Bulgarian Chemical Communications, Volume 51, Issue 1, (pp. 25 – 30) 2019

Degradation of sulfonamides in aqueous solution by an electro/Fe^{2+}/peroxydisulfate process

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Received March 31, 2018; Revised August 30, 2018

Sulfonamide antibiotics with strong toxicity are difficult to degrade in aqueous media. In this study, electrochemical coupled with Fe^{2+} activation of peroxydisulfate (EC/Fe^{2+}/PS) was used to treat sulfamethoxazole (SMX). The removal efficiency of SMX was 89.4%. Acidic medium was favorable to the oxidative degradation of SMX. The best removal efficiency was at pH 3. Fe^{2+} concentration and plate spacing were optimized; too high or too low values were not beneficial to SMX degradation. To a certain extent, separately increasing the PS concentration, Na_2SO_4 concentration and current density could increase the removal rate of SMX. The free radical test showed that $SO_4^{\bullet-}$ played a leading role in acid conditions. It was found that the benzene ring structure of SMX was gradually destroyed. According to the data analysis, the kinetic model of the EC/Fe^{2+}/PS system was $C_t=C_0 \exp(-8.9921\times10^{-4} [Fe^{2+}]^{0.4383} [PS]^{0.7747} [Na_2SO_4]^{0.3382} [\text{current density}]^{0.4095} [\text{plate spacing}]^{0.8573} t)$. This study shows that the EC/Fe^{2+}/PS system can effectively degrade sulfonamide antibiotics in water. It provides an efficient and environmentally friendly treatment for removing sulfonamides from water.

Keywords: Electrochemistry; Fe^{2+}; Peroxydisulfate; Reaction kinetics; Sulfamethoxazole

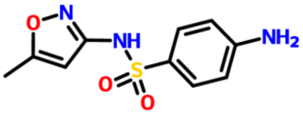
INTRODUCTION

In recent years, a new type of pollutants, such as pharmaceuticals and personal care products (PPCPs), has been frequently detected in various kinds of water bodies. PPCPs include human and animal medicines, cosmetics, sunscreens, spices, etc., with the characteristics of low concentration, strong toxicity and difficult removal [1]. Antibiotics are some of the most important pollutants in PPCPs. Sulfonamides (SAs) with chemotherapeutic effects are the earliest and most widely used antibiotics [2]. SAs pollution is mainly harmful to the microorganisms, aquatic animals and human health. Therefore, one of the hot issues in water treatment is how to effectively control and remove SAs.

Advanced oxidation has the advantages of strong reaction speed, high removal efficiency, no secondary pollution. Thus, advanced oxidation methods are widely used in the field of antibiotic treatment [3]. Activated peroxydisulfate (PS) technology is a new advanced oxidation method. Electrochemical technology combined with activated PS is a technology of PS activation based on the introduction of an electric field [4]. In the process, on the one hand, the organic matter is oxidized through the electrochemical reaction and degraded into small molecules. On the other hand, the organic matter is oxidized by strongly active free radicals produced by the activated PS (Eq. (1) and Eq. (2)) [5]. Previous studies have shown that the presence of an electric field activates part of the persulfate and allows the persulfate catalyst to be reused (Eq. (3)) [6]. In the study of electrochemical and persulfate oxidation, Fe^{2+} is usually used as a catalyst. According to the different types of Fe^{2+} production, the process is divided into three types. (i) direct addition of Fe^{2+} catalyzing the decomposition of PS to produce $SO_4^{\bullet-}$. That is followed by the reduction of Fe^{3+} at the cathode to Fe^{2+} for reuse [7]; (ii) Fe^{2+} is added by external Fe^{3+} reduction on the cathode to reproduce Fe^{2+} in the solution [8, 9]; (iii) Fe^{2+} is generated by the Fe electrode as the anode, activating PS to produce $SO_4^{\bullet-}$ [10].

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{\bullet-} + SO_4^{2-} \quad (1)$$
$$Fe^{2+} + SO_4^{\bullet-} \rightarrow Fe^{3+} + SO_4^{2-} \quad (2)$$
$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (3)$$

At present, applying the electrochemical synergistic persulfate technology (EC/Fe^{2+}/PS) to treat sulfa antibiotics has not been reported. Sulfamethoxazole (SMX) has been frequently detected in the environment. The structural formula of the SMX is as follows:



Formula 1.

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In this study, EC/Fe^{2+}/PS method was used to treat SMX in water. The effect and its impact factors were investigated. The reaction kinetics was also analyzed.

EXPERIMENTAL

SMX ($C_{10}H_{11}N_3O_3S$), PS ($Na_2S_2O_8$), 1, 2-naphthoquinone-4-sulfonic acid sodium salt ($C_{10}H_5NaO_5S$) and $FeSO_4 \cdot 7H_2O$ were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. All reagents were analytical grade. The electrochemical reactor was a glass beaker with an effective volume of 2000 mL. The anode was made of Ti/IrO_2-RuO_2-TiO_2 coated with ruthenium-titanium-iridium. The cathode was made of a stainless steel plate. The electrode plate size was 20 cm × 6 cm × 0.3 cm. Electric stirring method was adopted.

The initial concentration of SMX was 10 mg/L (40 μM). The removal of SMX was monitored at different conditions: PS, Fe^{2+}/PS, EC, EC/PS, and EC/Fe^{2+}/PS. The impact factors of the EC/Fe^{2+}/PS system were studied, such as SMX initial concentration, initial pH, Fe^{2+} concentration, PS concentration, electrolyte concentration, current density and plate spacing. The effect on PS residual rate was also studied. Excess *tert*-butanol and methanol were added to determine the types of free radicals [11]. In order to analyze the reaction product, samples were taken after a certain reaction time. Then the absorbance of the solution in a certain wavelength range was measured.

The concentration of SMX was determined by spectrophotometry using sodium 1, 2-naphthoquinone-4-sulfonate as the chemical derivative chromogenic reagent [12]. Removal efficiency was calculated as follows: removal efficiency (%) = $((C_0-C_t)/C_0) \times 100$, where C_0 and C_t are the concentrations of SMX at time 0 and t, respectively. The concentration of PS was determined using an iodometric titration method.

RESULTS AND DISCUSSION

Degradation efficiency of SMX in the EC/Fe^{2+}/PS process

The degradation of SMX was investigated under different conditions of PS, Fe^{2+}/PS, EC, EC/PS, EC/Fe^{2+}/PS. The results are shown in Fig. 1. As can be seen, SMX was hardly removed in the PS system. Comparatively, it was found that 23.28% of SMX was removed after 5 min of the reaction in the Fe^{2+}/PS system, but the removal efficiency did not further change. This suggested that Fe^{2+} could activate PS to produce $SO_4^{\bullet -}$, which would degrade the SMX. However, the degradation of SMX only occurred in the first few minutes of the reaction. The reason may be that Fe^{2+} was consumed in the reaction, indicated by the color change of the solution. No activating agent continued to activate PS in the system. In the EC system, the degradation efficiency of SMX was 50.45% after 60 min of reaction. The removal efficiency of SMX increased to 70.38% when PS was added to the system. This indicated that the electron transfer could activate PS to produce $SO_4^{\bullet -}$, which oxidized SMX [13].

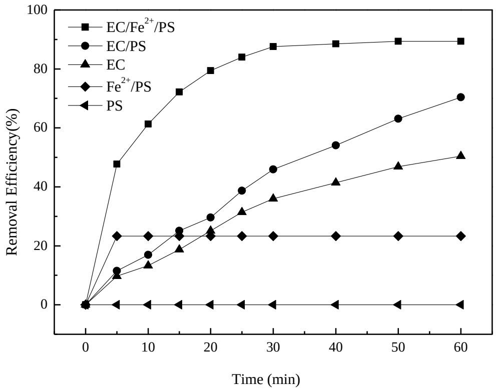

Fig. 1. Removal efficiency of SMX in the different systems

In the EC/Fe^{2+}/PS system, the degradation efficiency of SMX was 89.4%, which was higher than the sum of EC system (50.45%) and Fe^{2+}/PS system (23.28%). That suggested a synergistic effect between EC and Fe^{2+}/PS [7].

Effect of SMX initial concentration, initial pH, Fe^{2+} concentration and PS concentration

As can be seen from Fig. 2 (a), with the increase in SMX concentration, the degradation efficiency gradually decreased. When the concentration of PS was constant (2.5 mM), the number of active radicals generated by activation was limited (2.5 mM). When the concentration of SMX increased from 10 mg/L to 30 mg/L, a larger number of intermediate products were produced by oxidative degradation. Then the further degradation of intermediate products would consume the radicals. They would compete with the SMX, reducing the degradation efficiency of SMX.

The removal efficiency of SMX showed a downward trend as the initial pH value increased (Fig. 2 (b)). The highest degradation efficiency was at pH 3, reaching 87.59%. SMX removal efficiency was maintained at a high level when pH values were 3, 5, 7, 9. It was shown that the pH of the solution decreased to neutrality with the progress of the reaction [14]. This indicated that the PS activation system could apply to a wide range of initial pH values. At pH 11 the removal rate rapidly decreased. The remaining content of PS gradually increased as the pH increased from 3 to 11. That suggested that as the pH increased, less PS was decomposed in the system. The reason may be that in addition to the activation effect of Fe^{2+}, the PS was also catalyzed by acid to accelerate the $SO_4^{\bullet -}$ formation at low pH.

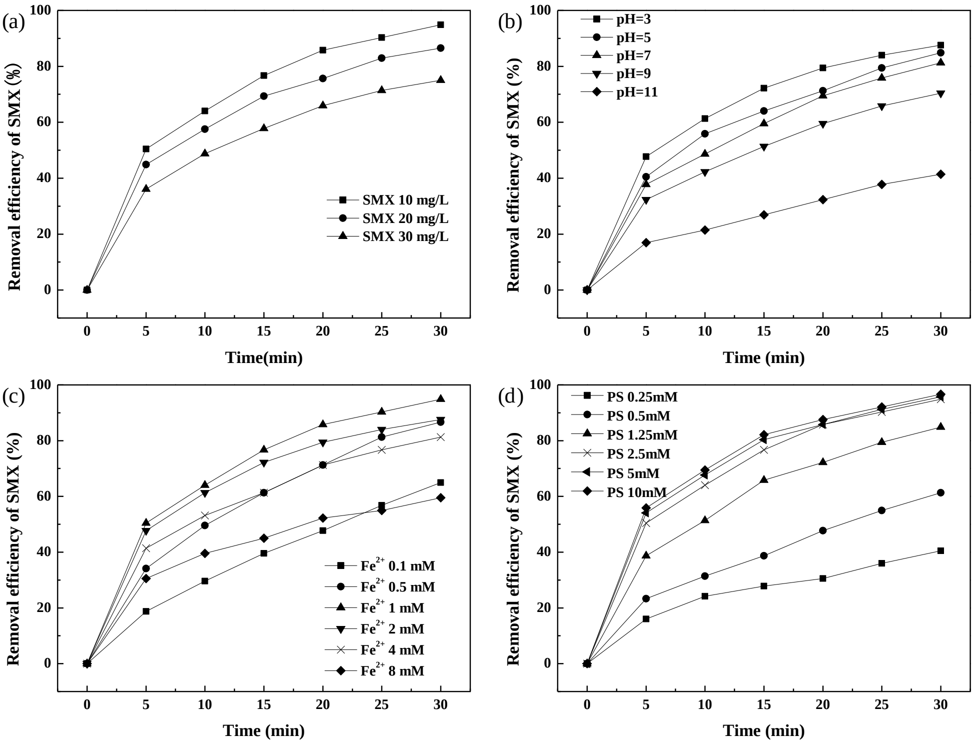

Fig. 2. Effect of the SMX initial concentration (a), initial pH (b), Fe^{2+} concentration (c) and PS concentration (d) on SMX removal efficiency in the EC/Fe^{2+}/PS system

A higher pH value was unfavorable for PS decomposition. Precipitation of Fe^{3+} would occur at the higher pH. That would weaken the reduction reaction of Fe^{3+}, dropping the generation rate of $SO_4^{\bullet-}$. Meanwhile, $SO_4^{\bullet-}$ would react with OH^- at the higher pH. Under alkaline conditions, the oxidation-reduction potential of $^{\bullet}OH$ (E_0 = 2.3) was lower than that of $SO_4^{\bullet-}$. $SO_4^{\bullet-}$ and $^{\bullet}OH$ also reacted and thus some active free radicals were consumed in the system with a higher pH. This suggested that at higher pH value the catalyst activity was reduced and, the concentration of active radicals in the solution decreased.

When the concentration of Fe^{2+} increased from 0.1 mM to 1.0 mM, the removal efficiency of SMX increased from 64.95% to 94.84% (Fig. 2 (c)). However, the removal rate of SMX showed a downward trend when the Fe^{2+} concentration changed from 2 mM to 8 mM. The remaining content of PS decreased as the concentration of Fe^{2+} increased. That implied that the catalytic reaction rate increased and the decomposition of PS was accelerated. Therefore, as the initial Fe^{2+} concentration increased from 0.1 mM to 1 mM, the removal rate of SMX significantly increased. When the concentration of Fe^{2+} was higher, the color of the reaction solution was deepened to brown. This may be because excessive Fe^{2+} was oxidized to Fe^{3+} by consuming sulfate radicals. Besides that a high concentration of $SO_4^{\bullet-}$ would undergo a self-quenching reaction, leading to inefficient use of $SO_4^{\bullet-}$. These results suggested that an appropriate amount of Fe^{2+} could promote SMX degradation, while excessive Fe^{2+} could inhibit SMX degradation. This conclusion was consistent with previous reports [15].

As the PS concentration increased from 0.25 mM to 2.5 mM, the SMX removal efficiency rapidly increased (Fig. 2 (d)). When the PS concentration went on increasing, the SMX removal efficiency little changed. It was found that increasing PS concentration decreased its own residual rate. PS residual rate was defined as (C_{ps-t}/C_{ps-0}), where C_{ps-t} and C_{ps-0} were the concentrations of PS at time t and 0, respectively. The reason may be that when the PS concentration was low, the probability of collision with the Fe^{2+} was relatively low. With the increase in PS concentration, the concentration of $SO_4^{\bullet-}$ gradually increased in the system. When the PS concentration reached to a certain range, increasing the PS concentration could reduce the PS residual rate, but the SMX oxidation rate was not obviously changed. This may be because the high concentration of PS could quickly produce a large number of free radicals. In addition to the self-quenching reactions, radicals also reacted with PS. Large amounts of PS were inefficiently degraded. The utilization efficiency of

PS and $SO_4^{\bullet -}$ was very low when PS was added in excess.

Effect of Na_2SO_4 concentration, current density and plate spacing

As shown in Fig. 3 (a), when Na_2SO_4 concentration was 0 mM, the removal efficiency of SMX was very low. When Na_2SO_4 concentration was 6 mM, the removal efficiency of SMX was obviously improved. When the concentration of Na_2SO_4 went on increasing, the removal efficiency of SMX gradually increased. When the Na_2SO_4 concentration was greater than 25 mM, the removal efficiency of SMX slightly increased.

As the current density increased, the removal efficiency of SMX also increased (Fig. 3 (b)). The reason may be that the electrochemical reaction between the electrodes would be more intense with the greater current density. Enhancement of electron transfer could promote the production of $SO_4^{\bullet -}$ by PS and increase the degradation rate of SMX [16].

The removal rate of SMX firstly increased and then decreased with the increase of plate spacing (Fig. 3 (c)). The removal rate reached 94.84% when the spacing reached 9 cm. After that, the removal rate showed a downward trend. The reason may be that the solution resistance became larger when the spacing increased to a certain value. Then the mass transfer efficiency decreased, leading to the downfall of the reaction rate [17].

Identification of oxidizing species and reaction products

The results suggest that reactive oxidizing species are produced in the EC/Fe^{2+}/PS system, leading to the enhanced degradation of SMX. To identify the generation of $^{\bullet}OH$ or $SO_4^{\bullet -}$, radical quenchers of *tert*-butanol and methanol were added to the system. *Tert*-butanol is an effective quencher of $^{\bullet}OH$, while methanol is a good quencher of both $SO_4^{\bullet -}$ and $^{\bullet}OH$ [18, 19].

It can be seen from Fig. 4 (a) that adding a quencher to the EC/Fe^{2+}/PS system has a significant effect on SMX degradation. When no quencher was added to the system, the removal rate of SMX was 94.84% in 30 min. The removal rate of SMX decreased to 83.06% as an excess of *tert*-butanol was added. This indicated the presence of $^{\bullet}OH$ in the system and played a role in the oxidation of SMX. The removal rate of SMX was 43.21% when adding excess methanol. The inhibition of SMX oxidation by methanol was much stronger than that by *tert*-butanol. These results indicated the presence of $SO_4^{\bullet -}$ in the system and $SO_4^{\bullet -}$ played a leading role in the process of SMX. The solution had a distinct absorption peak at a wavelength of 256 nm (benzene ring B) before the reaction (Fig. 4 (b)). The absorption peak decreased until it disappeared with the reaction. This indicated that SMX was oxidized and the benzene ring structure was gradually destroyed.

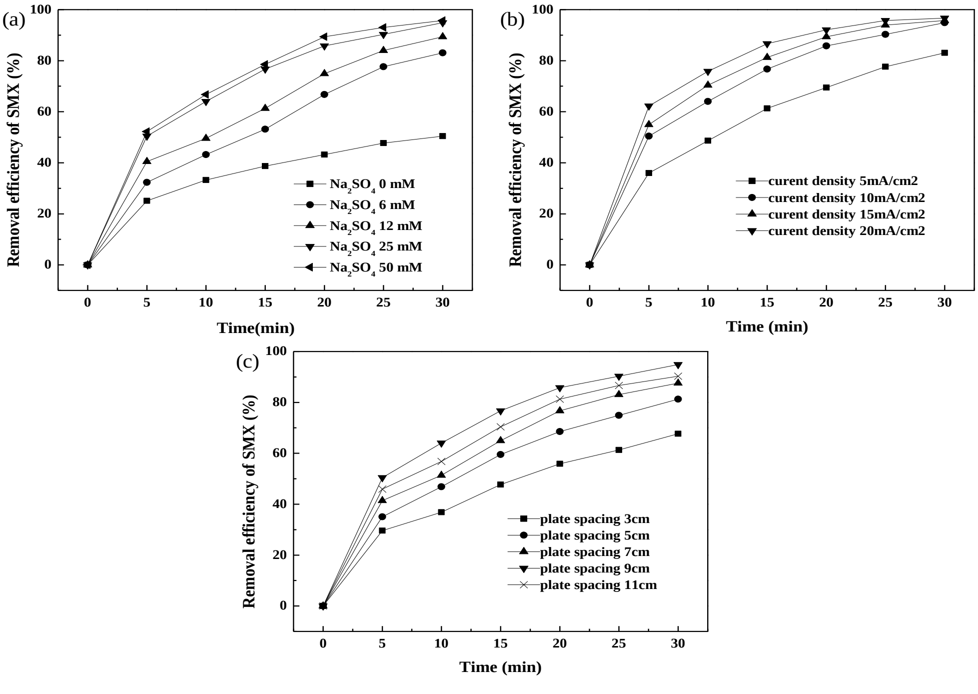

Fig. 3. Effect of Na_2SO_4 concentration (a), current density (b) and plate spacing (c) on SMX removal efficiency in the EC/Fe^{2+}/PS system

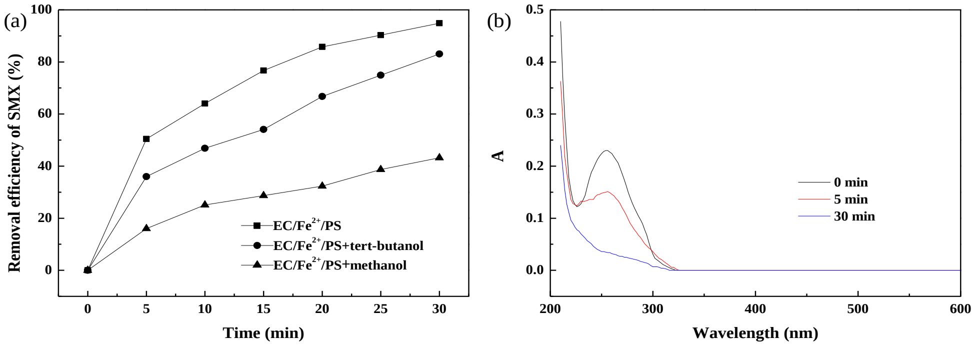

Fig. 4. Effect of quenchers on SMX degradation (a) and UV-vis spectrum during the reaction (b) in the EC/Fe^{2+}/PS system

Reaction kinetics of the EC/Fe^{2+}/PS system

The first-order kinetic equation was best to fit the reaction kinetics of the EC/Fe^{2+}/PS system. The reaction rate constant k is affected by several factors, such as [Fe^{2+}], [PS], [Na_2SO_4], [current density] and [plate spacing] at certain SMX concentration and pH conditions. Then the apparent correlation could be established:

$k=\mu[Fe^{2+}]^a\ [PS]^b\ [Na_2SO_4]^c\ [\text{current density}]^d\ [\text{plate spacing}]^e$

where μ, a, b, c, d, e are constants. In order to obtain these constants, the above results were subjected to statistical analysis. Then the reaction rate constant of k can be expressed as:

$k=8.9921\times10^{-4}[Fe^{2+}]^{0.4383}[PS]^{0.7747}[Na_2SO_4]^{0.3382}[\text{current density}]^{0.4095}[\text{plate spacing}]^{0.8573}$

So, the kinetic equation of SMX degradation in EC/Fe^{2+}/PS system can be expressed as:

$C_t=C_0\ \exp\ (-8.9921\times10^{-4}\ [Fe^{2+}]^{0.4383}\ [PS]^{0.7747}\ [Na_2SO_4]^{0.3382}\ [\text{current density}]^{0.4095}\ [\text{plate spacing}]^{0.8573}\ t)$.

From the above equation, the order of factors affecting the reaction rate is as follows: plate spacing > PS concentration > Fe^{2+} concentration > current density > Na_2SO_4 concentration under certain reaction conditions. Comparison between kinetic model and experimental data shows that the actual value was well fitted to this dynamic model.

CONCLUSIONS

The main results of this study showed that:

1. The EC/Fe^{2+}/PS system could effectively degrade SMX in aqueous medium. The acidic conditions were favorable to SMX degradation. The optimal values of Fe^{2+} concentration and plate spacing were 1 mM and 9 cm, respectively. When the values were higher than the optimal values, the removal efficiency decreased and the processing cost increased. The removal efficiency increased with the separate increase in PS concentration, Na_2SO_4 concentration and current density.

2. The results of the free radical test showed that $SO_4^{\bullet-}$ played a leading role in the EC/Fe^{2+}/PS system. The benzene ring structure of SMX was destroyed in the reaction. The reaction kinetic equation was obtained:

$C_t=C_0\ \exp\ (-8.9921\times10^{-4}\ [Fe^{2+}]^{0.4383}\ [PS]^{0.7747}\ [Na_2SO_4]^{0.3382}\ [\text{current density}]^{0.4095}\ [\text{plate spacing}]^{0.8573}\ t)$.

These results show that sulfonamide antibiotics could be effectively oxidized in the EC/Fe^{2+}/PS system. This study provides an efficient and environmentally friendly treatment for removing sulfonamides in water.

Acknowledgement: *This work was financially supported by Doctoral Research Start Fund Project of Liaoning Province (201501070), Department of Education Scientific Research General Project of Liaoning Province (L2015451), and Scientific Research Project of Shenyang Jianzhu University (2017023). We would like to thank Timothy R. Filley for language correction.*

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