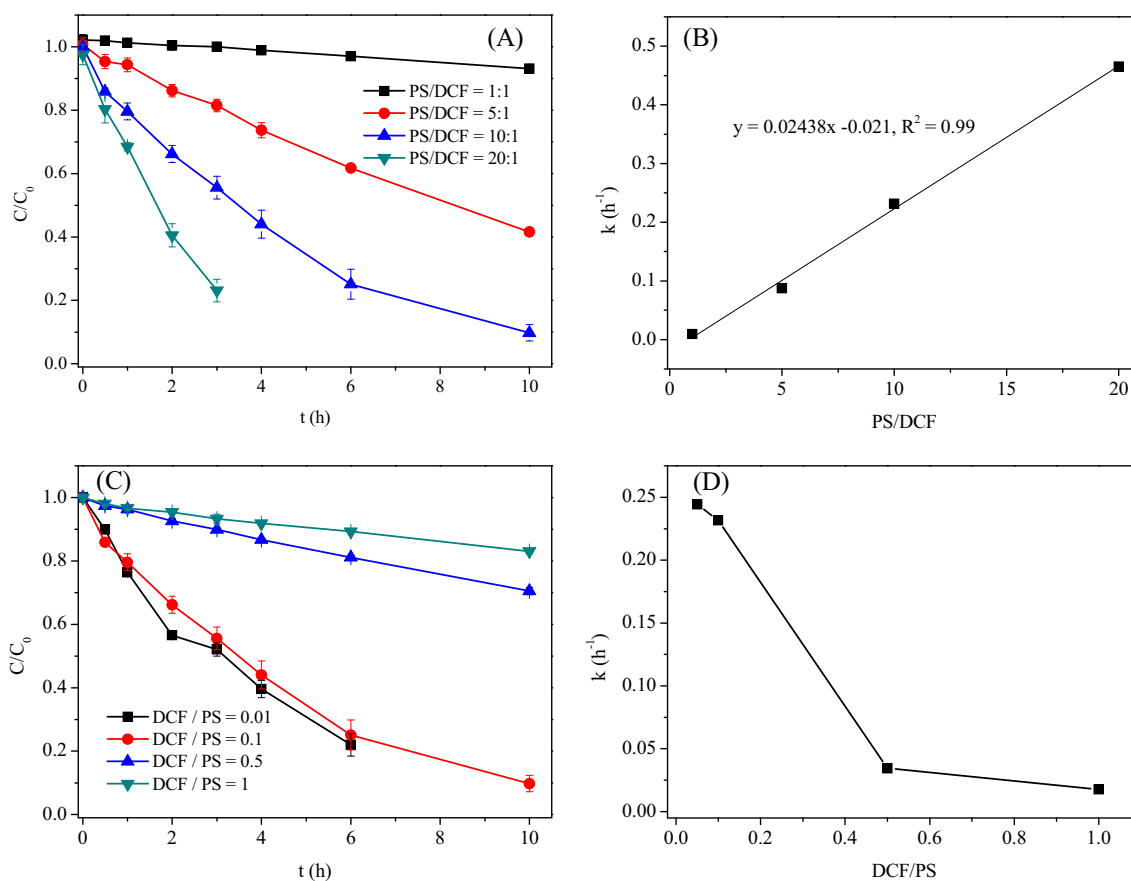
Fig. 3 Degradation of diclofenac at different initial dosage of PS (**a**) and DCF (**c**). (**b**): degradation rate constants derived from (**a**), (**d**): degradation rate constants derived from (**c**). Experimental conditions: temperature=60 °C, pH=7, (**a**) and (**b**): $[DCF]_o$=0.047 mM, $[PS/DCF]_0$=1–20, (**c**) and (**d**): $[PS]_0$=0.47 mM, and $[DCF/PS]_0$=0.01-1. The *error bars* represent the standard deviation of three replicate samples

to sustain the degradation of DCF at a low concentration. However, the rate constants rapidly decreased from 0.2316 to 0.0344 h^{-1} as DCF/PS increased from 0.1 to 0.5, and further slightly decreased to 0.0177 h^{-1} when the ratio increased to 1. The overall amount of reactive radicals was theoretically constant at the fixed PS concentrations with identical reaction conditions. Hence, the proportion of degraded DCF was small relative to the total dosage at a high initial concentration of DCF (Tan et al. 2012). $SO_4^{\cdot-}$ was the restriction factor and a higher concentration of PS was required for efficient DCF degradation. According to the result that a lower initial DCF dosage induced a faster DCF degradation, a rapid degradation of DCF at an environmental concentration was expected when thermally activated PS was applied in DCF-contaminated environment remediation.
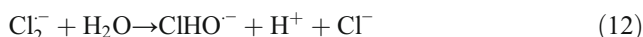
Effect of solution matrix

Effect of Cl^-

Although DCF has been previously reported to be highly reactive with $SO_4^{\cdot-}$, the effect of the solution matrix on their reaction has not been investigated before. Cl^- and HCO_3^- are the common ions in groundwater, and the reactivity of PS in contaminated groundwater might be affected by the background ions. Effect of Cl^- and HCO_3^- on the degradation of DCF by the thermally activated PS was evaluated. As shown in Fig. 4, DCF degradation was obviously influenced by the coexisting Cl^- ions. DCF degradation increased at Cl^- concentrations ranging from 1 to 10 mM, but slightly decreased when Cl^- concentration exceeded 10 mM, i.e., exhibiting a promoting effect on DCF degradation at low concentration, but an inhibitory effect at high concentrations, which was consistent with the previous study about the degradation of *p*-nitrosodimethylaniline by activated PS (Bennedsen et al. 2012). During the activated PS system, Cl^- could react with $SO_4^{\cdot-}$ to generate reactive chloride species (Eqs. 7–12) (Liang et al. 2006), which could also be involved in the propagation reactions with PS and increase the overall generation of $SO_4^{\cdot-}$. On the other hand, the Cl^- ions and the reactive species might reduce the recombination frequency of $SO_4^{\cdot-}$. Moreover, the produced reactive chloride species was potentially capable of degrading the contaminant (Bennedsen et al. 2012). Such influence might dominate at low concentrations of Cl^- (0–10 mM), thus promoting the degradation of DCF. However, when Cl^- exceeded 10 mM, chloride radicals might further react with the excess Cl^- to generate presumed less reactive chloride species, e.g., $Cl_2^{\cdot-}$, thus inhibitory degradation of DCF was observed. Therefore, Cl^- in groundwater played a significant role in the contaminant removal
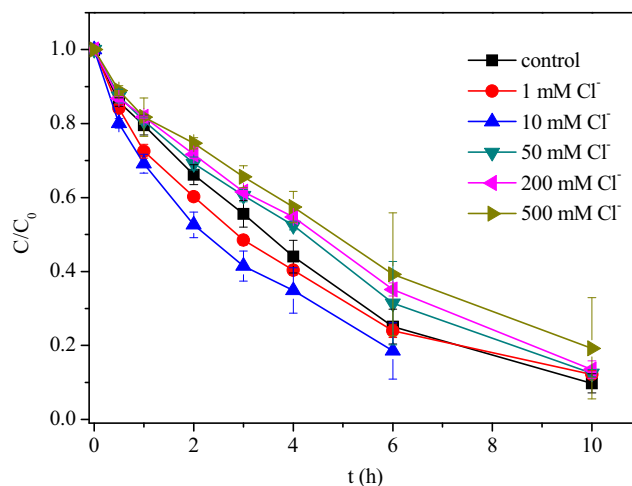
Fig. 4 Effect of Cl^- on diclofenac degradation. Experimental conditions: $[DCF]_0=0.047$ mM, $[PS]_0=0.47$ mM, temperature$=60$ °C, and pH$=7$. The *error bars* represent the standard deviation of three replicate samples
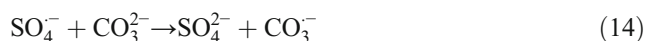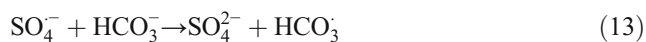
by the activated PS and should not be strictly considered as a scavenger.

$$SO_4^{\cdot-} + Cl^- \rightarrow SO_4^{2-} + Cl^{\cdot} \tag{7}$$

$$Cl^{\cdot} + Cl^- \rightarrow Cl_2^{\cdot-} \tag{8}$$

$$2Cl_2^{\cdot-} \rightarrow Cl_2 + 2Cl^{\cdot} \tag{9}$$

$$Cl^{\cdot} + H_2O \rightarrow ClHO^{\cdot-} + H^+ \tag{10}$$

$$ClHO^{\cdot-} \rightarrow HO^{\cdot} + Cl^- \tag{11}$$

$$Cl_2^{\cdot-} + H_2O \rightarrow ClHO^{\cdot-} + H^+ + Cl^- \tag{12}$$

Effect of HCO_3^-

Effect of HCO_3^- on the degradation of DCF was also investigated, and the result is shown in Figure S2. As seen, HCO_3^- of up to 20 mM did not affect DCF degradation by thermally activated PS. HCO_3^- could react with $SO_4^{\cdot-}$ to generate reactive radical species, e.g., $HCO_3^{\cdot}$ and $CO_3^{\cdot-}$ (Eqs. 13–15). Considering the pK_a for deprotonation reaction (Eq. 15) is 9.5, $HCO_3^{\cdot}$ was expected to be the the dominant radical species at pH 7, also previously verified by ESR spectra (Chawla and Fessenden 1975). However, based on the much slower reaction rate of $SO_4^{\cdot-}$ with HCO_3^- ($k=1.6\times10^6$ M^{-1} s^{-1} (Tan et al. 2012)) than DCF ($k=9.2\times10^9$ M^{-1} s^{-1} (Mahdi Ahmed et al. 2012)), the contribution of $HCO_3^{\cdot}$ towards DCF degradation was negligible. Although the significant inhibitory effect of HCO_3^- was previously reported on 1,1,1-trichloroethane degradation by the thermally activated PS, the adverse effect could be attributed to the variation of pH derived from HCO_3^- (Gu et al. 2011). In that study, the pH of the reaction solution without buffer addition was determined to rapidly increase to the alkaline pH after the addition of HCO_3^-. The adverse effect of HCO_3^- in the activated PS system increased

with increasing pH (Liang et al. 2006). The negligible effect of HCO_3^- on the contaminant degradation was also observed in other studies about the degradation of TCE (Liang et al. 2006) and p-nitrosodimethylaniline (Bennedsen et al. 2012) by activated PS, during which the solution pH levels were buffered at a neutral pH and the contaminant degradation was independent of HCO_3^- concentration. Therefore, pH variation should be specially considered when exploring the effect of HCO_3^-.

$$SO_4^- + HCO_3^- \rightarrow SO_4^{2-} + HCO_3^{\cdot} \qquad (13)$$

$$SO_4^- + CO_3^{2-} \rightarrow SO_4^{2-} + CO_3^{\cdot -} \qquad (14)$$

$$HCO_3^{\cdot} \rightarrow H^+ + CO_3^{\cdot -} \qquad (15)$$

Effect of NOM

NOM, e.g., HA, has always existed in groundwater, so its effect on the degradation of DCF was also evaluated in this work (Fig. 5). The result indicated that DCF degradation was slightly inhibited in the presence of HA. 1 ppm of HA had a slightly adverse effect on DCF removal, and the inhibitory effect further increased when HA increased from 1 to 20 ppm. The adverse impact of HA on contaminant degradation was also observed in the degradation of benzotriazole (Roshani and Leitner 2011) and cylindrospermopsin (He et al. 2013) by activated PS. HA could compete with DCF for $SO_4^{\cdot-}$, thus a portion of $SO_4^{\cdot-}$ was consumed by HA instead of the target contaminant. Higher amounts of HA could consume more $SO_4^{\cdot-}$, thus having a lower contaminant removal.

Performance of DCF oxidation in the real groundwater

Degradation of DCF by thermally activated PS was investigated in the real groundwater (Fig. 6). The result indicated that degradation of DCF in the real groundwater was faster than the DI water buffered at pH 8. The initial pH of groundwater was around pH 8, but could gradually decrease to pH 4.2 during the reaction. According to results discussed earlier in the "Effect of pH" section, a lower pH was favorable for the degradation of DCF. Hence, a faster degradation of DCF in the real groundwater might be attributed to the decrease of pH during the reaction. To further explore the degradation of DCF in the real groundwater, we also compared DCF degradation in groundwater to that in DI water at pH 8, but without a buffer. The degradation performance in the two samples was comparable (Fig. 6). Noting that pH of the DI water during the reaction decreased faster than that in groundwater, finally to pH 3.5. The alkaline species in groundwater might contribute to slightly buffer the solution pH, retarding the pH decrease during the reaction. The inorganic carbon detected in groundwater (1.3 mM) confirmed the presence of alkaline species.
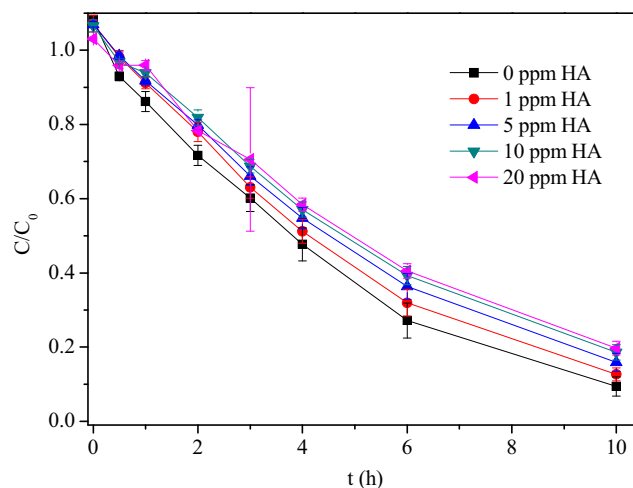
Fig. 5 Effect of HA on diclofenac degradation. Experimental conditions: $[DCF]_0 = 0.047$ mM, $[PS]_0 = 0.47$ mM, temperature=60 °C, and pH=7. The *error bars* represent the standard deviation of three replicate samples

Some common metal ions were also determined to be present in groundwater, such as Fe (0.921 µg/l), Cu (0.062 µg/l), and Co (0.032 µg/l), which might be the potential activator for PS (Anipsitakis and Dionysiou 2004). Moreover, Cl^- was measured to be 2.1 mM in groundwater, favoring the degradation of DCF according to the result in section 3.4.1. Therefore, the negative effect of a smaller pH variation due to the alkaline species might be comparable to the positive effect from the metal ions and Cl^-, resulting in the similar degradation trend of DCF in groundwater and DI water without the buffer. Although DCF was one of recalcitrant pharmaceuticals, thus persistent in the environment, our results indicated that thermally activated PS was effective in oxidizing DCF in the real groundwater.
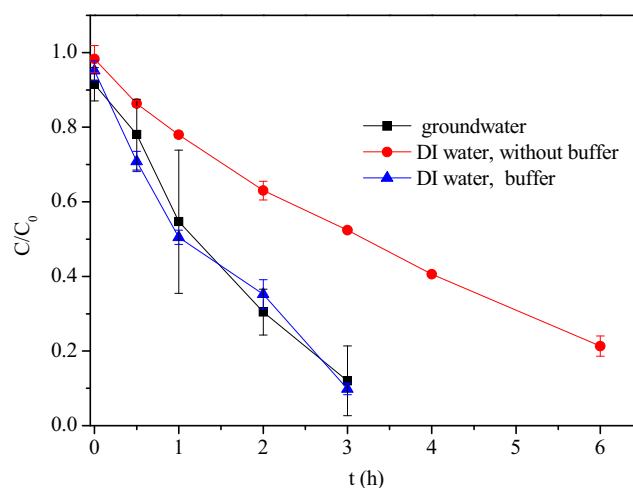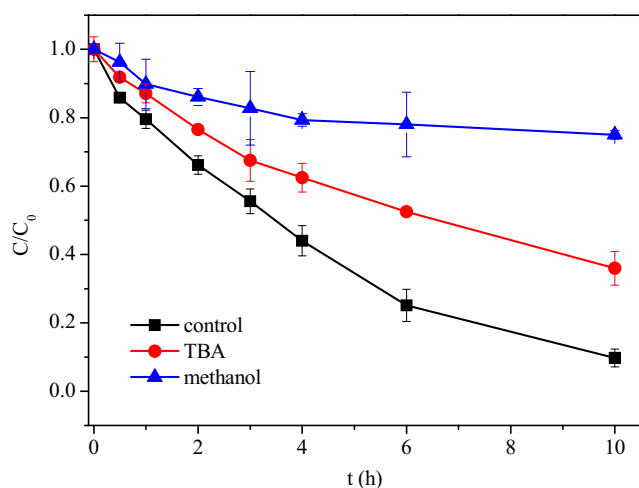

Fig. 6 Degradation of DCF by thermally activated PS in real groundwater. Experimental conditions: $[DCF]_0 = 0.047$ mM, $[PS]_0 = 0.47$ mM, temperature=60 °C, and pH=7. The *error bars* represent the standard deviation of three replicate samples

Identification of the dominant radicals

In the activated PS system, both of SO_4^- and $HO\cdot$ were possibly responsible for the degradation of contaminants. To clarify the dominant radicals for DCF degradation, alcohols were used as the probe during the reaction. Alcohols with and without α-hydrogen have different reactivity and rate constants towards radical species. For example, tert-butyl alcohol (TBA, without α-hydrogen) reacts with OH^- at the rate constants (6.0×10^8 M^{-1} s^{-1}) much faster than $SO_4^{\cdot -}$ (8.4×10^5 M^{-1} s^{-1}), while methanol reacts with OH^- and $SO_4^{\cdot -}$ at a high and comparable rate constants, and the rate constants were 9.7×10^8 M^{-1} s^{-1} and 1.1×10^7 M^{-1} s^{-1} for OH^- and $SO_4^{\cdot -}$, respectively (Yan et al. 2011). The addition of the alcohol could quench the radicals and affect the degradation rate of DCF, thus we could identify the dominant radicals by the extent of the rate decrease. As shown in Fig. 7, the degradation of DCF was significantly influenced with the addition of two radical quenchers. The inhibition of DCF degradation efficiency was 65 and 26 % with methanol and TBA, respectively. With the same amount of TBA, a relatively small drop of the degradation efficiency in comparison with methanol, indicating $SO_4^{\cdot -}$ might be the dominant radical species for DCF degradation by thermally activated PS.

Toxicity variation during DCF degradation

The toxicity of DCF degradation solution was assessed based on the inhibition on the growth of *Vibrio qinghaiensis sp. – Q67* (Zhang et al. 2015). As shown in Fig. 8, DCF alone had a significantly inhibitory effect on the growth of photobacteria, and the luminescence was almost completely inhibited. A
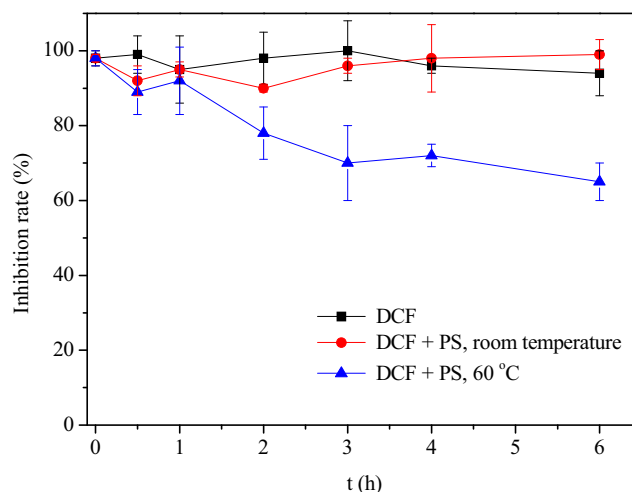
Fig. 8 Toxicity variation during degradation of diclofenac by thermally activated PS. The *error bars* represent the standard deviation of three replicate samples

high toxicity of DCF at the concentration lower than that used in this work was also previously confirmed in the evaluation of its toxicity to zebrafish embryo, during which concentration of DCF over 10.13 μM was lethal to all the embryos, while 3.78 μM DCF exhibited genetic and developmental toxicity (Chen et al. 2014). After the addition of PS at room temperature, the inhibitory effect of the photobacteria was not alleviated, because negligible PS was activated at the room temperature, and an ignorable degradation of DCF was observed within 6 h. In the thermally activated PS system, the inhibition of luminescence decreased gradually along the reaction (Fig. 8). Meanwhile, about 70 % degradation of DCF was observed within 6 h (Fig. 1). The lower toxicity of the DCF solution in the thermally activated PS system implied that transformation products of DCF were less toxic than the parent compound. Transformation products of DCF towards $SO_4^{\cdot -}$ oxidation was specially explored in a previous study, where eight transformation products were identified. The reaction was proposed to start from a one electron transfer from DCF to $SO_4^{\cdot -}$, followed by a multistep transformation involving decarboxylation, hydroxylation, and bond cleavage reactions to mineralization (Mahdi Ahmed et al. 2012). Therefore, the thermally activated PS process was effective for degradation and detoxification of DCF, thus it was a promising alternative ISCO approach for DCF-contaminated groundwater remediation.

Conclusions

This work demonstrated that thermally activated PS could effectively oxidize recalcitrant pharmaceuticals, like DCF, in groundwater. The degradation of DCF was well-fitted with the pseudo-first-order kinetics, highly temperature-

Fig. 7 Effect of radical quenchers (methanol and TBA) on diclofenac degradation. Experimental conditions: $[DCF]_0 = 0.047$ mM, $[PS]_0 = 0.47$ mM, $[alcohol] / [DCF] = 1000$, temperature = 60 °C, and pH = 7. The *error bars* represent the standard deviation of three replicate samples

dependent from 50–70 °C, and pH-dependent from pH 5 to 9. Higher temperatures or acidic condition were favorable for the degradation of DCF. The oxidation reaction exhibited excellent Arrhenius behavior with activation energy of about 157.63 kJ·mol^{-1}. The effect of Cl$^-$ on the degradation of DCF was also concentration-dependent, exhibiting a positive effect at low Cl$^-$ concentrations, but a negative effect at high concentrations. HCO$_3^-$ had a negligible effect on DCF removal, while HA slightly inhibited DCF degradation. SO$_4^{\cdot-}$ was recognized as the main reactive species responsible for DCF oxidation. The acute toxicity tests with bioluminescent assay indicated that toxicity of the DCF solution gradually decreased by thermally activated PS oxidation. Therefore, the thermally activated PS was effective in the detoxification of DCF and thus was a highly promising technique for the remediation of DCF-contaminated groundwater.

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