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Degradation of Diuron by Electrochemically Activated Persulfate

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Abstract An electrochemically activated persulfate (EC/PS) system was proposed for the degradation of herbicide diuron in this study. In the EC/PS system, the ferrous ions (Fe^{2+}) produced from iron electrode can activate persulfate to generate sulfate radical ($SO_4^{\cdot-}$) as well as hydroxyl radical ($OH^{\cdot}$). The results showed that the degradation of diuron was significantly enhanced in the EC/PS system, compared to electrocoagulation, persulfate, and Fe^{2+}/PS process. Both of $SO_4^{\cdot-}$ and OH^{-} contributed to the degradation of diuron in the EC/PS system according to the radical scavenging studies. The pseudo first-order rate constants of diuron increased with increasing the applied currents and dosages of persulfate. pH affected the degradation of diuron indirectly through the speciation of iron and resulted in higher removal efficiency in acidic condition than in alkaline condition. Chloride, carbonate, and bicarbonate in real water inhibited the degradation of diuron dramatically through consuming $SO_4^{\cdot-}$ and OH^{-} and abided by the order of $CO_3^{2-}>HCO_3^{-}>Cl^{-}$. This study demonstrates that the EC/PS system is a novel, efficient, promising, and environmental-friendly method to treat diuron contamination.

1 Introduction

Diuron [N-(3,4-dichlorophenyl)-N, N-dimethylurea], a kind of broad-spectrum herbicide, is widely used in agricultural areas to control annual and perennial broad-leaf, as well as grassy weeds. And it has been used for more than 40 years worldwide (Carrier et al. 2009; Gao et al. 2009; Tan et al. 2012a, b). Diuron could contaminate the surface water by agricultural runoffs and wastewater generated from diuron manufacturing plants (Chiron et al. 2000; Romero et al. 2010). Moreover, diuron is chemically stable, and its half-life in water is about 2 weeks (Guardiola et al. 2012; Huovinen et al. 2015). The US EPA has classified diuron as a "known/likely" human carcinogen. Diuron also ranges from moderately toxic to highly toxic to aquatic organisms and may cause long-term adverse effects to the aquatic environment. Due to the toxic and harmful impacts to the human beings and aquatic organisms, the wastewater effluent containing diuron should be cautiously disposed prior to release into the environment (Chen and Huang 2015; Messeguer 2011).
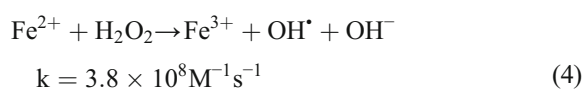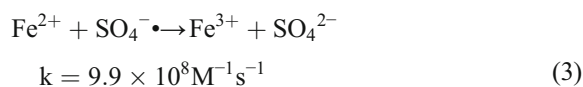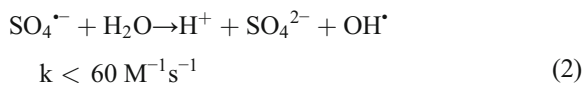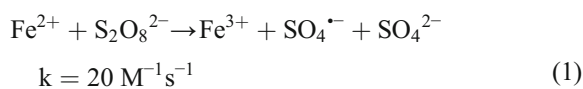
With the development of water treatment technologies, advanced oxidation processes (AOPs) are becoming popular and have been widely used to treat diuron in

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wastewater owing to its recalcitrance for biodegradation (Chen and Huang 2015). AOP are a promising alternative for degrading diuron mainly based on the high oxidation ability of hydroxyl radicals (OH^-) or sulfate radical (SO_4^-) generated by the chemical reaction in the aqueous solutions (Bu et al. 2016; Chu et al. 2015; Tan et al. 2013). Among all the AOPs, electrochemically activated persulfate (EC/PS) process has been considered as a potential technology in water treatment due to its high efficiency (Govindan et al. 2014; Lin et al. 2013; Wu et al. 2012).

Although the EC/PS system is still not widely known, more attention have been paid as it is relatively inexpensive, nontoxic, and effective compared to other typical activators, such as heat-, photo-, metal-, chelated metal-, quinone-, phenols-, hydrogen peroxide-activated persulfate. In the EC/PS system, Fe^{2+} is released from a sacrificial iron electrode at a specified rate under direct current. And electro-generation of hydrogen peroxide (H_2O_2) may occur in the EC systems. Therefore, both SO_4^- and OH^- are generated in the system based on the Reaction Nos. 1 to Nos. 4 (Luo et al. 2015; Yu et al. 2004; Yuan et al. 2013). SO_4^- are very strong aqueous oxidizing species with a redox potential estimated to be 2.6 V, similar to that of the OH^-, 2.7 V (Vicente et al. 2011; Wacławek et al. 2016). Moreover, SO_4^- have a longer half-life than OH^- because of their preference for electron transfer reaction, while OH^- can participate in a diversity of reaction with equal preference (Anipsitakis and Dionysiou 2004; Furman et al. 2010; Govindan et al. 2014). Therefore, SO_4^- are more selective than OH^- for the oxidation of many organic contaminants (Bu et al. 2016; Neta et al. 1988).

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{\bullet-} + SO_4^{2-}$$
$$k = 20\ M^{-1}s^{-1} \tag{1}$$

$$SO_4^{\bullet-} + H_2O \rightarrow H^+ + SO_4^{2-} + OH^{\bullet}$$
$$k < 60\ M^{-1}s^{-1} \tag{2}$$

$$Fe^{2+} + SO_4^{-}\bullet \rightarrow Fe^{3+} + SO_4^{2-}$$
$$k = 9.9 \times 10^8 M^{-1}s^{-1} \tag{3}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^-$$
$$k = 3.8 \times 10^8 M^{-1}s^{-1} \tag{4}$$

So far, the degradation kinetics and mechanism of diuron in the EC/PS system have not been investigated. Therefore, the objectives of this study are (1) to study the degradation kinetics of diuron in the EC/PS system, (2) to identify the main activated radical species responsible for diuron degradation, (3) and to evaluate the influential factors on diuron degradation performance.

2 Materials and Methods

2.1 Materials and Reagents

All the chemicals used in the experiments were analytical reagent grade. The solutions were prepared by ultrapure water (18.2 $M\Omega \cdot cm$) deionized by an ELGA purelab water system. Diuron (≥99.0 %) was obtained from Aladdin Co., Ltd. (Shanghai, China). Methyl alcohol (MeOH) and acetonitrile (HPLC grade, ≥99.9 %) were purchased from Sigma-Aldrich Chemical Co., Ltd. (USA). Sodium persulfate ($Na_2S_2O_8$, ≥99.5 %), sodium sulfate (Na_2SO_4, ≥99.5 %), ferrous sulfate ($FeSO_4 \cdot 7H_2O$, ≥99.0 %), tertiary butanol (TBA, ≥98.0 %), sodium chloride (NaCl, ≥99.0 %), sodium carbonate (Na_2CO_3, ≥98.0 %), and sodium bicarbonate ($NaHCO_3$, ≥99.0 %) were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

2.2 Experimental Procedures

A series of experiments were conducted in a glass beaker containing 200-mL solution and were performed at constant current controlled by a direct current (DC) power supply. The sacrificial iron plates with dimensions of 5 cm × 2 cm were employed as electrode material and set in parallel at a distance of 2 cm. The total submerged area of electrodes was 6 cm² (3 cm × 2 cm) in the electrolytic cell.

The stock solution of diuron was prepared before the experiments. The required experimental concentrations of solutions were diluted with ultrapure water when necessary. $Na_2S_2O_8$ stock solution was freshly prepared promptly prior to use. The concentration of diuron in the experiments was fixed at 10 μM. 0.5 mM Na_2SO_4 was added into the beaker as a background electrolyte to raise the solution conductivity. Before the reactions, pH of the diuron solutions was adjusted to 7.0 by adding 0.1 M NaOH or H_2SO_4, except for the effect of initial pH. At predetermined time intervals, samples were

collected and mixed immediately with appropriate amounts of methanol to quench the residual oxidants. Then, the samples were filtered with 0.45-μm filter membranes before analysis. All the experiments were performed at least in duplicate. Data in figures presented as the mean value of the tested data, and error bars indicated one standard deviation.

2.3 Chemical Analysis

The concentrations of diuron were measured by high-performance liquid chromatography (HPLC, Agilent 1260, USA) equipped with a Symmetry C18 column (150 mm × 4.6 mm × 5 μm, Agilent, USA) and a VWD detector (Agilent, USA) set at 254 nm. An ultrapure water/acetonitrile (v:v = 35:65) mixture was used as the mobile phase with a constant flow of 0.8 mL/min, and the injection volume was 10 μL.

3 Results and Discussion

3.1 Degradation of Diuron in the EC/PS System

To investigate the degradation efficiency of diuron, a set of comparative experiments were carried out by uEC alone, PS alone, and EC/PS system. As shown in Fig. 1, the concentrations of diuron remain unchanged when treated by PS alone, and the removal rate of diuron was almost negligible owing to the low oxidation ability of PS. Similarly, only 15 % of diuron was degraded in 15 min in the EC process as seen in Fig. 1. And the removed part was probably attributed to the surface chelation or electrostatic attraction of $Fe(OH)_n$ precipitates produced in the system. However, the EC/PS system significantly promoted the removal efficiency of diuron, and more than 77 % of diuron was degraded within 15 min in the samples with 0.5 mM initial PS concentration. The high removal efficiency was achieved in the EC/PS system because Fe^{2+} produced on the iron electrode can activate persulfate to generate $SO_4^{\cdot-}$ and $OH^{\cdot}$. The results demonstrated that combination of EC and PS can significantly enhance the degradation efficiency of diuron.

To further investigate the mechanism of the EC/PS system, a comparison between the EC/PS system and the Fe^{2+}-activated persulfate (Fe^{2+}/PS) system was conducted. The added Fe^{2+} concentrations in the Fe^{2+}/PS
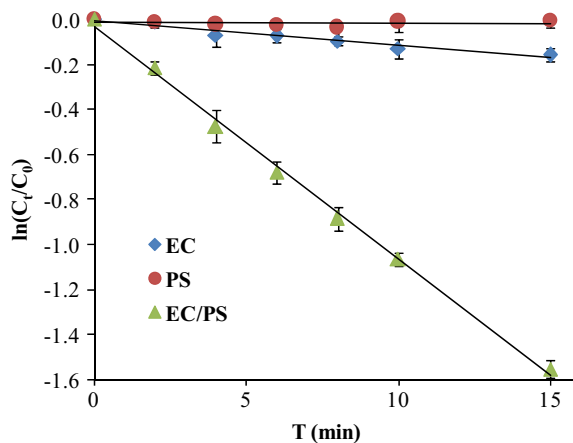

Fig. 1 Comparison of diuron degradation by PS, EC and EC/PS system. Experimental conditions: applied current = 30 mA, $[Diuron]_0 = 10$ μM, $[PS]_0 = 0.5$ mM, initial pH = 7.0, reaction time = 15 min

system were calculated via the following Faraday's law with a reaction time of 15 min.

$$C = \frac{I \times t}{F \times Z \times V} \qquad (5)$$

where, C is the generated molecular concentration of Fe^{2+} (mol/L), Z is the number of electrons (2 equivalents/mol), F is Faraday's constant (96485.3 Coulombs/mol), I is the given current (A), t is the reaction time (s), and V is the volume of electrolyte (L).

As shown in Fig. 2, different from the EC/PS system, the diuron degradation did not increase as the added Fe^{2+} concentration in the Fe^{2+}/PS system. And the optimum mole ratio of Fe^{2+} to PS was about 1:1, which was similar to other studies focusing on Fe^{2+}/PS system or Fe^{2+}/PMS system (Rastogi et al. 2009; Tan et al. 2012a, b). Figure 2 also reveals that the removal rates of diuron by the Fe^{2+}/PS system were always lower than that by the EC/PS system at all the applied currents. This phenomenon could be ascribed to the different utilization of Fe^{2+} between the two systems. In the Fe^{2+}/PS system, excess Fe^{2+} would compete with diuron for $OH^{\cdot}$ and $SO_4^{\cdot-}$ and, thus, hindered the diuron degradation (Cao et al. 2008; Usman et al. 2014; Xu and Li 2010). However, in the EC/PS system, Fe^{2+} was generated gradually from the iron electrode, which assured the optimal utilization of both Fe^{2+} and PS.
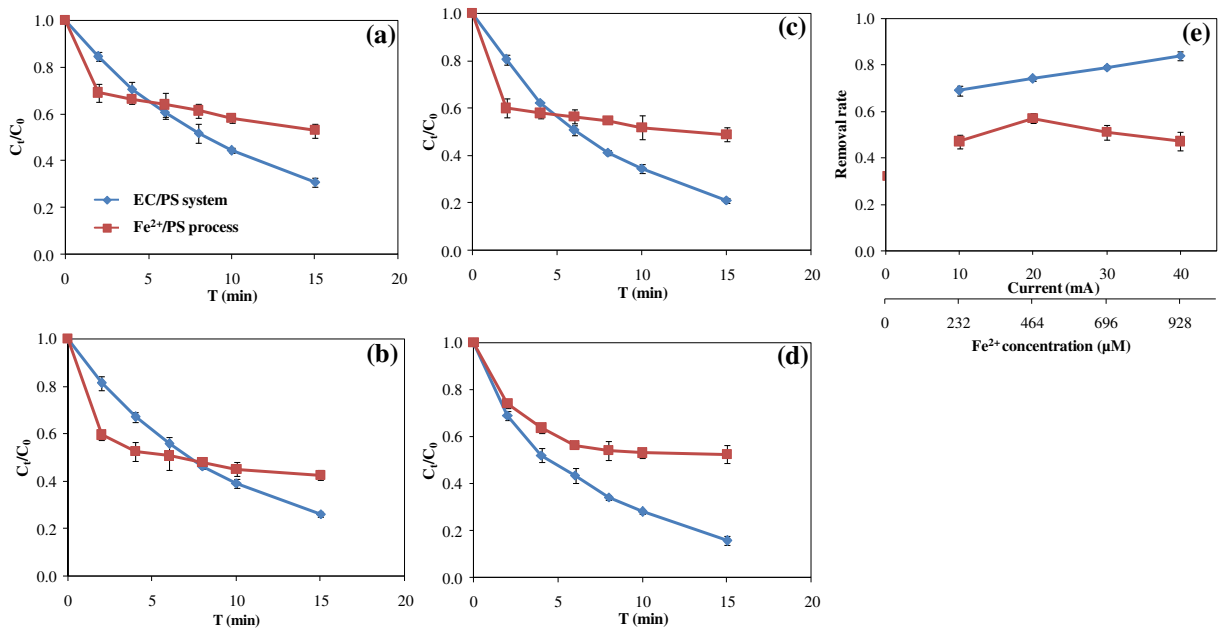
Fig. 2 Comparison of diuron degradation by the EC/PS and Fe^{2+}/PS process under similar reaction conditions. **a** $I_0 = 10$ mA, $[Fe^{2+}]_0 = 232$ μM; **b** $I_0 = 20$ mA, $[Fe^{2+}]_0 = 464$ μM; **c** $I_0 = 30$ mA, $[Fe^{2+}]_0 = 696$ μM; **d** $I_0 = 40$ mA, $[Fe^{2+}]_0 = 928$ μM; **e** overall removal rate. Experimental conditions: $[Diuron]_0 = 10$ μM, $[PS]_0 = 0.5$ mM, initial pH = 7.0, reaction time =15 min

3.2 Role of Sulfate Radical and Hydroxyl Radical in the EC/PS System

To identify the role of $SO_4^{\cdot-}$ and $OH^{\cdot}$ on the degradation of diuron in the EC/PS system, two scavengers, MeOH and TBA, were used in further experiments. TBA is an effective quencher for $OH^{\cdot}$ ($k = 6.0 \times 10^8$ $M^{-1}s^{-1}$), but not for $SO_4^{\cdot-}$ ($k = 4.0 \times 10^5$ $M^{-1}s^{-1}$), while MeOH is considered as an effective scavenger for both $SO_4^{\cdot-}$ ($k = 1.1 \times 10^7$ $M^{-1}s^{-1}$) and $OH^{\cdot}$ ($k = 9.7 \times 10^8$ $M^{-1}s^{-1}$) (Buxton et al. 1988; Neta et al. 1988; Xie et al. 2015). Therefore, the difference of degradation rate of diuron in the presence of scavengers could be used to distinguish the role of $SO_4^{\cdot-}$ and $OH^{\cdot}$.

Figure 3 shows the coexistence of MeOH or TBA inhibited the degradation of diuron in the EC/PS system. Initially, the pseudo-first-order rate constants of diuron degradation decreased rapidly. With further increasing the dosages of MeOH or TBA, the decreasing speed of the pseudo-first-order rate constants reduced dramatically. As shown, the pseudo-first-order rate constants decreased from 0.099 to 0.029 min^{-1} with increasing the concentration of TBA from 0 to 50 mM. While the pseudo-first-order rate constants decreased more rapidly from 0.099 to 0.020 min^{-1} with increasing the concentration of MeOH from 0 to 50 mM. These results suggested that both $SO_4^{\cdot-}$ and $OH^{\cdot}$ are existing in the EC/PS system and responsible for the diuron degradation.

3.3 Effect of Applied Current

Figure 4 illustrated the degradation efficiency of diuron by the EC/PS system at different applied currents ranging from 10 to 40 mA. The results showed that the diuron degradation in the EC/PS system was current-dependent. As the applied current increased from 10 to 40 mA, the removal rate of diuron significantly increased from 69 to 84 % within 15 min, and the pseudo-first-order rate constant increased from 0.078 to 0.102 min^{-1}, accordingly. As shown in the insert image of Fig. 4, a linear correlation between diuron degradation rate constants and applied currents on the iron electrode is determined as:

$$k_{obs} = 0.001 \times I_0$$
$$+ 0.063 \quad (I_0 = 10-40 \text{ mA}) \quad R^2$$
$$= 0.990 \tag{6}$$

where k_{obs} and I_0 are the pseudo-first order degradation constant (min^{-1}) and the applied current (mA),
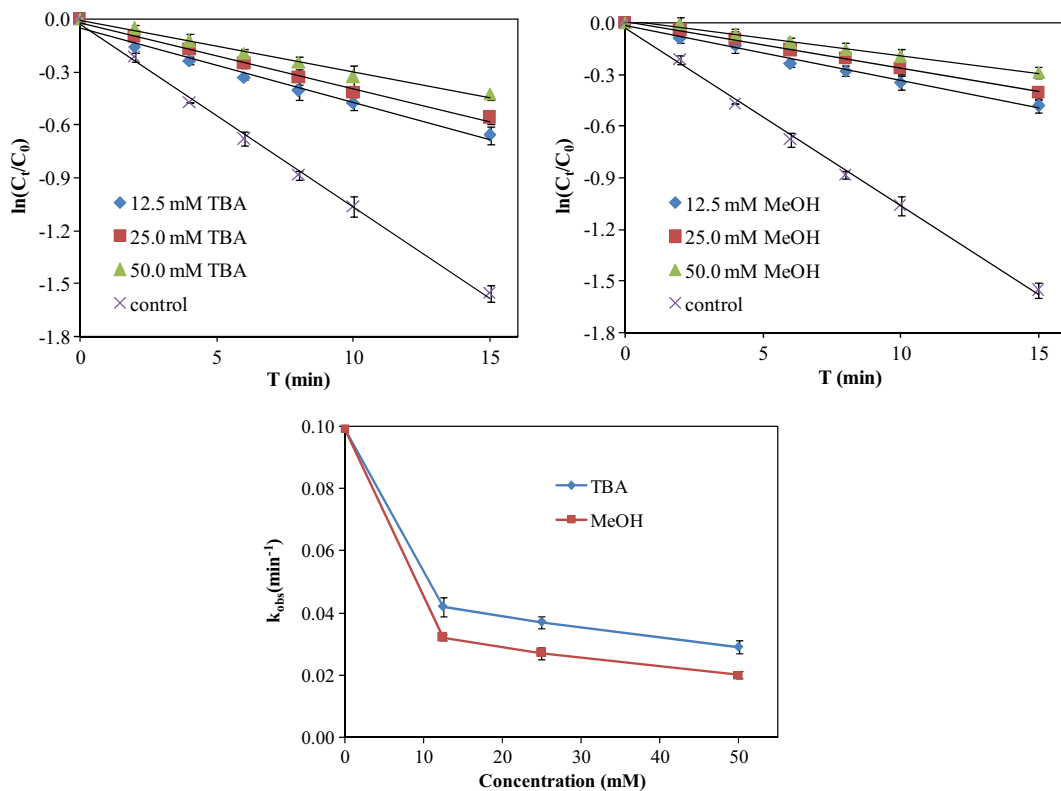
Fig. 3 Effects of co-existing TBA and MeOH on the pseudo-first-order rate constants of diuron. Experimental conditions: applied current = 30 mA, [TBA] = 0–50 mM, [MeOH] = 0–50 mM, $[Diuron]_0 = 10~\mu M$, $[PS]_0 = 0.5$ mM, initial pH = 7.0, reaction time =15 min

respectively. A rational explanation for this phenomenon is that increasing the applied current would accelerate the generation of ferrous ions from iron electrode, and then improve the decomposition of the persulfate to generate more sulfate radicals, which account for the increase of diuron removal rate. Similar phenomenon was observed by Antonin et al. who studied on the incineration of ciprofloxacin using an electrochemical method (Antonin et al. 2015).

3.4 Effect of PS Dosage

The effect of initial PS dosage on the degradation of diuron was evaluated by conducting experiments at PS dosages ranging from 0.10 to 1.00 mM. In the absence of PS, the removal efficiency of diuron was minimal within 15 min (seen in Fig. 1). However, the removal efficiency increased significantly with the addition of PS as shown in Fig. 5. The degradation rates under various PS dosages all followed pseudo-first-order kinetics. When the PS dosage increased from 0.10 to 1.00 mM,

the degradation rate constants increased accordingly from 0.014 to 0.247 min^{-1}. Persulfate is a source of sulfate radicals in the EC/PS system, and more reactive radicals would be generated to degrade diuron
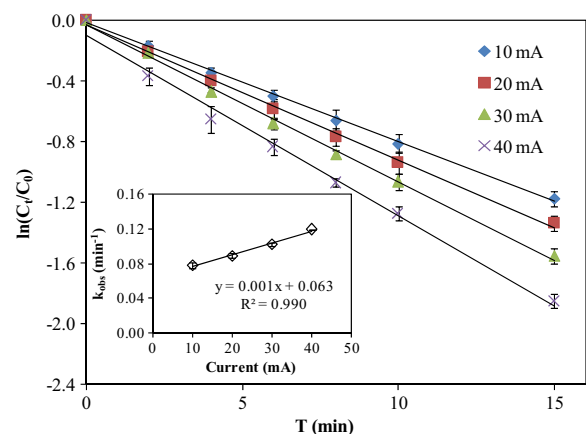

Fig. 4 Diuron degradation in the EC/PS system under different applied currents. Experimental conditions: $[Diuron]_0 = 10~\mu M$, $[PS]_0 = 0.5$ mM, initial pH = 7.0, reaction time =15 min

at higher PS dosage. Similar results were reported by Zhao et al. (2012) who researched on the transformation of refractory pollutants by electro-Fenton process. Furthermore, as the insert image of Fig. 5 presented, the degradation rate constant also exhibited a linear trend as a function of PS dosage in this study (k_{obs} = 0.254 $[PS]_0$–0.015, $[PS]_0$ = 0.1–1.0 mM, R^2 = 0.991).

3.5 Effect of Initial pH

The speciation of iron differs in different solution pH and, thereby, the initial pH is a key factor that influences the degradation efficiency in the EC/PS system (Lakshmanan et al. 2009). Figure 6 shows the degradation of diuron in the EC/PS system among different initial pH (3.0~11.0). Obvious degradation of diuron was observed in acidic condition, and the optimum pH was at 3.0 in this study, which is consistent with Fenton-like oxidation (Sheng et al. 1999). As the initial pH increased from 3.0 to 11.0, the diuron degradation rate constants decreased from 0.154 to 0.008 min^{-1}. This is because that when the initial pH was at and above 2.5, $FeOH^{2+}$ and $Fe(OH)_3$ occupy a dominant part instead of Fe^{2+}, and the formation of $FeOH^{2+}$ and $Fe(OH)_3$ decreased the concentration of free Fe^{2+}, thus decreasing the activation of sulfate radicals through reaction 1. Besides, the regeneration of Fe^{2+} from ferric ions at the cathode was also inhibited, further slowing down the degradation

rate of diuron. Therefore, a conclusion could be drawn that the EC/PS system could be better applied in acidic condition than in alkaline condition.

3.6 Effect of Coexisting Anions

Chloride (Cl^-), carbonate (CO_3^{2-}), and bicarbonate (HCO_3^-) are common anions present in real surface water and may affect the degradation efficiency of diuron in the EC/PS system. In this study, the concentrations of different anions were fixed at 0.5 mM. As shown in Fig. 7, the presence of Cl^-, CO_3^{2-}, and HCO_3^- inhibited the diuron degradation to different degrees, which could be ascribed to their scavenging effect on $SO_4^{\cdot-}$ and $OH^\cdot$ as the following reactions (Buxton et al. 1988; Luo et al. 2015).
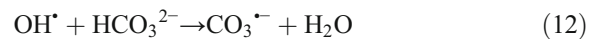
$$SO_4^{\cdot-} + Cl^- \rightarrow SO_4^{2-} + Cl^\cdot \tag{7}$$

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

$$SO_4^{\cdot-} + CO_3^{2-} \rightarrow CO_3^{\cdot-} + SO_4^{2-} \tag{9}$$

$$OH^\cdot + CO_3^{2-} \rightarrow CO_3^{\cdot-} + OH^- \tag{10}$$

$$SO_4^{\cdot-} + HCO_3^{2-} \rightarrow CO_3^{\cdot-} + HSO_4^- \tag{11}$$

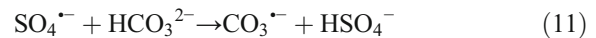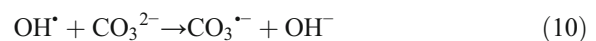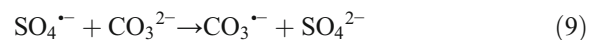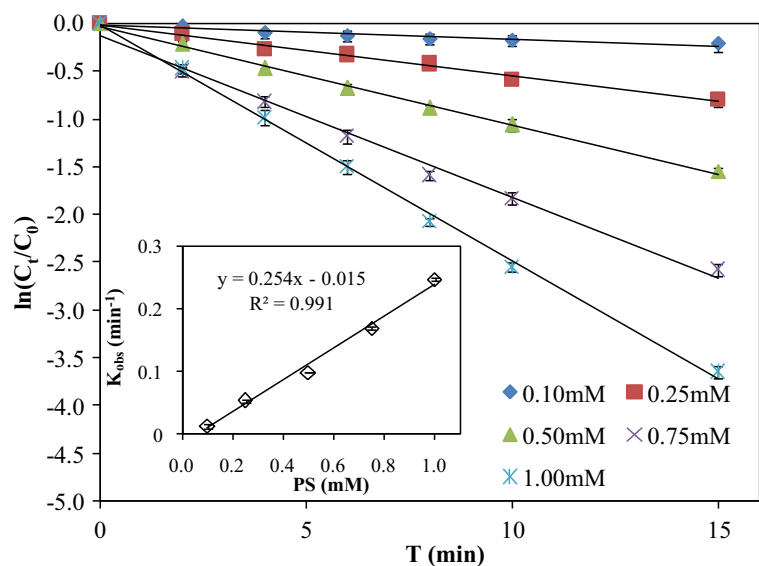$$OH^\cdot + HCO_3^{2-} \rightarrow CO_3^{\cdot-} + H_2O \tag{12}$$

Fig. 5 Diuron degradation in the EC/PS system under different persulfate dosages. Experimental conditions: applied current = 30 mA, $[Diuron]_0$ = 10 μM, initial pH = 7.0, reaction time = 15 min
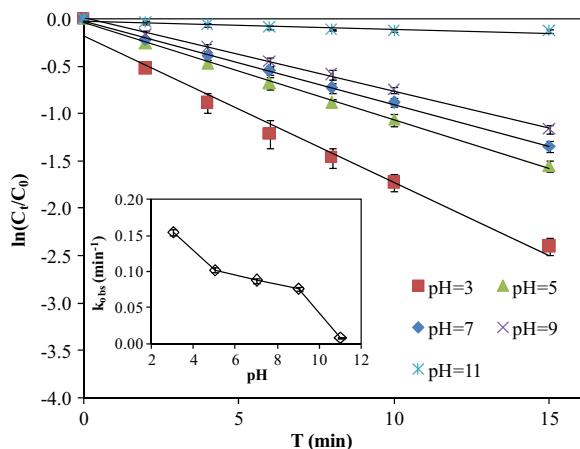
Fig. 6 Diuron degradation in the EC/PS system under different initial solution pH. Experimental conditions: applied current = 30 mA, [Diuron]$_0$ = 10 μM, [PS]$_0$ = 0.5 mM, reaction time = 15 min

Besides, the pseudo-first-order rate constants were calculated to be 0.086, 0.072, and 0.046 min^{-1} in the presence of Cl$^-$, HCO$_3^-$, and CO$_3^{2-}$, respectively. This can be reasonably explained by the redox potential of different radicals, and it may abide by the following order: SO$_4^{\cdot-}$ > OH$^\cdot$ > Cl$^\cdot$ > CO$_3^{\cdot-}$. Therefore, the inhibiting effect of diuron degradation was in the order of CO$_3^{2-}$ > HCO$_3^-$ > Cl$^-$.

3.7 Mineralization of Diuron in the EC/PS System

The changes of TOC and diuron removal efficiency were investigated with initial diuron concentration 10 μM, persulfate concentration 1.0 mM, applied current 40 mA, initial pH 3.0. As shown in Fig. 8, the removal efficiency of diuron increased quickly and approximately 2 % of diuron was detected in 10 min, and there was nearly no diuron existed as the reaction proceeded. However, the TOC removal efficiency was only 10.8 % after 10 min reaction. The TOC removal efficiency achieved about 22.5 % when the reaction time extended to 30 min, implying that mineralization of diuron was poor and only 22.5 % of diuron was mineralized to CO$_2$ and H$_2$O in the EC/PS system, which is consistent with other studies (Tan et al. 2012a, b). The results indicated that most of diuron transformed to its intermediate by-products instead of CO$_2$ and H$_2$O in the EC/PS system and, thus, optimized persulfate dosage, applied current, or reaction time is needed to completely mineralize diuron into inorganics.
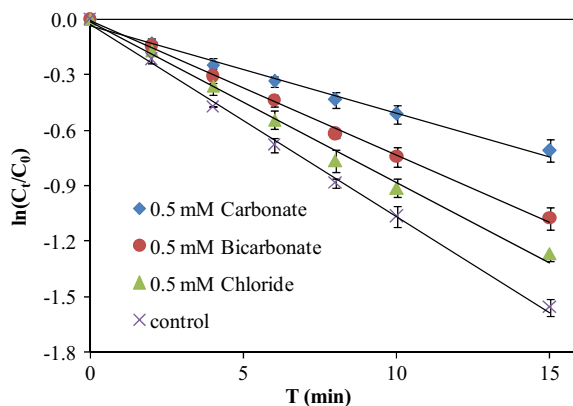

Fig. 7 Diuron degradation in the EC/PS system under different common anions. Experimental conditions: applied current = 30 mA, [Diuron]$_0$ = 10 μM, [PS]$_0$ = 0.5 mM, initial pH = 7.0, reaction time = 15 min

4 Conclusions

This study showed that diuron in water can be removed effectively by the electrochemically activated persulfate (EC/PS) system, and the removal efficiency is better than in EC alone, PS alone, and Fe^{2+}/PS process. The radical scavenging studies using MeOH and TBA further indicated that both SO$_4^{\cdot-}$ and OH$^\cdot$ contributed to the degradation of diuron in the EC/PS system. Increasing the applied current and PS dosage increased the degradation of diuron. pH affected the degradation of diuron and faster degradation occurred in acidic condition. Chloride, carbonate, and bicarbonate are likely to be radical scavengers in real water, and the inhibiting effect was in the order of CO$_3^{2-}$ > HCO$_3^-$ > Cl$^-$. Of course, further studies will be followed when using the EC/PS system to control diuron pollution.
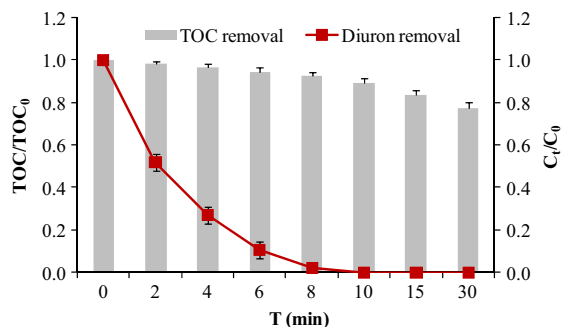

Fig. 8 The change of TOC and diuron removal efficiency with reaction time in the EC/PS system. Experimental conditions: applied current = 40 mA, [Diuron]$_0$ = 10 μM, [PS]$_0$ = 1.0 mM, initial pH = 3.0, reaction time = 30 min

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