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$FeCeO_x$ catalyzed ultrasonic degradation of diclofenac: Influencing factors, kinetics, and mechanism

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ABSTRACT

This paper studied the removal of diclofenac in $FeCeO_x$ catalyzed ultrasonic system. The effects of initial pH, temperature, ultrasonic density and $FeCeO_x$ dosage were investigated. Under optimum conditions (pH of 6, temperature of 298 K, ultrasonic density of 2.4 W/cm^3, and $FeCeO_x$ dosage of 0.7 g/L), more than 80% removal of diclofenac was achieved within 10 min. The kinetic of $FeCeO_x$ catalyzed ultrasonic process fitted Behnajady model very well and the reaction rate constant achieved 0.595 min^{-1}. The dechlorination efficiency was more than 70% and the kinetic of dechlorination followed pseudo-second order model. The reaction mechanism was proposed based on the existence of surface cerium and iron and the abundant oxygen vacancies in the $FeCeO_x$ catalyst. Ce(III) and Fe(III) could accept the electrons transferred by oxygen vacancy and the generated $^1O_2$ could attack diclofenac molecules, resulting in their mineralization to inorganic products.

Keywords: Diclofenac; $FeCeO_x$; Ultrasound; Kinetic; Mechanism

1 Introduction

Diclofenac is a non-steroidal anti-inflammatory pharmaceutical and is used world-wide for the relief of analgesic, antiarthritic and antirheumatic pains [1]. Diclofenac can be partially eliminated (21–40%) in wastewater treatment plants [2], and the incomplete removal causes its occurrence in rivers, lakes and groundwater [3]. Thus, diclofenac is one of the most commonly detected pharmaceuticals in aquatic environment [4,5]. Recent research demonstrated that diclofenac can lead to renal lesions and alterations of the fishes even at a concentration of 5 μg/L [6]. Therefore, the need for more effective method is imperative for removing diclofenac from water.

Sono catalytic process, a novel advanced oxidation technology, has received increasing attention for the removal of pharmaceuticals from water [7]. During the sono catalytic process, the cavitation and "hot spot" effects under ultrasound irradiation are enhanced by providing additional nucleation sites of catalyst, which is beneficial to the generation of active species and degradation of organic molecules [8]. Many catalysts have been studied in sono catalytic process for degradation of diclofenac in water [9,10]. Results show that the influence factors and reaction mechanism of sono catalytic process are different with various catalysts. Wang et al. studied the catalytic activities of CeO_2/TiO_2,

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SnO_2/TiO_2 and ZrO_2/TiO_2 in the sono catalytic process and found that the key sono catalytic mechanism of semiconductor catalyst was the inhibition of recombination of electron hole pairs [11]. Guyer and Ince et al. found the synergy of reactive iron super oxide nano particles and ultrasound with enhanced mass transfer and continuous cleaning of the metal surface. The catalyst plays a dominant role in sono catalytic process [10].

In our previous study [12], $FeCeO_x$ was synthesized by an ultrasonic impregnation method and exhibited an excellent performance in catalyzing an ultrasonic system in water. Fe and Ce ions with different valences coexisted in dynamic equilibrium and $FeCeO_x$ showed excellent chemical stability in the ultrasonic process. Thus, the sono catalytic system with $FeCeO_x$ as catalyst was worth of further research. This work was performed to investigate the influencing factors, reaction kinetics and mechanism in sono catalytic process with $FeCeO_x$ catalyst. Effects of pH, temperature, ultrasonic density and $FeCeO_x$ dosage were investigated in detail. Kinetics of diclofenac degradation and dechlorination in sono catalytic process were analyzed. Reaction mechanism was proposed based on the microcosmic character of $FeCeO_x$ and performances of active species addition.

2. Experimental

2.1. Reagents and materials

All chemicals used were of analytical grade and used without further purification. Ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$) and sodium hydroxide (NaOH) were purchased from Xilong Chemical Co. Ltd, China. Cerous nitrate ($Ce(NO_3)_3{\cdot}6H_2O$) was purchased from Tianjin Guangfu Fine Chemical Institute, China. Diclofenac was purchased from Tokyo Chemical Industry Co. Ltd, Japan. Hydrogen peroxide (H_2O_2, 30%, *V/V*) and sulfuric acid (H_2SO_4, 98%) were obtained from Beijing Chemical Works, China. Sodium persulfate ($Na_2S_2O_8$) were obtained from Sinophram Chemical Reagent Co., Ltd, China. The solutions were prepared with deionized water, which was purified using a Millipore Milli Q UV Plus system.

2.2. Synthesis of $FeCeO_x$

$FeCeO_x$ catalyst was prepared using a ultrasonic impregnation method according to previous report [12]. The CeO_2 was prepared by precipitation method and then dipped in a $FeCl_2{\cdot}4H_2O$ solution under ultrasonic irradiation and the mixture was subsequently filtered. The solid after calcination in a muffle furnace was the final $FeCeO_x$ catalyst.

2.3. Determination of diclofenac removal

The reaction solution was adjusted with diluted NaOH and H_2SO_4 to the desired initial pH and a final volume of 100 ml. The certain dose of the $FeCeO_x$ catalyst was added into the reaction solution. Then the solution was immersed by ultrasonic probe with approximately 1.5 cm below the liquid level. The ultrasonic frequency was stable at 20 kHZ. At stated time, 1.0 ml of supernatant from the sample solution was analyzed after filtration with a 0.45 μm membrane filter. Control experiments were performed under identical conditions. The reaction temperature was controlled by a Yiheng DK-600A constant temperature instrument by circulating water. Chloride ions were determined with a Thermo Scientific DIONEX ICS-600 ion chromatograph (IC), which was equipped with a C18 reversed phase column (4 mm × 250 mm I.D.). Diclofenac was determined with a Waters e2695 high-performance liquid chromatography instrument (HPLC), which was equipped with a C18 reversed phase column (4.6 mm × 150 mm I.D.). Elution conditions: mobile phase was composed of a 70/30 v/v acetonitrile and acetic acid solution (0.2%); flow rate: 1 ml/min; injection volume: 10 μL; column temperature: 30°C; λ_{max}: 275 nm.

3. Results and discussion

3.1. Diclofenac degradation in different reaction systems

To evaluate the efficiency of the $FeCeO_x$-catalyzed ultrasonic process, the removal performance of diclofenac in different systems was investigated. Fig. 1 shows that the diclofenac removal efficiencies with ultrasound alone and $FeCeO_x$ alone were 22% and 60%, respectively, in 30 min. In the $FeCeO_x$/ultrasound system, about 80% diclofenac was removed in 30 min, indicating that $FeCeO_x$ could catalyze the ultrasonic process to remove diclofenac in water. In order to determine the role of Fe ions and CeO_2 in the catalytic process, Fe^{2+} and CeO_2 were added in the ultrasonic system. The diclofenac removal with ultrasound/Fe^{2+} system was similar to ultrasound alone, indicating that Fe^{2+} was not functional. About 50% diclofenac removal efficiency was achieved with ultrasound/CeO_2 system, indicating that CeO_2 played a role in the ultrasonic process. Since Fe^{2+} ions entered into the lattice of $FeCeO_x$, a new form of Fe was generated and led to the excellent removal efficiency of diclofenac in the ultrasonic process. Thus, the synergy effect of Fe-doped CeO_2 was produced in $FeCeO_x$.

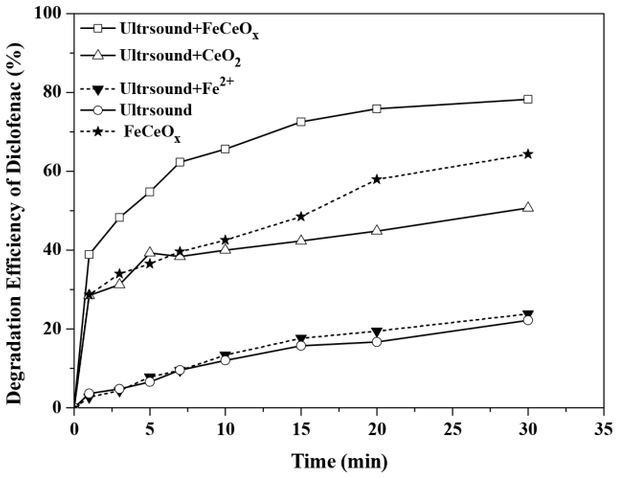

Fig. 1. Removal of diclofenac by CeO_2 and $FeCeO_x$ in presence of ultrasound. Experimental conditions: pH = 5, $FeCeO_x$ dosage = 0.5 g/L, CeO_2 dosage = 0.5 g/L, ultrasonic density = 1.5 W/cm^3, [DCF] = 20 mg/L, [Fe^{2+}] = 1 mmol/L, temperature = 298 K.

3.2. Influences of operation parameters on diclofenac removal

3.2.1. Effect of pH

Experiments were conducted to investigate the effect of pH on diclofenac removal in ultrasonic process and the pH range was within 4–8, which is the typical range for diclofenac removal. Due to the solubility of diclofenac in water, a pH below 4 was not considered here. As shown in Fig. 2, pH significantly affected the removal efficiency of diclofenac. The best removal performance of diclofenac was achieved at pH 6, especially at the first 10 min. Although the diclofenac removal efficiencies were almost the same in 30 min at pH 6 and pH 4, pH 4 was not preferred due to the acidic condition, which would increase the cost and damage the instrument. Therefore, pH 6 was chosen for the following study.

3.2.2. Effect of temperature

Generally, the reaction rate is higher at higher temperature. However, as shown in Fig. 3, at certain temperature range (278–318 K), the temperature had little effect on diclofenac degradation in sono catalytic process, which is of advantage in practical application. The phenomenon is resulting from comprehensive function of multiple factors in sono catalytic process, including adsorption-desorption, cavitation, degradation at solid liquid interface and in liquid phase. The effect of temperature on each function is different. Hamdaoui et al. found that desorption of p-chlorophenol from activated carbon increased with temperature increasing from 294 to 334 K in the presence of ultrasound [13]. The cavitation effect may be also inhibited by the solution temperature, because the rising of temperature leads to degassing of the solution due to volatilization of gas bubbles, which may reduce the number of gas nuclei to form cavitation bubbles in ultrasonic system. The degradation at solid liquid interface and in liquid phase can be enhanced with temperature rising. This may be ascribed to the higher mass transfer rate, resulting in the enhanced formation rate of free radical and reaction rate of free radicals with the target pollutant. The influence of temperature to the above functions may be counterbalanced or even overcome in certain temperature range (278–318 K). In this light, it is reasonable that the temperature had little effect on the diclofenac degradation in sono catalytic process.

3.2.3. Effect of ultrasonic density

Experiments were carried out to study the effect of ultrasonic density on the diclofenac removal in ultrasonic process. The results are shown in Fig. 4. The diclofenac removal efficiency increased with increasing ultrasonic density from 1.2 to 2.4 W/cm^3, and about 80% of diclofenac was removed

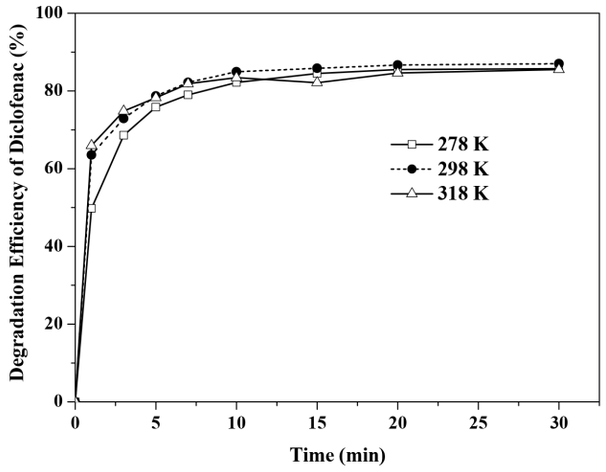

Fig. 3. Effect of solution temperature on diclofenac degradation in ultrasonic process catalyzed by $FeCeO_x$. Experimental conditions: [Diclofenac] = 20 mg/L, $FeCeO_x$ dosage = 0.5 g/L, pH = 6, ultrasonic density = 3.0 W/cm^3.

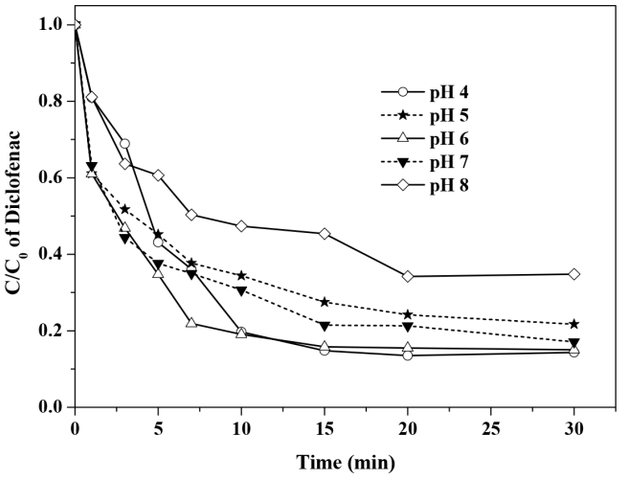

Fig. 2. Effect of pH on diclofenac degradation in ultrasonic process catalyzed by $FeCeO_x$. Experimental conditions: [DCF] = 20 mg/L, $FeCeO_x$ dosage = 0.5 g/L, ultrasonic density = 3.0 W/cm^3, temperature = 298 K.

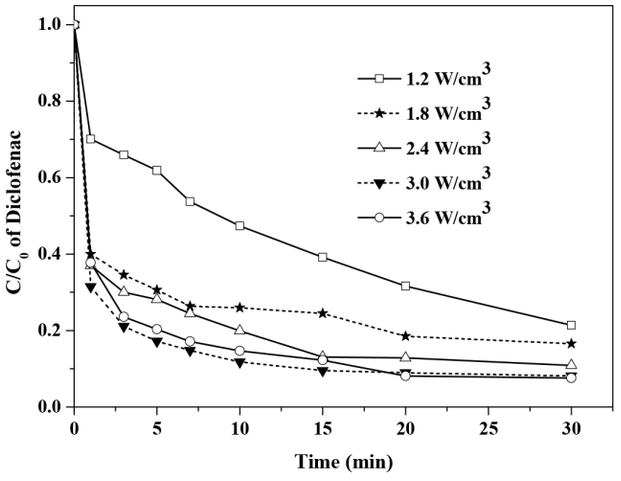

Fig. 4. Effect of ultrasonic density on diclofenac degradation in ultrasonic process catalyzed by $FeCeO_x$. Experimental conditions: [DCF] = 20 mg/L, $FeCeO_x$ dosage = 0.5 g/L, pH = 6, temperature = 298 K.

in 30 min. The phenomenon could be explained by that the cavitation effect was enhanced with the ultrasonic density increase, which led to a higher collapse temperature and more hydroxyl free radicals [14]. The diclofenac removal efficiency kept stable when the ultrasonic density increasing from 2.4 to 3.6 W/cm^3. The excessive ultrasonic density might lead to intensive cavitation effect, which could scatter the energy. Thus, ultrasonic density of 2.4 W/cm^3 was chosen in the following experiments.

3.2.4. Effect of $FeCeO_x$ dosage

The effect of $FeCeO_x$ dosage in the range of 0.1–1.0 g/L on diclofenac removal was investigated. As shown in Fig. 5, the degradation efficiency of diclofenac increased significantly with increasing $FeCeO_x$ dosage from 0.1 to 1.0 g/L in the first 10 min. As the reaction occurred at the interface of $FeCeO_x$ and water, the more $FeCeO_x$ was added, the more adsorptive and reactive sites were available. Thus, higher removal efficiency could be achieved with an increased $FeCeO_x$ dosage. As the diclofenac removal efficiency with $FeCeO_x$ dosage of 0.7 g/L was almost the same as 1.0 g/L at 10 min, the $FeCeO_x$ dosage of 0.7 g/L was preferred.

In general, the conditions of pH 6, temperature of 298 K, ultrasonic density of 2.4 W/cm^3 and $FeCeO_x$ dosage of 0.7 g/L were chosen as the optimum conditions in the following study. Under these conditions, more than 80% of the diclofenac was removed within 10 min. In comparison to other studies [15,16], a higher and faster removal efficiency of diclofenac was achieved with $FeCeO_x$ catalyst in ultrasonic process.

3.3. Reaction kinetic

Kinetic study for removal of diclofenac was investigated in ultrasound alone and $FeCeO_x$/ultrasound system. As seen in Fig. 6, the reaction kinetic of ultrasound alone followed pseudo-first-order model and the correlation coefficient was 0.996. The kinetic equation is as follows:

$$In\left(\frac{C}{C_o}\right) = -kt \tag{1}$$

where C, C_0, k and t are the diclofenac concentration at time t (min), initial dye concentration (mg/L), rate constant (min^{-1}), and ultrasonic time (min), respectively. The value of k is an apparent reaction rate and can be obtained directly from the regression analysis of the linear curves in the plot. The pseudo-first-order reaction rate constant of ultrasound was 0.007 min^{-1}, which is as similar with other ultrasonic degradation studies [17].

As heterogeneous reaction occurred in the $FeCeO_x$ catalyzed ultrasonic process, the kinetic model would be different with the ultrasound alone system. We developed the reaction kinetic in $FeCeO_x$/ultrasound system by Behnajady model [18]. The kinetic equation is as follows:

$$\frac{C}{C_o} = \frac{t}{(m+bt)} \tag{2}$$

where C_0 is the initial concentration of diclofenac (mg/L); C is the concentration at time (t) (mg/L); m and b are the two dimensionless characteristic constants of model relating to the initial removal rate and maximum oxidation capacities, respectively. The reaction rate constant can be written as in Eq. (3):

$$\frac{t}{\left(1-\frac{C}{C_0}\right)} = m + bt \tag{3}$$

As shown in Fig. 6, the kinetic of $FeCeO_x$ catalyzed ultrasonic process fitted Behnajady model very well and the correlation coefficient was 0.999. As m is the constant of the initial degradation rate of diclofenac, the reaction rate can be calculated as 0.595 min^{-1}. The reaction rate enhanced by approximately 85 times in the $FeCeO_x$ catalyzed ultrasonic process comparing with ultrasound alone. Comparing with other studies [19], $FeCeO_x$ also exhibited excellent catalytic performance and diclofenac achieved a fast degradation rate.

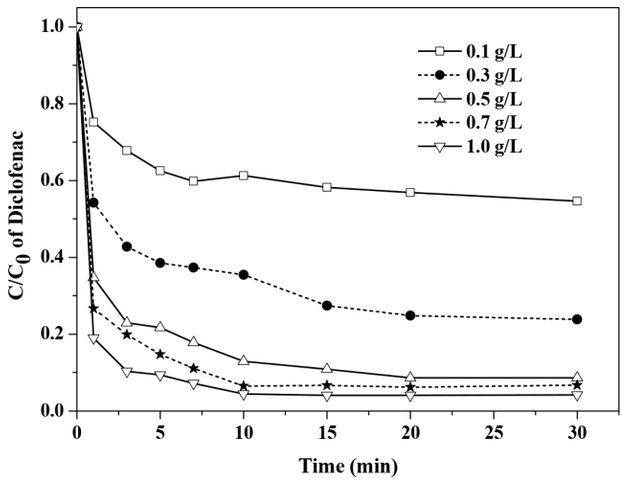

Fig. 5. Effect of $FeCeO_x$ dosage on diclofenac degradation in ultrasonic process. Experimental conditions: [DCF] = 20 mg/L, pH = 6, ultrasonic density = 2.4 W/cm^3, temperature = 298 K.

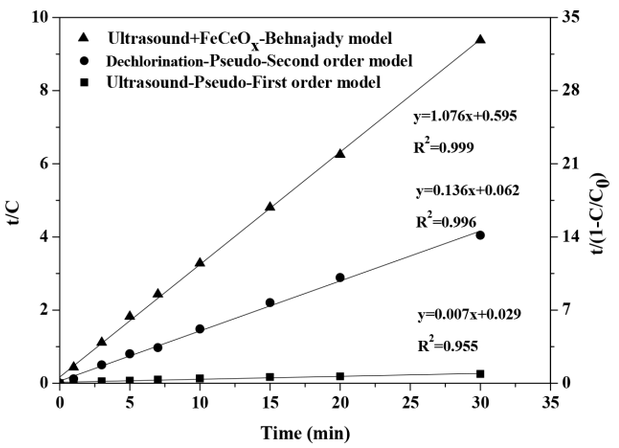

Fig. 6. Reaction kinetic of diclofenac in sonocatalytic process. Experimental conditions: [DCF] = 20 mg/L, $FeCeO_x$ dosage = 0.7 g/L, pH = 6, ultrasonic density = 2.4 W/cm^3, temperature = 298 K.

As diclofenac degraded in the catalytic ultrasonic process, dechlorination would be occurred. Thus, we measured the chloride ion concentration after the reaction, and found that the dechlorination efficiency was more than 70%, indicating that chemical degradation, not absorption was the main reason diclofenac removed from the water. Besides, the kinetic of dechlorination followed pseudo-second order model with the correlation coefficient of 0.996. The kinetic equation is as follows:

$$\frac{t}{C} = \frac{1}{KC_e^2} + \left(\frac{1}{C_e}\right)t \quad (4)$$

where C, C_e, k and t are the diclofenac concentration at time t (min), equilibrium concentration (mg/L), rate constant (min^{-1}), and ultrasonic time (min), respectively. The reaction rate constant of dechlorination was calculated as 0.299 min^{-1}, which showed relatively fast dechlorination efficiency in sono catalytic process. Soufan et al. also considered the chlorination kinetic of diclofenac followed a second-order reaction model [20].

The different fitted reaction kinetic models indicated that reaction occurred in $FeCeO_x$ catalyzed ultrasonic process was different with ultrasound system. In a heterogeneous sono catalytic process, reactions may occur on the catalyst surface, in the solution and in the interior of cavitation bubbles. Chong et al. reported that Fe and Ce ions with different valences coexist in dynamic equilibrium and the oxygen vacancy in lattice of $FeCeO_x$ also participated in the ultrasonic process [21]. Thus, the reactions on the $FeCeO_x$ surface and in its interior indeed occurred, which might affect the reactions in the solution and in the interior of cavitation bubbles, comparing to ultrasound alone system.

3.4. Reaction mechanism

The most common active species in AOPs are hydroxyl radicals (•OH), super oxide radical anion ($O_2^{\bullet-}$) and singlet oxygen ($^1O_2$). To verify the roles of these active species to the ultrasonic process catalyzed by $FeCeO_x$, •OH were detected by EPR trapping measurement. In addition, scavengers of benzoquinone and sodium azide were employed to quench $O_2^{\bullet-}$ and $^1O_2$, respectively. As seen in Fig. 7a, •OH radicals were trapped by EPR, which indicated that •OH were the intermediate oxidative species in the reaction process. As seen in Fig. 7b, when benzoquinone was added to the solution, the diclofenac removal efficiency decreased by approximately 10% during the period of 1–15 min. The change in trend demonstrates that $O_2^{\bullet-}$ participated in the reaction. The addition of sodium azide inhibited diclofenac degradation efficiency by approximately 60%, indicating that $^1O_2$ played an important role in the removal of diclofenac.

Since the generation of $^1O_2$ has great relationship with the oxygen vacancies in catalyst [22] e, $FeCeO_x$ also played an important role in this study. Therefore, it is worthy to detect the main function species in the $FeCeO_x$ catalyzed ultrasonic process. In order to detect the main function species in the $FeCeO_x$ catalyzed ultrasonic process, Fe^{2+} ions were added into the diclofenac solution. As seen in Fig. 7c, the addition of Fe^{2+} ions could enhance the diclofenac removal efficiency in the catalytic ultrasonic process. As described in Section 3.1, Fe^{2+} ions were not function under ultrasound

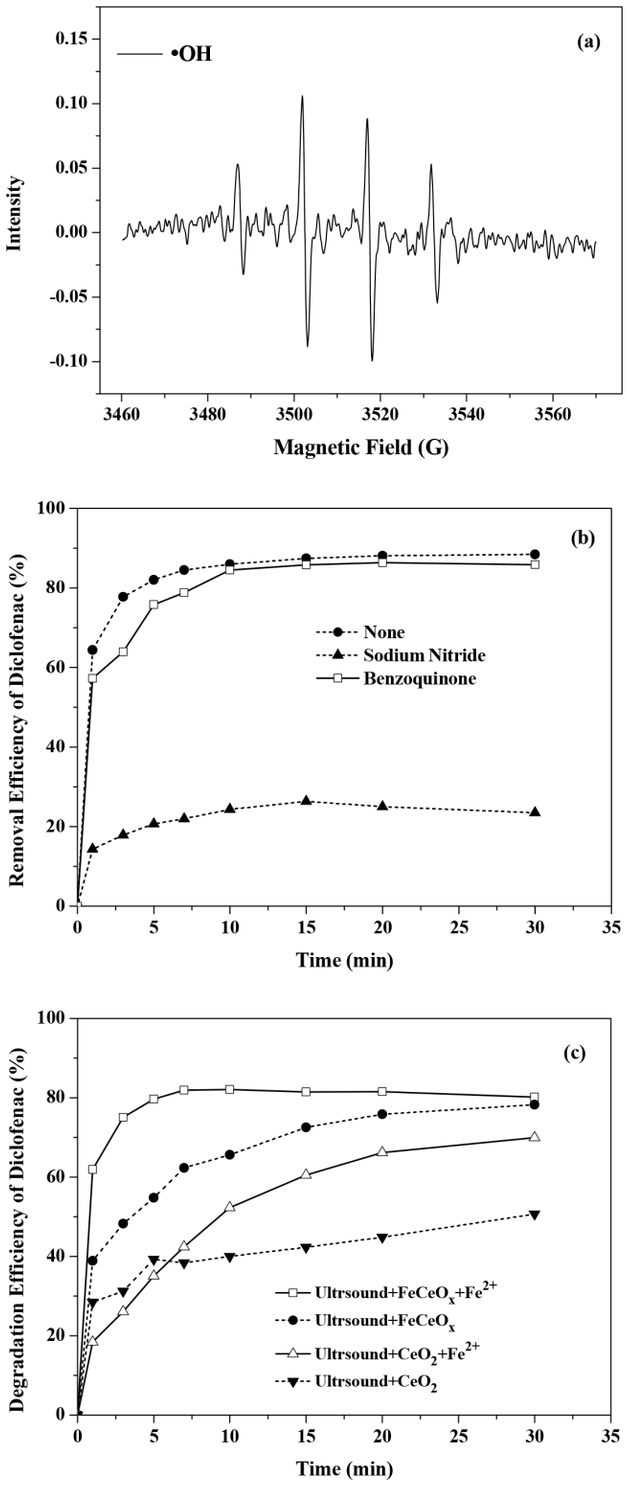

Fig. 7. Active species trapping in the reaction process (a) •OH radicals were trapped by EPR., (b) Effect of radicals scavenger addition, (c) Effect of Fe^{2+} addition. Experimental conditions: [DCF] = 20 mg/L, pH = 6, $FeCeO_x$ dosage = 0.7 g/L, CeO_2 dosage = 0.5 g/L, ultrasonic density = 2.4 W/cm^3, temperature = 298 K, [sodium nitride] = 10.0 mmol/L, [benzoquinone] = 10.0 mmol/L, [Fe^{2+}] = 1 mmol/L.

irradiation. Thus, the addition of Fe^{2+} ions mainly affected the function of $FeCeO_x$ material. As reported before [21], the valence changes of Ce (III), Ce (IV), Fe (III) and Fe (II) in $FeCeO_x$ after reaction, and the oxygen vacancies in $FeCeO_x$ also decreased after the reaction. Thus, the addition of Fe^{2+} ions might enhance the valence changes of Fe, Ce elements and mobility of oxygen vacancies, which could accelerate the electron transfer in the reaction process. Therefore, the diclofenac removal was enhanced by the addition of Fe^{2+} ions. Furthermore, the characteristic of $FeCeO_x$ played an important role in catalytic ultrasonic process.

Based on above analyses, we proposed a mechanism for diclofenac degradation in the $FeCeO_x$ catalyzed ultrasonic process. As shown in Fig. 8, under ultrasonic irradiation, water molecules are firstly converted into •OH and •H in the cavitation bubbles [23]. Then, the electrons (e^-) can react with the adsorbed oxygen molecule (O_2) on the surface of $FeCeO_x$, producing super oxide anion oxide ($O_2^{\bullet-}$). As a strong oxidative intermediate, $O_2^{\bullet-}$ can also react with •OH and H^+ to produce $^1O_2$. $^1O_2$ can also be generated by lattice oxygen via the reduction of oxygen dissolved in solution or the combination of $O_2^{\bullet-}$ under acidic conditions [24]. Ce(III) and Fe(III) existing in the $FeCeO_x$ catalyst could accept the electrons transferred by oxygen vacancy. Finally, the generated $^1O_2$ could attack diclofenac molecules, resulting in their mineralization to inorganic products. The reactions are listed in Eqs. (5)–(12), in which "))))" denotes ultrasonic irradiation:

$$H_2O+))) \rightarrow \cdot OH + \cdot H \quad (5)$$

$$O_{2(ads)} + e^- \rightarrow O_2^{\cdot-} \quad (6)$$

$$O2^{\cdot-} + \cdot OH \rightarrow {}^1O_2 + OH^- \quad (7)$$

$$2O_2^{\cdot-} + 2H^+ \rightarrow {}^1O_2 + H_2O_2 \quad (8)$$

$$O2^{\cdot-} + H_2O_2 \rightarrow {}^1O_2 + \cdot OH + OH^- \quad (9)$$

$$O_{Vac} + O_2^{\cdot-} + H^+ \rightarrow {}^1O_2 + \cdot OH \quad (10)$$

$$Ce(III) + O_{Vac} + O_2 + H^+ \rightarrow Ce(IV) + {}^1O_2 + \cdot OH \quad (11)$$

$$Fe(III) + 2O_{Vac} + e^- \rightarrow Fe(II) + O_2 \quad (12)$$

4. Conclusions

The removal of diclofenac in water was conducted in a $FeCeO_x$ catalyzed ultrasonic system. More than 80% diclofenac was removed within 10 min under optimum conditions (pH 6, temperature 298 K, ultrasonic density 2.4 W/cm^3, and $FeCeO_x$ dosage 0.7 g/L). The kinetic of $FeCeO_x$ catalyzed ultrasonic process fitted Behnajady model very well and the kinetic of dechlorination followed pseudo-second order model. $FeCeO_x$ played an important role in catalytic ultrasonic process. The existence of surface cerium and iron and the abundant oxygen vacancies in the $FeCeO_x$ catalyst were responsible for the effective removal of diclofenac in ultrasonic process.

Acknowledgements

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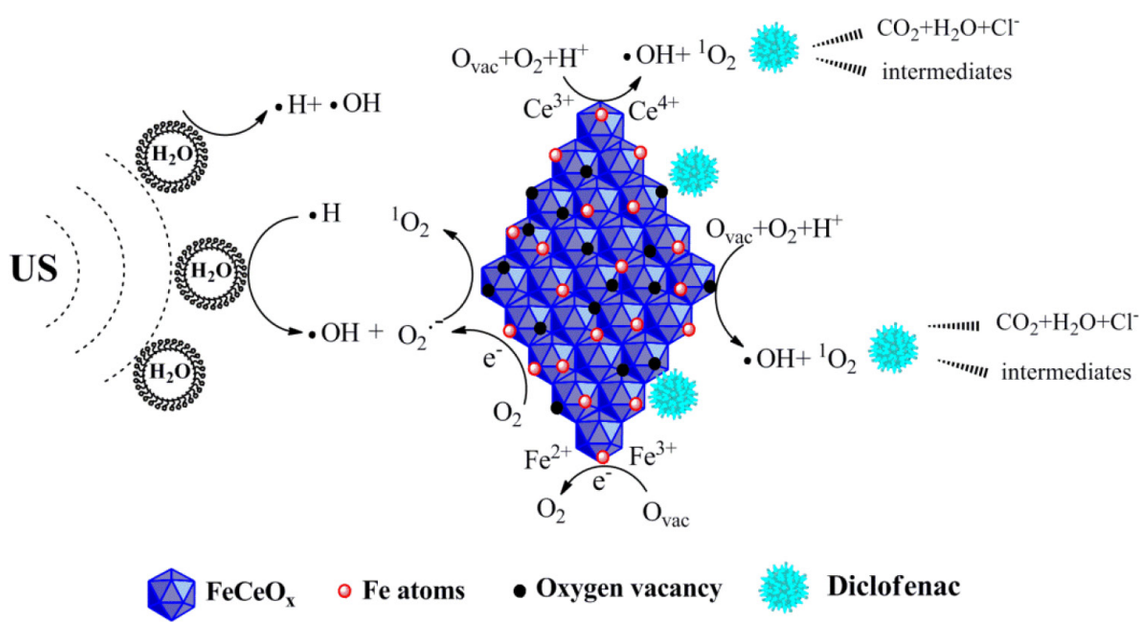

Fig. 8. Schematic diagram of reaction mechanism in sono catalytic process catalyzed by $FeCeO_x$.

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