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Original Research

Removal of Sulfonamides in Water Using an Electro/Peroxydisulfate System Catalyzed with Activated Carbon

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Abstract

Sulfonamides are frequently detected in surface water and groundwater, which have the characteristics of low concentration, high toxicity, and being difficult to remove. In this study, an electro/peroxydisulfate system catalyzed with activated carbon (EC/AC/PS) was used to treat sulfamethoxazole (SMX). The results showed that the removal efficiency of SMX was 88.5% by the EC/AC/PS system. An increase of SMX concentration led to a decrease of SMX degradation efficiency, followed by an increase of intermediate products. Acidic conditions improved the degradation of SMX with optimum pH value of 5. A separate increase of AC concentration, PS concentration, and current density would enhance the degradation efficiency of SMX. But the extent was limited when reaching a certain level. There was an optimum plate spacing of 9 cm for SMX degradation efficiency. After repeating the use of AC 4 times, the removal efficiency of SMX still exceeded 80%. The free radical experiments showed that $SO_4^{\bullet-}$ played a leading role. The benzene ring structure of SMX was gradually decomposed with reaction. According to data analysis, the reaction kinetic model was $C_t = C_0\exp(-1.100\times10^{-3}[AC]^{0.4471}[PS]^{0.6397}[\text{current density}]^{0.5658}[\text{plate spacing}]^{0.8405}t)$. This study implied that the EC/AC/PS process could effectively remove sulfonamide antibiotics in water, which was an environmentally friendly treatment method.

Keywords: activated carbon, electrochemistry, peroxydisulfate, sulfonamides

Introduction

Pharmaceuticals and personal care products (PPCPs) have been recently detected in surface water and groundwater, attracting more and more attention. They have low concentrations, strong toxicity, and are difficult to remove [1]. Antibiotics are an important PPCP pollutant. Although presented in trace amounts in water, antibiotics show a long-lasting state due to their poor degradability and constant input. Their residues can flow into groundwater or surface water, and even accumulate in the soil. Through the food chain they will threaten human health [2]. At present, many countries have detected antibiotic contamination [3-4]. Previous studies have shown that sulfonamides (SAs)

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with chemotherapeutic effects are the earliest and most widely used antibiotics [5].

Advanced oxidation methods are usually used in the field of antibiotic treatment [6]. Advanced oxidation technology relies on strong oxidizing free radical species, and it has the advantages of strong oxidation activity and low selectivity to pollutants. And it can remove some organic pollutants that could not be easily degraded by traditional oxidation methods [7]. One of the advanced oxidative methods is activated peroxydisulfate (PS) technology. The PS dissolves in water and ionizes to produce $S_2O_8^{2-}$. In the presence of an activator, $S_2O_8^{2-}$ is activated to produce $SO_4^{\bullet -}$ [8-9]. The PS activation methods include thermal activation, transition metal ions activation, UV activation, activated carbon activation, and microwave activation [10-13].

Activated carbon (AC) has a wide range of sources and low prices [14]. A method for activating PS to treat organic wastewater by electrochemical synergistic activated carbon was first used in a previous study that combined electro with PS catalyzed with activated carbon (EC/AC/PS) to treat organic wastewater. The anode was Ti/IrO_2-RuO_2-TiO_2 and the cathode was stainless steel. The pH of the reaction solution was adjusted to 3-7, the PS concentration was 2.50 to 10 mM, the concentration of Na_2SO_4 was 50 mM, the amount of the activated carbon was 0.25-0.75 g/L, and the current density was 4-16 mA/cm^2. In this condition, the decolorization efficiency of yellow-orange II would be up to 87.1% with the initial concentration of 100 mg/L. The decolorization efficiency of yellow-orange II was only 21.2% after 1 h reaction if just-activated carbon was present in the system. In the AC/PS system, the decolorization efficiency of yellow-orange II reached 70.2%. These results indicated that the electrochemical technology could significantly enhance the activation of PS by activated carbon to remove yellow-orange II. They could also reduce processing costs [15-16].

In this study, the PS oxidative method catalyzed with activated carbon was combined with electrochemical technology. The treatment target was sulfamethoxazole (SMX), which had been frequently detected in the environment. The effective and impact factors on degradation efficiency of SMX were investigated in the EC/AC/PS system, and the kinetics of reaction were also analyzed.

Materials and Methods

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 AC were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. AC was soaked in 5% hydrochloric acid to wash out the ash and impurities on its surface. Then it was repeatedly washed with deionized water and dried in an oven at 105ºC. The activated carbon after n times used was denoted as AC_n (initial AC was AC_0). All other reagents were analytical grade. Na_2SO_4 was added as a supporting electrolyte. The experiments were performed in a glass beaker with an effective volume of 2000 mL. The 20 cm × 6 cm × 0.3 cm electrode plate anode (Ti/IrO2-RuO2-TiO2 coated with ruthenium titanium iridium) and same-sized electrode plate cathode (stainless steel) were used. The electric stirring method provided mixing of the solution. A direct current (DC) power supply was used to supply constant current conditions.

The degradation efficiency of SMX was investigated at five different conditions of PS, AC, EC, AC/PS, and EC/AC/PS. The impact factors of EC/AC/PS system on SMX removal efficiency were analyzed, such as SMX initial concentration, initial pH, AC concentration, time of AC reuse, PS concentration, current density, and plate spacing. At the same time, the PS residual rate was also analyzed. To determine the types of free radical, excess tert-butanol and methanol were added [17]. The absorbance of the solution in a certain wavelength range was measured in order to analyze reaction products.

The method of sodium 1, 2-naphthoquinone-4-sulfonate as the chemical derivative chromogenic reagent was used to determine the concentration of SMX by Spectrophotometry [18]. The degradation efficiency of SMX was calculated according to Equation (1):

$$\text{Degradation efficiency (\%)} = ((C_0 - C_t)/C_0) \times 100 \quad (1)$$

…where C_0 and C_t are the concentrations of SMX at times 0 and t, respectively. An iodometric titration method was used to determine the concentration of PS [19].

Results and Discussion

Degradation Efficiency of SMX in Different Processes

In order to explore the effect of AC activation on PS and the effect of EC/AC/PS on SMX treatment, five different systems of PS, AC, EC, AC/PS, and EC/AC/PS were analyzed. It can be seen from Fig. 1 that when the solution only added PS, the degradation efficiency of SMX was almost zero after 80 min reaction. While 12.41% SMX was removed when only adding AC after 80 min reaction, indicating that AC had a certain degree of adsorption on the target pollutants. The removal efficiency of SMX in the AC/PS system was much higher than that of AC and PS alone after an 80-min reaction, implying that AC could effectively activate PS to produce $SO_4^{\bullet -}$ free radicals to remove SMX. When EC was applied alone, the degradation efficiency of SMX reached 55.89% after the 80-min reaction. The removal efficiency of SMX

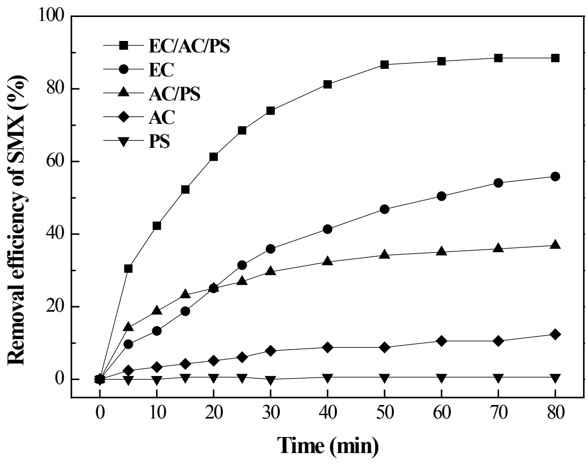

Fig. 1. Removal efficiency of SMX in different systems.

reached 88.50% under test conditions of the EC/AC/PS system, and was higher than the sum of AC/PS and EC. These results showed that the activation rate of PS was increased under an electrical field, suggesting the synergistic effect between them [20].

Effects of SMX Initial Concentration, Initial pH, AC Concentration and Reuse Times on Degradation Efficiency of SMX in EC/AC/PS System

As can be seen from Fig. 2 a), the removal efficiency of SMX decreased as the concentration of SMX increased. The reason may be that when the concentration of pollutants was high, only parts of it could be removed under the condition of limited free radicals in the system. In addition, the concentration of intermediate products greatly increased with the increase of SMX concentration. These intermediates required the consumption of electric energy and free radicals. Therefore, the removal rate of the system became lower the higher the initial concentration of SMX during the same period.

As can be seen from Fig. 2 b), as the initial pH value increased, the degradation efficiency of SMX first increased and then decreased. When the pH value was 5, the degradation efficiency reached the maximum. At the pH values of 3, 5, 7, and 9, the removal efficiencies of SMX were good, which were 88.68%, 89.40%, 83.97%, and 75.82%, respectively. This indicated that the EC/AC/PS system could maintain a high degradation efficiency of SMX within a wide range of initial pH [21]. When the initial pH was 11, SMX degradation efficiency rapidly decreased to 46.83%. Combined with the effect of pH on the residual rate of PS, the residual PS concentration gradually increased as the initial pH increased from 3 to 11. This demonstrated that the acidic and neutral conditions were more beneficial to the decomposition of PS, resulting in more active free radicals to degrade SMX. When pH was 5, the removal efficiency of SMX was the best. This may because too high or too low pH is not conducive to the adsorption of SMX by activated carbon. Under alkaline conditions, the adsorption of organic

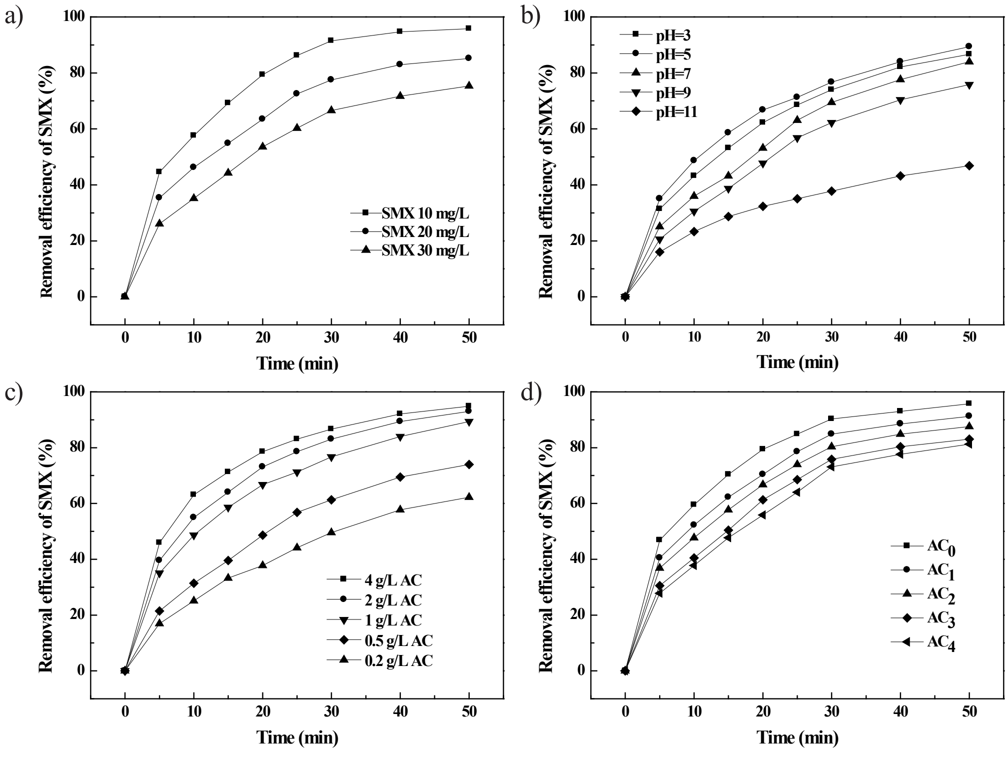

Fig. 2. Effect of SMX initial concentration a), initial pH b), AC concentration c), and reuse times d) on SMX degradation efficiency in the EC/AC/PS system.

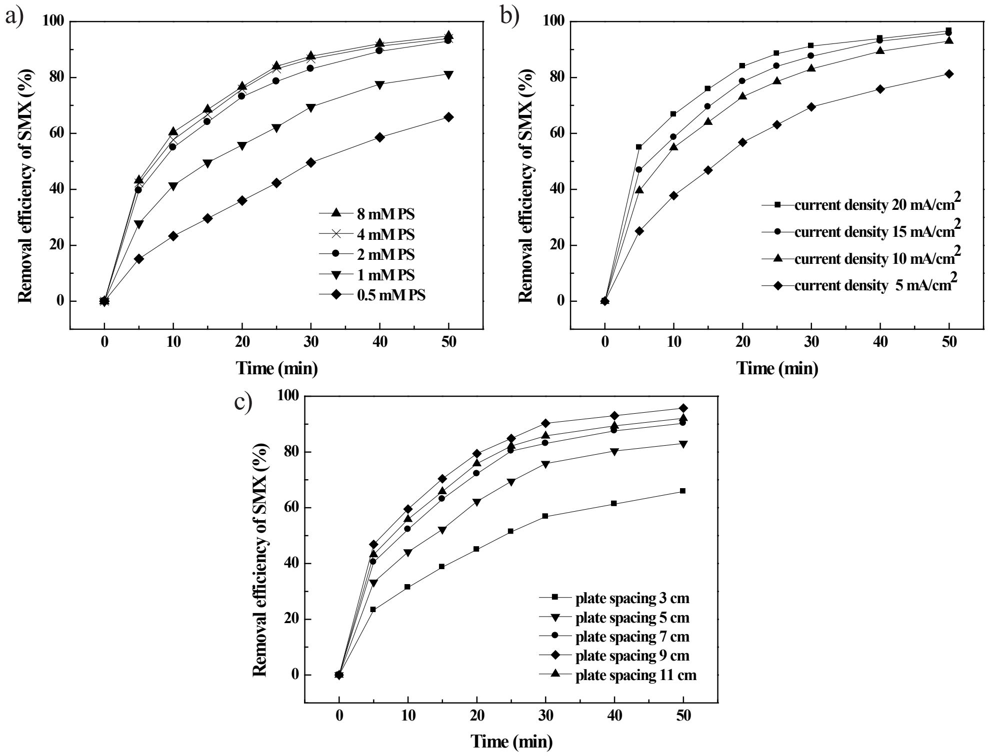

Fig. 3. Effect of PS concentration a), current density b), and plate spacing c) on SMX degradation efficiency in the EC/AC/PS system.

matter on the activated carbon surface was less. And the $SO_4^{\bullet -}$ would react with a large amount of $^{\bullet}OH$, resulting in reducing the free radicals in alkaline conditions [22]. Thus the conditions of electrochemical oxidation, activated carbon adsorption, and the formation of free radicals were best for degrading SMX when pH was 5.

As can be seen from Fig. 2 c), the removal efficiency of SMX gradually increased from 55.89% to 93.93% as the AC concentration increased from 0.2 g/L to 4 g/L in the EC/AC/PS system. When the concentration of AC increased, the residual efficiency of PS decreased, indicating an increase in PS decomposition. The reason could be analyzed from the activation and adsorption properties of activated carbon. On one hand, as the concentration of AC increased, the rate of catalytic decomposition of PS accelerated and generated more $SO_4^{\bullet -}$. On the other hand, as the concentration of activated carbon increased, adsorption capacity would increase, then more pollutants would be adsorbed [23-24]. Although the removal efficiency of SMX was better when more activated carbon was added, the SMX was adsorbed to the AC inside. Then the SMX would not be oxidized and degraded by $SO_4^{\bullet -}$. Therefore, the concentration of AC is not as good as possible. Considering the adsorption of activated carbon and the removal efficiency of SMX, the concentration of AC was controlled at 2 g/L in the EC/AC/PS system.

As can be seen from Fig. 2 d), with the increase of AC repeated use times, the degradation efficiency of SMX gradually decreased. The degradation efficiency of SMX reached 95.74% in AC_0 condition of EC/AC/PS system. The removal rate of SMX was 81.25% in AC_4 condition after reacting for 50 min. When increased reuse times of AC, the activation effect on PS was weakened. But the decline extent was not obvious. This may be because more SMX was adsorbed inside the porous structure of the AC as reuse time increased. The results would reduce the chances of contact between the AC and PS, decreasing the effect of activating PS. In addition, with the increase of reuse times, the adsorption sites on the surface were more occupied. Thus the adsorption of SMX on activated carbon would be reduced. A previous study [25] explained that the main reason for the deactivation of activated carbon was the adsorption of organic substances on the surface of activated carbon. But the deactivation of activated carbon could be reduced by increasing the concentration of PS [26]. This would increase the reuse time of activated carbon and reduce the treatment cost. In this study, the removal efficiency of SMX was more than 80% even in AC_4 condition, indicating that the reused AC still had a good catalytic effect. This may be because the electric field has a regenerative effect on activated carbon.

Effect of PS Concentration, Current Density, and Plate Spacing on Degradation Efficiency of SMX in the EC/AC/PS System

As can be seen from Fig. 3 a), when the concentration of PS increased from 0.5 mM to 2 mM, the removal efficiency of SMX greatly increased from 65.85% to 92.12%. When the concentration of PS continuously increased to 4 mM and 8 mM, the degradation efficiencies of SMX were 93.93% and 94.84% after 50 min of reaction, respectively. Degradation efficiency did not change significantly. The PS residual efficiency decreased with the increase of its concentration. When the concentration of PS was more than 2 mM, the residual efficiency gently varied. When other conditions were constant, $SO_4^{\bullet -}$ increased as the concentration of PS increased in the system. Therefore, when the concentration of PS increased from 0.5 mM to 2 mM, the degradation efficiency of SMX increased obviously. Previous studies [25] showed that pollutant removal efficiency increased slightly with the increase of PS concentration when it reached a certain value. The reason may be due to the self-quenching reaction when the concentration of PS continued to increase. Meanwhile, $S_2O_8^{2-}$ would also consume part of $SO_4^{\bullet -}$, leading to a decrease in $SO_4^{\bullet -}$ concentration. When adding more than 4 mM PS in this study, the $SO_4^{\bullet -}$ and $S_2O_8^{2-}$ concentrations were relatively high. Then the above phenomena would play the role of weakening the oxidative degradation of SMX. Therefore, the removal efficiency did not significantly improve when adding more than 4 mM PS. With comprehensive consideration of treatment effect and cost, the suitable PS concentration was 2 mM in the EC/AC/PS system.

As Fig. 3 b) showed, the removal efficiency of SMX increased with the current density increasing. When the current density increased from 5 mA/cm^2 to 10 mA/cm^2, the degradation efficiency of SMX increased from 78.53% to 92.12%. Then the degradation efficiency increased gradually while current density continued to increase. The PS decomposition rate increased with the current density increasing. First, as current density increased, the electrochemical reaction of contaminants became more intensive between electrodes, accelerating the rate of oxidative degradation and improving electrolysis efficiency [27]. At the same time, some research showed that the electric field could promote the regeneration of AC and enhance the ability of activation PS [28]. Thus, the removal efficiency of SMX increased with the current density increasing. However, when the current density reached a certain value, removal efficiency little increased with current density increasing. This may be because of the secondary reaction or thermal effect in the system when the current density was too high. These reactions would consume more current than at low current densities.

As can be seen from Fig. 3 c), the degradation efficiency of SMX tended to increase first and then decrease with the increase of plate spacing. When plate spacing was 3 cm, the degradation efficiency of SMX was relatively low. Increasing the plate spacing to 5 cm, the degradation efficiency of SMX increased significantly. When the plate spacing further increased to 9 cm, the degradation efficiency of SMX reached the maximum of 95.74%. When the plate spacing was more than 9 cm, the degradation efficiency of SMX tended to decrease slowly. When the other conditions were constant, the plate spacing mainly affect system resistance. When the plate spacing was small, resistance was small. Then the voltage was relatively small between the two plates. Thus the electrochemical reaction power was weak and SMX degradation efficiency was low. On the other hand, the regeneration effect on AC was few by electrochemistry. The rate of oxidation SMX would not improve. With the increase of plate spacing, electrochemical oxidation and free radical oxidation would strengthen. The removal efficiency of SMX would increase with plate spacing increasing. However, when plate spacing was too large, the resistance of the system was too large. The mass transfer efficiency of the solution became lower, and the degradation efficiency of SMX slowed. In this study, the best value of plate spacing was 9 cm.

Verification of Free Radicals and Reaction Products in the EC/AC/PS System

In order to verify the type of free radicals in the system, the effects of radical quenchers such as tert-butanol and methanol were investigated. Tert-butanol is an effective quencher of $^{\bullet}OH$ [29]. Methanol is a good quencher of both $SO_4^{\bullet -}$ and $^{\bullet}OH$ [30]. The addition of tert-butanol and methanol inhibited SMX degradation efficiency in the EC/AC/PS system (Fig. 4 a). When

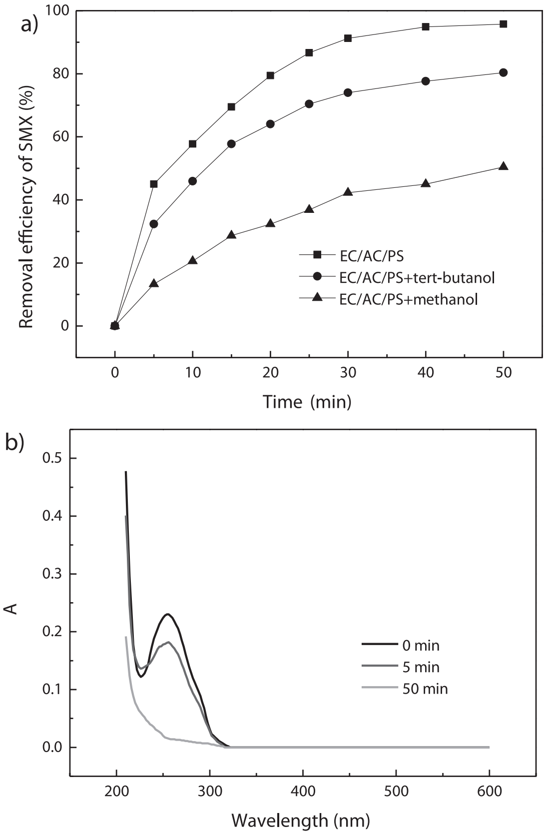

Fig. 4. Effect of scavengers on SMX degradation a) and UV-vis spectral changes with reaction time b) in the EC/AC/PS system.

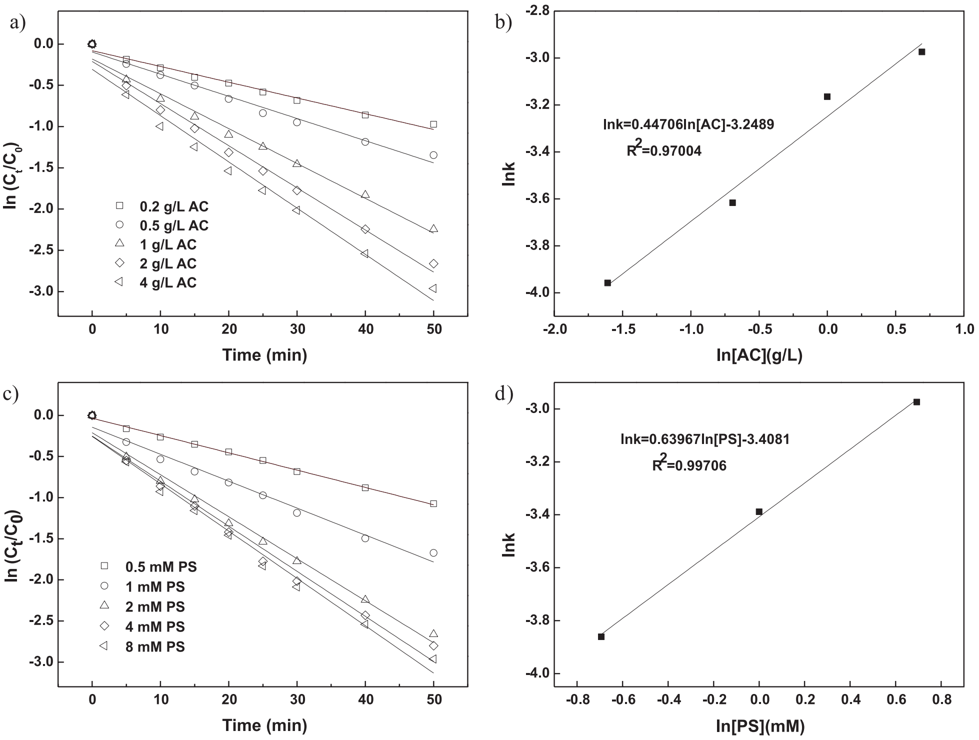

Fig. 5. Effect of AC a) and PS c) at varying concentrations on SMX decomposition and plot of lnk vs ln[AC] b), lnk vs ln[PS] d) in the EC/AC/PS system.

no quencher was added to the system, the degradation efficiency of SMX reached 95.74% after 50 min reaction. The addition of tert-butanol reduced SMX degradation efficiency by 15.4%, indicating the existence of $^{\bullet}$OH in the system. When adding an excessive amount of methanol, the degradation efficiency of SMX significantly decreased – by 45.29%. These results demonstrated that $SO_4^{\bullet-}$ played a leading role in the free radical oxidation of SMX.

Before the reaction, the solution had an obvious absorption peak at the 256 nm wavelength, implying benzene ring B structure (Fig. 4 b). The absorption peak weakened until disappearing with the reaction time, meaning that the SMX was gradually degraded and functional groups were damaged [31]. It was interesting that the absorbance suddenly increased at the wavelength of 230 nm and 300-320 nm after 5 min reaction, respectively. This indicated that intermediates were produced with the reaction. These peaks vanished after 50 min reaction, suggesting SMX substantially mineralized to the final products by oxidative degradation.

Kinetic Equation of Degradation SMX in the EC/AC/PS System

Reaction kinetics of the EC/AC/PS system was best to fit the first-order reaction kinetics equation according to the data analysis of SMX concentration with reaction time. The reaction rate constant of k is affected by several factors, such as [AC], [PS], [current density] and [plate spacing] under specific SMX initial concentration, pH, and electrolyte concentration conditions [32] that could be expressed as Equation (2):

$$k = \mu[AC]^a\,[PS]^b[\text{current density}]^c[\text{plate spacing}]^d \qquad (2)$$

… where μ, a, b, c, and d are constant. In accordance with getting these constant, data analysis was conducted. As can be seen from Fig. 5 a) and b), $k = 0.0388\ [AC]^{0.4471}$ when other factors were constant. Similarly, $k = 0.0331\ [PS]^{0.6397}$ as can be seen from Fig. 5 c) and d), $k = 0.0134\ [\text{current density}]^{0.5658}$ as can be seen from Fig. 6 a) and b), and $k = 0.00936\ [\text{plate spacing}]^{0.8405}$ as can be seen from Fig. 6 (c) and (d) under certain conditions separately.

In summary, the reaction rate constant of k can be expressed as:

$$k = 1.100\times10^{-3}[AC]^{0.4471}[PS]^{0.6397}[\text{current density}]^{0.5658}[\text{plate spacing}]^{0.8405} \qquad (3)$$

Then the kinetic equation of degradation SMX in EC/AC/PS system would be:

$$C_t = C_0\exp(-1.100\times10^{-3}[AC]^{0.4471}[PS]^{0.6397}[\text{current density}]^{0.5658}[\text{plate spacing}]^{0.8405}t) \qquad (4)$$

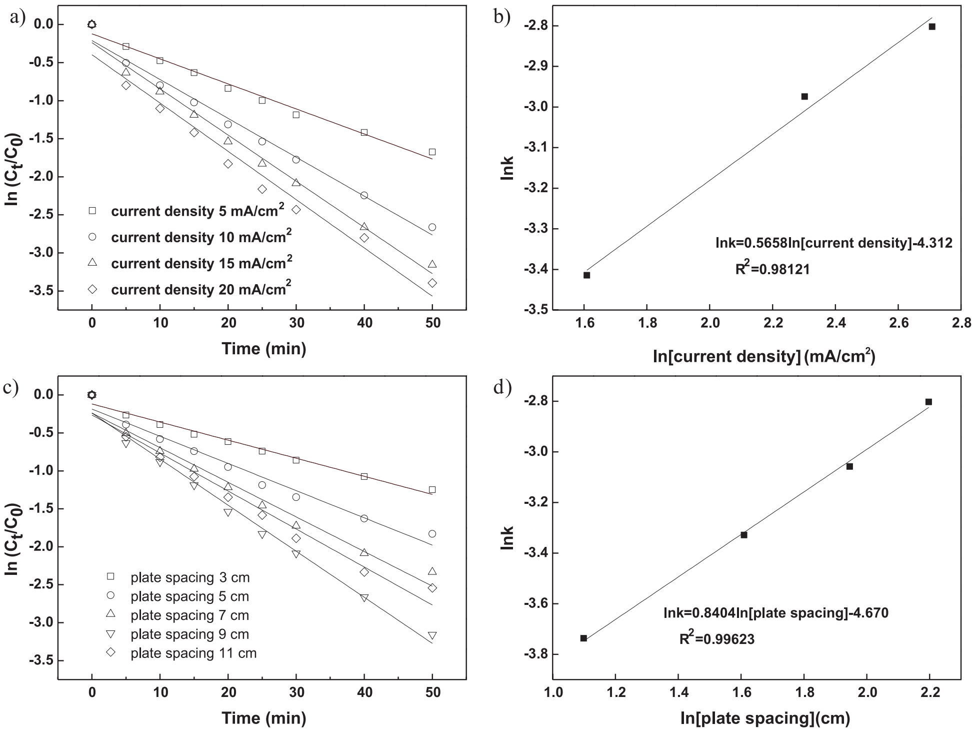

Fig. 6. Effect of current density a) and plate spacing c) at varying concentrations on SMX decomposition and plot of lnk vs. ln[current density] b), and lnk vs. ln[plate spacing] d) in the EC/AC/PS system.

From the equation, we can get the order of factors affecting the reaction rate: plate spacing>PS concentration>current density>AC concentration. The equation had been verified with actual values. They were fitted well.

Conclusions

In this study, an EC/AC/PS system was used to degrade SMX in water. The results showed that AC could activate PS to improve degradation efficiency of SMX. The removal efficiency of SMX by the EC/AC/PS system was higher than that of EC and AC/PS, respectively. This indicated that there was synergy between EC and AC/PS. The concentration of intermediate products would be higher with the higher concentration of SMX, which may compete with SMX for free radicals. Then the degradation efficiency of SMX was reduced. The optimum values of pH and plate spacing for SMX degradation were 5 and 9 cm, respectively. Removal efficiency decreased when the values were higher than the optimal value. Removal efficiency increased to a certain level and then changed little as AC concentration, PS concentration, and current density increased separately. Even with 4-times reused AC, the removal efficiency of SMX remained above 80%. Both $SO_4^{\bullet-}$ and $^{\bullet}OH$ were oxidizing SMX in the EC/AC/PS system, and $SO_4^{\bullet-}$ played a leading role. The benzene ring structure of SMX was damaged with the reaction. The reaction of SMX in the EC/AC/PS system fitted the first order reaction kinetics according to data analysis. Then the reaction kinetic equation was as follows: $C_t = C_0\exp(-1.100\times10^{-3}[AC]^{0.4471}[PS]^{0.6397}[\text{current density}]^{0.5658}[\text{plate spacing}]^{0.8405}t)$. The order of these impact factors was: plate spacing>PS concentration>current density>AC concentration. This study showed that sulfonamide antibiotics could be effectively removed by the EC/AC/PS process. It is an efficient and environmentally friendly method for sulfonamide degradation in water.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

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