Applied Catalysis B: Environmental 201 (2017) 573–581

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Elimination of sulfaclozine from water with $SO_4^{\bullet-}$ radicals: Evaluation of different persulfate activation methods

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A R T I C L E I N F O

Article history:
Received 22 April 2016
Received in revised form 16 August 2016
Accepted 19 August 2016
Available online 21 August 2016

Keywords:
Sulfaclozine
Sulfate radicals
Hydroxyl radicals
Persulfate activation
Competitive kinetics

A B S T R A C T

The evaluation of different persulfate activation methods (UV, solar light, electron, Fe(II)) on the degradation of sulfaclozine was investigated along with the effect of persulfate concentrations. UV/TiO_2/$K_2S_2O_8$ resulted in the highest degradation rate regardless persulfate concentrations. However, persulfate addition on the UV/TiO_2 system was not as efficient as expected and the use of radical scavengers showed that pH played an important role in the distribution of dominant radicals. It was found that at pH 7, hydroxyl and sulfate radicals were involved in the degradation of sulfaclozine, whereas at pH 11 no contribution of sulfate radicals was observed.

Following the formation of the six by-products of the first generation formed in UV/TiO_2 system, we obtained the formation of two by-products out of six in the UV/$K_2S_2O_8$ system and four in the UV/TiO_2/$K_2S_2O_8$ system but with different concentrations, confirming the hypothesis suggested about the intervention of $O_2^{\bullet-}$ in the degradation mechanism of sulfaclozine.

The second order rate constant of the reaction between sulfaclozine and $SO_4^{\bullet-}$ radicals was determined by a competitive kinetics method and two values of 7.5×10^9 M^{-1} s^{-1} and 1.7×10^{10} M^{-1} s^{-1} were obtained depending on the references used, and found to be close to those obtained between sulfaclozine and $^\bullet$OH radicals (7.2×10^9 M^{-1} s^{-1} and 5.9×10^9 M^{-1} s^{-1}).

1. Introduction

Sulfaclozine is a sulfonamide antibiotic (Fig. 1) widely used for the treatment of various poultry diseases. This antibiotic used in veterinary treatments is weakly absorbed from the gastrointestinal tract of animals and then, can be excreted intact in the environment and discharged into water cycles [1].

Furthermore, conventional wastewater treatment plants using biological treatments are not well adapted for removing biologically active molecules such as sulfonamide antibiotics [2–4] and therefore additional treatments such as the AOPs (Advanced Oxidation Processes) are often required [5,6].

In-situ chemical oxidation (ISCO) is an efficient technique used for the ground water remediation [7,8] involving the use of oxidants to remove organic pollutants from water. Several oxidants can be used for ISCO, but the main four are: persulfate, permanganate, hydrogen peroxide and ozone [7,9].

Recently, persulfate has also received attention for water remediation due to its high stability, aqueous solubility, high efficiency and relatively low cost [10,11]. Persulfate is a strong oxidant ($E^0(S_2O_8{}^{2-}/SO_4{}^{2-}) = 2.05$ V/ENH) [12] and can act directly as an oxidant but its rate of contaminants oxidation remains limited. In order to enhance its efficiency, persulfate has to be activated to generate more powerful sulfate radicals ($SO_4^{\bullet-}$). In this context, heat, UV, electron and transition metals (e.g., ferrous ion (Fe(II)) [12–16] were used.

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

$$S_2O_8{}^{2-} + h\upsilon \rightarrow 2SO_4{}^{\bullet-} \quad (2)$$

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

$$S_2O_8{}^{2-} + M^{n+} \rightarrow SO_4{}^{\bullet-} + SO_4{}^{2-} + M^{(n+1)+} \quad (4)$$

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http://dx.doi.org/10.1016/j.apcatb.2016.08.046
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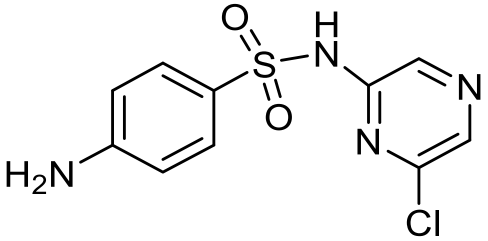

Fig. 1. Organic structure of sulfaclozine.

$SO_4^{\bullet-}$ radical is a stronger oxidant than persulfate ion ($E^0(SO_4^{\bullet-}/SO_4^{2-})$ = 2.6 V/ENH) [13,17] and has a high efficiency in the mineralization of organic pollutants. Moreover, it is efficient in removing halogen-substituted pollutants [18]. $SO_4^{\bullet-}$ engages at least three reaction modes with organic compounds: (i) by hydrogen abstraction from saturated carbon, (ii) by addition on a double bond and (iii) by electron transfer. Noting that the latter mechanism is not feasible by $^{\bullet}OH$ radicals with uncharged species [16]. Persulfate can also be activated by TiO_2 photocatalytic system by trapping the photogenerated electrons in the conduction band, Eq. (3). In this latter case the photocatalytic degradation should be enhanced due to the fact that the e^-/h^+ recombination rate will be reduced, further radical species will be present in the solution and some sulfate radicals could be turned into hydroxyl radicals Eq. (5) [13,19]:

$$SO_4^{\bullet-} + H_2O \rightarrow {}^{\bullet}OH + SO_4^{2-} + H^+ \qquad (5)$$

The rate-enhancing effect of adding $K_2S_2O_8$ to UV/TiO_2 system was clearly confirmed, for example, for pentachlorophenol [13], azo dyes [19], trichloroethylene [20] and imazalil [16].

It is well known that pH plays a very important role in the distribution of dominant radicals involved in the degradation mechanism [21]. In fact, $SO_4^{\bullet-}$ reacts with HO^- to form $^{\bullet}OH$ radicals with a rate constant of $6.5 \times 10^7\ M^{-1}\ s^{-1}$ under alkaline conditions according to the following reaction [22]:

$$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + {}^{\bullet}OH \qquad (6)$$

Thus, to determine the radicals most involved in the degradation mechanism, radical scavengers such as alcohol can be used. *Tert*–butanol can be used to scavenge mainly hydroxyl radicals ($k^{\bullet}OH = 5.2 \times 10^8\ M^{-1}\ s^{-1}$; $kSO_4^{\bullet-} = 8.4 \times 10^5\ M^{-1}\ s^{-1}$) [23,24], while methanol can be used to scavenge both hydroxyl and sulfate radicals ($k^{\bullet}OH = 1 \times 10^9\ M^{-1}\ s^{-1}$; $kSO_4^{\bullet-} = 1 \times 10^7\ M^{-1}\ s^{-1}$) [24,25].

The main objectives of this study were: (1) to determine the rate constant of the reaction between sulfaclozine and $SO_4^{\bullet-}$ radicals for comparison with $^{\bullet}OH$ radicals, (2) to study the degradation of sulfaclozine in different systems with different activation methods of persulfate (UV, solar light, UV/TiO_2, Fe(II)), (3) to study the effect of persulfate concentration in each system, (4) to carry out experiments at different pHs with and without scavengers in the UV/TiO_2/$K_2S_2O_8$ system to find out the most involved radicals in the degradation mechanism, and (5) to compare the by-products identified by LC–MS/MS in UV/TiO_2, UV/$K_2S_2O_8$ and UV/TiO_2/$K_2S_2O_8$ systems.

2. Materials and methods

2.1. Chemicals and reagents

Sulfaclozine sodium (99% purity) was purchased from Sigma-Aldrich and used as received. Titanium dioxide AEROXIDE TiO_2 P 25 was provided by Evonik Degussa with a specific BET area of $50\ m^2\ g^{-1}$, a mean particle size of 30 nm and crystal distribution of 80% anatase and 20% rutile (properties were given for the suppliers). Polyvinylidene fluoride PVDF filters (0.45 μm) were purchased from Millipore. Iron(II) sulfate, acetonitrile, NaOH, formic acid, potassium persulfate ($K_2S_2O_8$), methanol (LC–MS/MS grade) and *tert*-butanol were purchased from Sigma-Aldrich. Ultra pure water was obtained from a Millipore Waters Milli-Q water purification system. Other reagents were at least of analytical grade.

2.2. Experimental procedure

2.2.1. UV/TiO_2, UV/$K_2S_2O_8$ and UV/TiO_2/$K_2S_2O_8$ systems

Experiments were performed in an open Pyrex glass reactor (cut-off at 295 nm) with an inner diameter of 4 cm and height of 9 cm with a double walled cooling water jacket to keep the temperature of the solutions constant throughout the experiments (20 °C). An HPK 125 W Philips water cooled mercury lamp with a maximum emission wavelength of 365 nm and in a lower emission wavelength of 312 nm, was used as a light source. The radiant flux entering the irradiation cell was measured by a VLX-3W radiometer with a CX-365 detector (UV-A) and a value of $4\ mW\ cm^{-2}$ was found at the walls of the reactor. Adequate persulfate doses were added into 25 mL of sulfaclozine solution ($88\ \mu mol\ L^{-1}$) and the reaction solution was mixed by a magnetic stirrer to ensure homogeneity during the reaction. When needed, $2.5\ g\ L^{-1}$ of TiO_2 was added 20 min before irradiation to reach the adsorption-desorption equilibrium. To investigate the role of hydroxyl and sulfate radicals in the degradation of sulfaclozine, methanol and/or *tert*–butanol were added at the beginning of the experiments. The pH value (pH 11) was adjusted by adding concentrated solution of NaOH in the sulfaclozine solution. The first sample was taken out at the end of the dark adsorption period just before turning on the irradiation, in order to determine the bulk sulfaclozine concentration. This value was taken as the initial concentration for the photocatalytic experiment. During irradiation, the samples were with-drawn regularly from the reactor and filtered immediately through 0.45 μm PVDF membrane filters to remove TiO_2 particles.

2.2.2. Solar light/$K_2S_2O_8$ system

The degradation of 50 mL of sulfaclozine solution ($88\ \mu mol\ L^{-1}$) was carried out in a Pyrex reactor equipped with a solar light simulator (Suntest CPS+, Heraeus) and a 1.1 kW Xenon arc lamp. The solution was stirred with a magnetic stirrer bar and adequate persulfate doses were added just before the irradiation.

2.2.3. Fe(II)/$K_2S_2O_8$ system

Experiments were performed in a conical flask under mechanical stirring at room temperature (20 °C). Adequate persulfate and Fe(II) doses were added into 50 mL of sulfaclozine solution ($88\ \mu mol\ L^{-1}$). The reaction solution was mixed by a magnetic stirrer to ensure homogeneity during the reaction. It is noteworthy that although Fenton and Fenton-like systems are more efficient at pH > around 3 (at pH □ 4 ferric ions precipitate as ferric hydroxide $Fe(OH)_3$ which is very stable ($Ks = 10^{-38}$) limiting the reduction of Fe(III) to Fe(II) and the regeneration of Fe(II)), we have worked in this study at pH 7 since sulfaclozine is rapidly hydrolyzed at acidic pH [26].

It should be noted that, in these systems, control experiments were carried out and the removal of the substrate was considered negligible and that the most of the measurements were repeated up to 3 times and the error for those repeated were less than 5%

2.3. Analytical methods

2.3.1. HPLC-DAD

The concentration of sulfaclozine during the degradation was determined using Shimadzu VP series HPLC system equipped with a