

*Original Research*

# Degradation Of Tetracycline Antibiotic in Water by an Electro/Peroxydisulfate System Catalyzed with Fe<sup>2+</sup> Loaded on Activated Carbon

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## Abstract

Tetracycline is a well-known emerging contaminant which affects water environment. In this study, an electro/peroxydisulfate system catalyzed with Fe<sup>2+</sup> loaded on granular activated carbon (EC/Fe-GAC/PS) was used to treat tetracycline hydrochloride (TCH). Experimental results indicated that the removal efficiency of TCH was 86.12% by the EC/Fe-GAC/PS system. When TCH initial concentration was less than 20 mg/L, the removal efficiency of TCH was similar. The removal efficiency of TCH reached highest value when initial pH was 3, Fe-GAC concentration was 0.5 g/L and plate spacing was 9 cm, respectively. When the concentrations of PS and Na<sub>2</sub>SO<sub>4</sub> reached 3.0 mmol/L and 25 mmol/L, respectively, the removal rate of TCH was the highest. When the current density increased to 20 mA/cm<sup>2</sup>, the degradation efficiency of TCH began to decline. When the plate spacing is 9cm, the residual amount of TCH is the lowest. In a certain range, separately increasing of PS concentration, Na<sub>2</sub>SO<sub>4</sub> concentration, and current density would enhance the degradation efficiency of TCH. The free radical experiments showed that SO<sub>4</sub><sup>-</sup> played a leading role in acid conditions. According to data analysis, the reaction kinetic model of EC/Fe-GAC/PS system fitted first-order reaction kinetic model. The order of factors affected reaction efficiency was: plate spacing>current density>PS concentration>Fe-GAC concentration>Na<sub>2</sub>SO<sub>4</sub> concentration in the EC/Fe-GAC/PS system. This study showed that the EC/Fe-GAC/PS process was an efficient, environmental friendly and feasible way to degrade the tetracycline antibiotics in water.

**Keywords:** catalyst, activated carbon, electrochemistry, persulfate, tetracycline

## Introduction

In recent years, the ecological risks and environmental impacts caused by pharmaceuticals and personal care products (PPCPs) have attracted people's attention. Tetracycline (TC) is one kind of PPCPs and is widely used in medicine, animal husbandry and aquaculture industry [1-4]. It is the second most widely used antibiotic in the world and is toxic with low concentration and difficult removal [5, 6]. Toxicity of antibiotics can be assessed using the *Vibrio fischeri* bioluminescence inhibition bioassay. The luminescence of *Vibrio fischeri* is regulated by an intercellular signaling mechanism based on bacterial population density called quorum sensing, a phenomenon related to production of antibiotics [7]. Bioassays based on higher plants can also detect the toxicity of sewage, such as the onion genetic model considered promising, which has positive results for hospital wastewater, anti-toxic agents, industrial wastewater, and pharmaceuticals [8]. In addition, higher plants represented by broad bean can also play a role in detecting the ecotoxicity of antibiotics. The advantages of higher plants are that they are easy to grow and handle, they can be used for experiments without sterile conditions, the experimental results are easy to distinguish, and the speed of cell division is fast [9]. The bacterial growth inhibition method is used as a screen to detect antibiotic residues. Its advantages are that it is relatively cheap, fast and allows the analysis of large numbers of samples [10]. TC could penetrate into the soil and flow into groundwater or surface water, polluting surface water and groundwater [11], causing great harm to the ecosystem and human health [12-15]. Antibiotics have strong biological toxicity to aquatic organisms such as crucian carp and zebrafish. It can inhibit the translation activity of chlorophyll in plants and cause the death of plants in serious cases. Irreversible damage to mammalian reproductive system. It can also induce and spread drug resistance genes [16]. Therefore, finding out an effective technique to control and remove TC in water is an important problem.

Advanced oxidation methods use strong oxidizing free radicals to degrade organic matter, and have the advantages of strong reaction speed, low pollution and large processing range [17]. Advanced oxidation technology is commonly used in antibiotic treatment. Activated peroxydisulfate (PS) technology is an advanced oxidation method, it has the advantages of good stability, low price, mild reaction products [18]. 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  $SO_4^{\cdot-}$  [19,20]. The PS activation methods include thermal activation, transition metal ions activation, UV activation, activated carbon activation, and microwave activation [21-23].

Loaded activated carbon utilizes the rich pores and relatively large specific surface area of activated carbon, and some materials were loaded on the surface

of activated carbon in the form of molecules or lattices [24]. And it improves the chemical properties of the activated carbon surface, enhances the purification effect of wastewater, solves the problem of difficult material recovery, and enhances the utilization efficiency of materials [25].

On the other hand, activated carbon was loaded with metal ions can reduce the activation energy of the reaction system and improve the activation performance and stability of the catalyst [26]. Previous studies have used activated carbon to support Fe-Mn ions (Fe-Mn/AC) to prepare catalysts, and acid red 3R (AR3R) was used as the target pollutant. The effects of different loadings of Fe-Mn, the mass of Fe-Mn/AC, the concentration of PS and the concentration of AR3R on its degradation were investigated. The results show that when Fe-Mn catalyst is formulated in a ratio of 2:3, its ability to activate PS to degrade AR3R is the strongest. When the concentration of AR3R is 40 mg/L, the concentration of PS is 2.5 g/L, and the dosage of catalyst is 0.25 g, the decolorization efficiency of AR3R is 96.79% after 3 h [27]. These results indicated that the removal effect of AR3R by activated carbon was loaded with metal ions was obviously enhanced. Nevertheless, the electrochemical treatment (EC) of organic wastewater with metal ions supported on activated carbon is seldom, especially for the TC degradation.

In this study the PS oxidative method catalyzed with  $Fe^{2+}$  loaded on activated carbon was combined with electrochemical technology to treat tetracycline hydrochloride in water. We compared the removal rates of tetracycline hydrochloride (TCH) under six different systems: PS alone,  $Fe^{2+}$  loaded on granular activated carbon (Fe-GAC), peroxydisulfate catalyzed with  $Fe^{2+}$  loaded on granular activated carbon (Fe-GAC/PS), EC alone, EC/PS, and EC/Fe-GAC/PS. We also studied the effects of different influencing factors, such as the initial concentration of TCH, initial pH value of the system, Fe-GAC dosage, PS concentration,  $Na_2SO_4$  concentration, current density and electrode spacing, on the treatment of TCH in the EC/Fe-GAC/PS system. Finally, we use scavengers to explore the free radicals that play a role in the reaction system, and analyze the oxidation mechanism and the reaction kinetics.

## Materials and Methods

TCH ( $C_{22}H_{24}N_2O_8 \cdot HCl$ ), PS ( $Na_2S_2O_8$ ), ferrous sulfate heptahydrate ( $FeSO_4 \cdot 7H_2O$ ), granular activated carbon (GAC) and other the materials and reagents were of at least analytical grade. Details of materials and reagents are listed in Table 1. The GAC was cleaned with distilled water to remove the ash and impurities on its surface. Then it was repeatedly cleaned by an ultrasonic cleaner and dried in an oven at 115°C. The experimental water was a self-prepared tetracycline hydrochloride solution, which was prepared by mixing TCH powder and distilled water in a fixed ratio. 2.7802 g

Table 1. Details of main materials and reagents.

Reagent name	Purity grade	Origin
Tetracycline hydrochloride (C <sub>22</sub> H <sub>24</sub> N <sub>2</sub> O <sub>8</sub> ·HCl)	Analytical grade	Shanghai McLean
Peroxydisulfate (Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> )	Analytical grade	Shanghai McLean
Ferrous sulfate heptahydrate (FeSO <sub>4</sub> ·7H <sub>2</sub> O)	Analytical grade	Tianjin Regent
Activated carbon (GAC)		Tianjin Regent
Anhydrous sodium sulfate (Na <sub>2</sub> SO <sub>4</sub> )	Analytical grade	Tianjin Regent
Sodium hydroxide (NaOH)	Analytical grade	Sinopharm Group
Concentrated sulfuric acid (H <sub>2</sub> SO <sub>4</sub> )	Analytical grade	Sinopharm Group
Sodium bicarbonate (NaHCO <sub>3</sub> )	Analytical grade	Tianjin Regent
Potassium iodide (KI)	Analytical grade	Tianjin Regent
Tert-butanol (C <sub>4</sub> H <sub>10</sub> O)	Analytical grade	Shanghai McLean
Ethanol (C <sub>2</sub> H <sub>6</sub> O)	Analytical grade	Tianjin Fuyu

FeSO<sub>4</sub>·7H<sub>2</sub>O, 5 g dried GAC and 50 ml distilled water place in a beaker. The beaker was put in an oven at 115°C for 8 hours, took it out for repeated cleaning, dried it to obtain Fe-GAC. The reaction vessel was a 2000 ml glass beaker. The anode and cathode were respectively composed of Ti/IrO<sub>2</sub>-RuO<sub>2</sub>-TiO<sub>2</sub> coated with ruthenium titanium iridium and a stainless-steel plate. The electrode plate size was 20 cm × 6 cm × 0.3 cm. The DC stabilized current power supply provides current, the solution was mixed by means of electric agitation.

The removal efficiency of TCH was detected in six different systems of PS, Fe-GAC, Fe-GAC/PS, EC, EC/PS, EC/Fe-GAC/PS. The impact factors of the EC/Fe-GAC/PS system were investigated on TCH degradation efficiency were analyzed, such as TCH initial concentration, initial pH, Fe-GAC concentration, PS concentration, Na<sub>2</sub>SO<sub>4</sub> concentration, current density and plate spacing. In the meantime, the PS residual rate was also analyzed. Excess trapping agent (ethanol and tert-butanol) were added to analyze the species of free radicals [28]. Because the absorption line of the TCH solution fluctuates unstable around the wavelength of 276 nm, and the absorption peak is easily disturbed by the outside world at the wavelength of 276 nm, the concentration of TCH was measured by ultraviolet-visible spectrophotometer at a wavelength of 356 nm [29].

The removal efficiency (P/%) of TCH was calculated according to Eq. (1),

$$P (\%) = ((C_0 - C_t) / C_0) \times 100 \quad (1)$$

where C<sub>0</sub> and C<sub>t</sub> are the initial concentration of TCH and concentration at reaction time t, respectively. The concentration of PS was determined by iodine titration [30]. The operation method is as follows: add color developer (0.2 g NaHCO<sub>3</sub> and 4 g KI), then add distilled

water to the specified scale, mix and shake well, after fully reacting for 15 min, measure the absorbance value of solutions of different concentrations in a spectrophotometer with a wavelength of 352 nm.

The reusable performance is an important indicator to evaluate whether the catalyst has practical application value, and reflects the stability of the catalyst. We can through five consecutive degradation experiments. The experimental conditions are as follows: the initial concentration of TCH is 20 mg/L, the initial pH = 3, the dosage of Fe-GAC is 0.5 g/L, the concentration of PS is 2.5 mmol/L, the concentration of Na<sub>2</sub>SO<sub>4</sub> is 25 mmol/L, the current density is 15 mA/cm<sup>2</sup>, the electrode plate is The spacing is 9 cm, the reaction is 60 min. After each reaction, it was left standing for 2 hours and then washed with ultrapure water for several times until no TCH was detected in the supernatant. The adsorption was performed again and the data was recorded. The adsorption capacity of tetracycline hydrochloride was analyzed to judge the reusability of the material.

## Results and Discussion

### Degradation Efficiency of TCH in Different Processes

In order to explore the effect of Fe-GAC activation on PS and the effect of EC/Fe-GAC/PS on TCH treatment, six different systems of PS, Fe-GAC, EC, Fe-GAC/PS, EC/PS and EC/Fe-GAC/PS were analyzed. As depicted in Fig. 1, within 60 min, the removal efficiency of TCH was almost zero when only adding PS. When Fe-GAC was added alone, 10.69% of TCH was removed after 60min, indicating that Fe-GAC had a certain degree of adsorption on the target pollutants. Iron is a transition metal with a special valence electron structure. Its variable valence state and special properties make

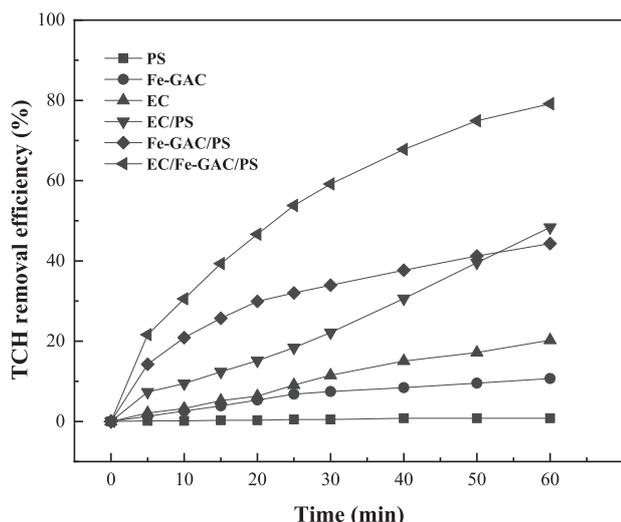


Fig. 1. Removal efficiency of TCH in different systems.

the oxygen atoms on the catalyst surface more active [31]. The removal efficiency of TCH in the Fe-GAC/PS system was much higher than that of Fe-GAC and PS alone and was reach 44.32% after 60 min reaction, indicating that Fe-GAC could activate PS to produce  $\text{SO}_4^{\bullet-}$  free radicals to remove TCH. When EC was used alone, the removal efficiency of TCH after 60 min was 20.25%. The removal efficiency of TCH in EC/Fe-GAC/PS system was 34.83% higher than that in Fe-GAC/PS system and was higher than the sum of Fe-GAC/PS and EC, reaching 79.15%, suggesting the synergistic effect between them. That is to say, in the whole reaction system, the migration of electrons is generated by the plate reaction, so that  $\text{SO}_4^{\bullet-}$  produced by PS, and Fe-GAC activation of PS can also produce  $\text{SO}_4^{\bullet-}$ . The result of this is that the removal rate of TCH is improved under the condition that the amount of  $\text{SO}_4^{\bullet-}$  increases significantly. At the same time, due to the existence of EC, the high-valence iron ions on the surface of Fe-GAC will be reduced to low-valence ferrous ions, which promotes the activation of PS to generate  $\text{SO}_4^{\bullet-}$  [32].

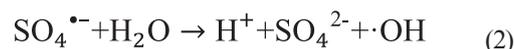
#### Degradation Efficiency of TCH under Different TCH Concentrations

As can be seen from Fig. 2a), the difference of TCH degradation effect was very small (75-79%) at the initial concentration of TCH was less than 20 mg/L. When the concentration of TCH increased to 30 mg/L, the removal efficiency of TCH decreased. The reason may be that in the case of limited free radicals in the system, increasing the TCH content will exceed the removal capacity of the reaction system, and too much TCH cannot be combined with the adsorption sites on the Fe-GAC surface, resulting in a significant decrease in the removal efficiency of TCH. In addition, the surface of Fe-GAC absorbed a large number of organic pollutants, reduced the contact area between Fe-GAC

and PS, resulting in lower to produce free radicals. As a result, the number of  $\text{SO}_4^{\bullet-}$  radicals generated by PS activation decreased, which affected the degradation of TCH.

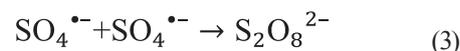
#### Degradation Efficiency of TCH under Different pH Conditions

As can be seen from Fig. 2b), as the initial pH value decreased from 9.0 to 3.0, the removal efficiency of TCH gradually increased, but the increase was small. The maximum removal efficiency of TCH was 81.25% when pH was 3.0. Combined with the effect of PH on the residual rate of PS, the residual PS concentration was similar and the fluctuation was only about 7%. At the same time, the pH value of the solution continued to drop and finally stabilized at about 2.8 during the reaction. The reason could be that  $\text{H}^+$  was produced in water under the action of  $\text{SO}_4^{\bullet-}$  (Eq (2)). Finally, the pH value of the whole reaction system will be stable. Therefore, TCH removal efficiency had little relationship with initial PH value in EC/Fe-GAC/PS system [33].



#### Degradation Efficiency of TCH under Different Dosage of Fe-GAC

As can be seen from Fig. 2c), as the Fe-GAC concentration increased, the degradation efficiency of TCH first increased and then decreased. When the Fe-GAC concentration was 0.1 g/L, 0.3 g/L, 0.5 g/L and 0.7 g/L, TCH removal efficiency were 65.66%, 73.1540%, 83.14% and 79.90%, respectively. According to the influence of Fe-GAC concentration on the residual rate of PS, the residual concentration of PS decreased as the Fe-GAC concentration increased, but the decrease degree was smaller. The content of catalyst Fe-GAC is not proportional to the removal of TCH. This may because as the concentration of Fe-GAC increased, the rate of catalytic degradation of PS accelerated and generated more  $\text{SO}_4^{\bullet-}$ . Coupled with more catalyst surface binding sites, the content of TCH was significantly reduced under the influence of both. However, excessive  $\text{SO}_4^{\bullet-}$  caused self-quenching reaction (Eq (3)) [34]. Therefore, the degradation effect of TCH was best when Fe-GAC concentration was 0.5 g/L.



#### Degradation Efficiency of TCH under Different PS Concentrations

As can be seen from Fig. 2d), with the increase of PS concentration from 0.5 mmol/L to 3.0 mmol/L, TCH

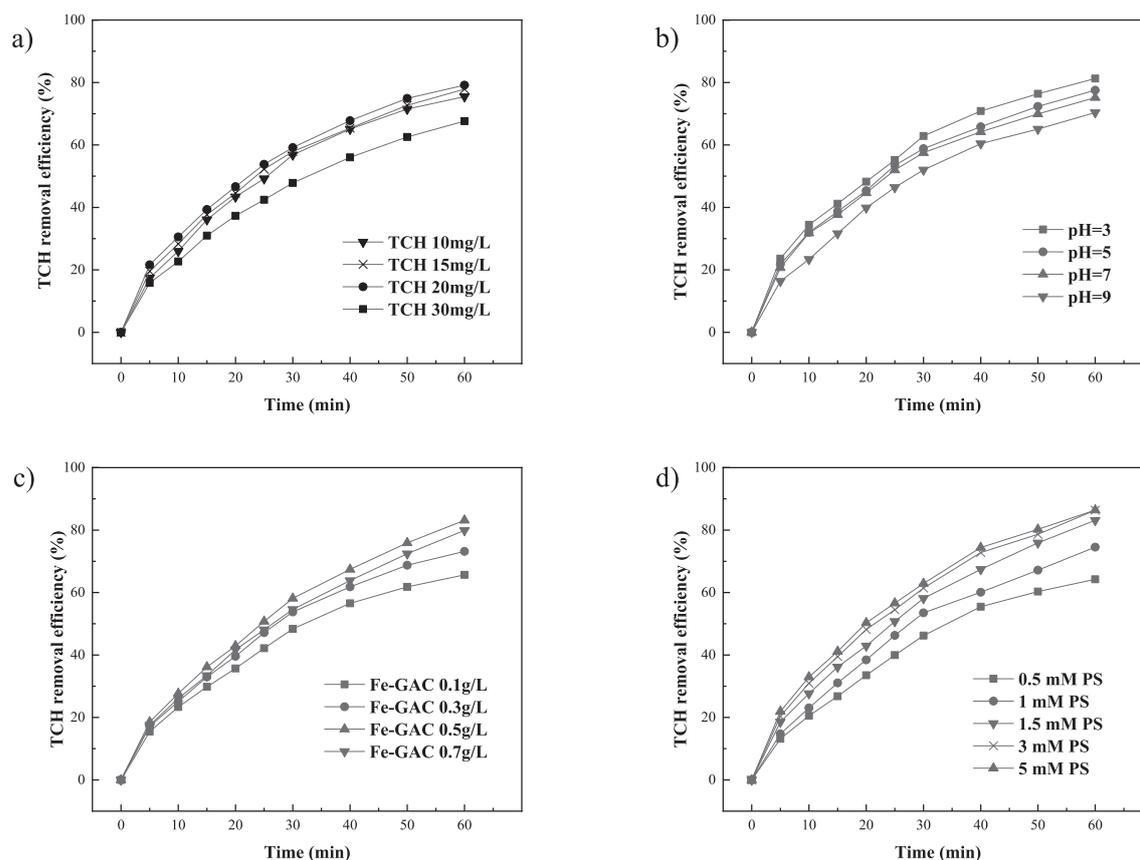
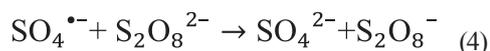


Fig. 2. Effect of the TCH initial concentration a), initial pH b), Fe-GAC concentration c) and PS concentration d) on TCH degradation efficiency.

removal efficiency gradually increased. When the PS concentration was increased to 5.0 mmol/L, the removal efficiency of TCH was almost unchanged compared with 3.0 mmol/L. The change trend of PS residual rate was consistent with that of PS concentration. The reason could be analyzed from two aspects. On one hand, as the concentration of PS increased, the contact probability of PS with Fe-GAC increased and generated more  $\text{SO}_4^{\cdot-}$ . On the other hand, excessive  $\text{SO}_4^{\cdot-}$  was quenched (Eq (4)). Meanwhile,  $\text{S}_2\text{O}_8^{2-}$  would also consume part of  $\text{SO}_4^{\cdot-}$ , leading to a decrease in  $\text{SO}_4^{\cdot-}$  concentration, which led to decrease in reaction  $\text{SO}_4^{\cdot-}$  with TCH. Hence, the removal efficiency did not significantly improve when adding 5 mmol/L PS. With comprehensive consideration of treatment effect and cost, the suitable PS concentration was 3.0 mmol/L in the EC/Fe-GAC/PS system.



#### Effect of $\text{Na}_2\text{SO}_4$ Concentration, Current Density and Plate Spacing on Degradation Efficiency of TCH in EC/Fe-GAC/PS System

As shown in Fig. 3a), with the increase of electrolyte  $\text{Na}_2\text{SO}_4$  concentration, TCH removal efficiency gradually increased in the system. When  $\text{Na}_2\text{SO}_4$

concentration exceeded 25 mol/L, TCH removal efficiency hardly increased.

In the concentration range of 0~25 mmol/L, when the concentration of  $\text{Na}_2\text{SO}_4$  in the solution is gradually increased, the ions with conductivity in the solution increase, the conductivity of the system is enhanced, and the ion transfer rate in the solution is accelerated. This will increase the amount of  $\text{SO}_4^{\cdot-}$ , thereby increasing the TCH removal rate. When the concentration of  $\text{Na}_2\text{SO}_4$  exceeds 25 mmol/L, the solution resistance decreases, and the voltage decreases under the condition of constant current. Low voltage leads to poor oxidation effect of TCH. Therefore, the electrolyte concentration can only be increased within a reasonable concentration range.

The removal of TCH was increased from 71.06% to 86.38% (Fig. 3b) as current density increased from 5 to 15  $\text{mA}/\text{cm}^2$ . When the current density was increased to 20  $\text{mA}/\text{cm}^2$ , the removal efficiency of TCH was almost similar to that of 15  $\text{mA}/\text{cm}^2$  after 60 min. The reason may be that the efficiency of electron transfer became faster with the current density increased. On the one hand this could promote PS to produce  $\text{SO}_4^{\cdot-}$ . On the other hand, it can promote the generation of  $\cdot\text{OH}$ , and the higher the concentration, the better the oxidation reaction effect. Under the combined action of these two, the TCH removal efficiency was improved. However,

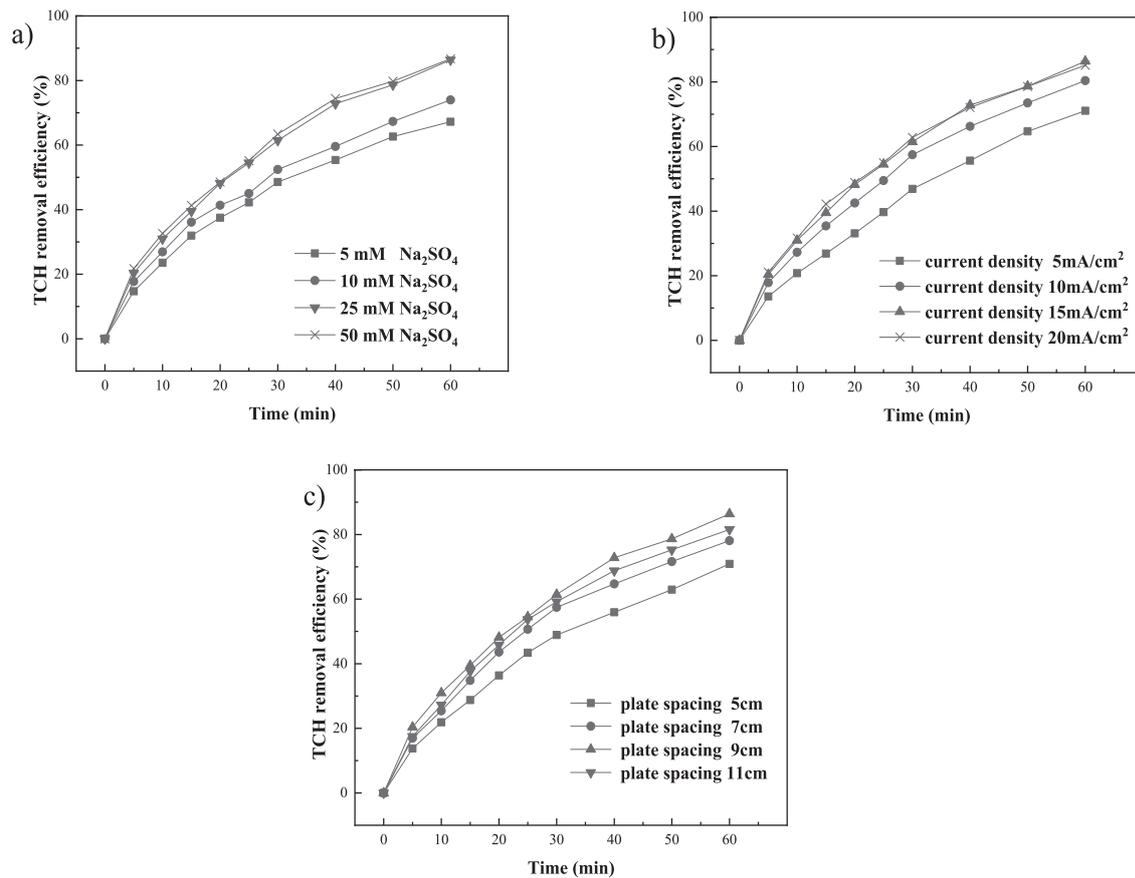
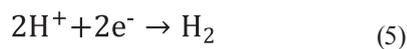


Fig. 3. Effect of Na<sub>2</sub>SO<sub>4</sub> concentration a), current density b) and plate spacing c) on TCH degradation efficiency.

a high current density may produce some side effects, such as hydrogen production (Eq. (5)) and slowed down the removal of TCH [35]. Because H<sup>+</sup> competes for electrons to activate persulfate, this competition results in lower SO<sub>4</sub><sup>•-</sup> levels.



The resistance of the solution is related to the distance between the plates, which directly affects the conductivity of the reaction system. The removal of TCH was increased from 70.91% to 86.38% (Fig. 3c) as plate spacing increased from 5 to 9 cm. When the degradation efficiency dropped to 81.54% with plate spacing of 11 cm. The reason may be that the resistance of the system increased and the electron transfer was difficult when plate spacing was too large, leading to reduce removal efficiency. And plate spacing affected the energy consumption of the system, therefore, in this study plate spacing of 9 cm was employed.

#### Verification of Free Radicals in the EC/Fe-GAC/PS System

The SO<sub>4</sub><sup>•-</sup> and ·OH were active substances present in persulfate systems [36, 37]. In order to verify the type of free radicals in the system, the effects of radical quenchers such as tert-butanol (t-BuOH) and ethanol

(EtOH) were investigated. Since the rate constant of the reaction of t-BuOH with ·OH is about 1000 times the rate constant of the reaction with t-BuOH and SO<sub>4</sub><sup>•-</sup>, it can be considered that Tert-Butanol is an effective quencher of ·OH [38]; Because the molecular structure of ethanol (EtOH) contains α-H, it can react with SO<sub>4</sub><sup>•-</sup> and ·OH at the same time, so it can be considered that ethanol is a common quencher of SO<sub>4</sub><sup>•-</sup> and ·OH [39].

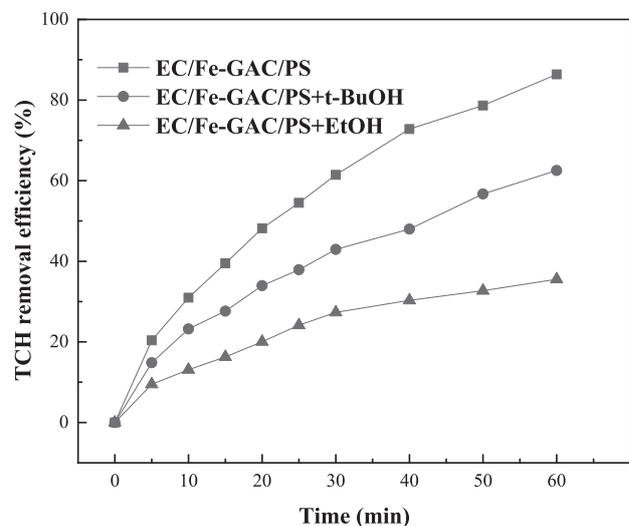


Fig. 4. Effect of scavengers on TCH degradation.

It can be seen from the Fig. 4 that adding tert-butanol and ethanol to the EC/Fe-GAC/PS system had an inhibitory effect on the removal of TCH. When no quencher was added into the system, removal efficiency of TCH was 86.38%. The addition of tert-Butanol reduced the removal efficiency of TCH to 62.12%, which proved that  $\cdot\text{OH}$  with oxidation exists in the system. When ethanol was added, the removal efficiency of TCH was 35.53%. The results showed that  $\text{SO}_4^{\cdot-}$  existed in the system and  $\text{SO}_4^{\cdot-}$  had a stronger effect in the oxidation process in the process of TCH.

### Analysis of Oxidation Mechanism of EC/Fe-GAC/PS System

Studies have shown that  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  can remove pollutants mainly through electron transfer, addition reaction and hydrogen extraction reaction in EC/Fe-GAC/PS system [40]. However, there are also studies that  $\cdot\text{OH}$  degrades organic pollutants through addition reactions and hydrogen extraction reactions, while  $\text{SO}_4^{\cdot-}$  mainly completes the oxidation process of the system through electron transfer [41]. The degradation

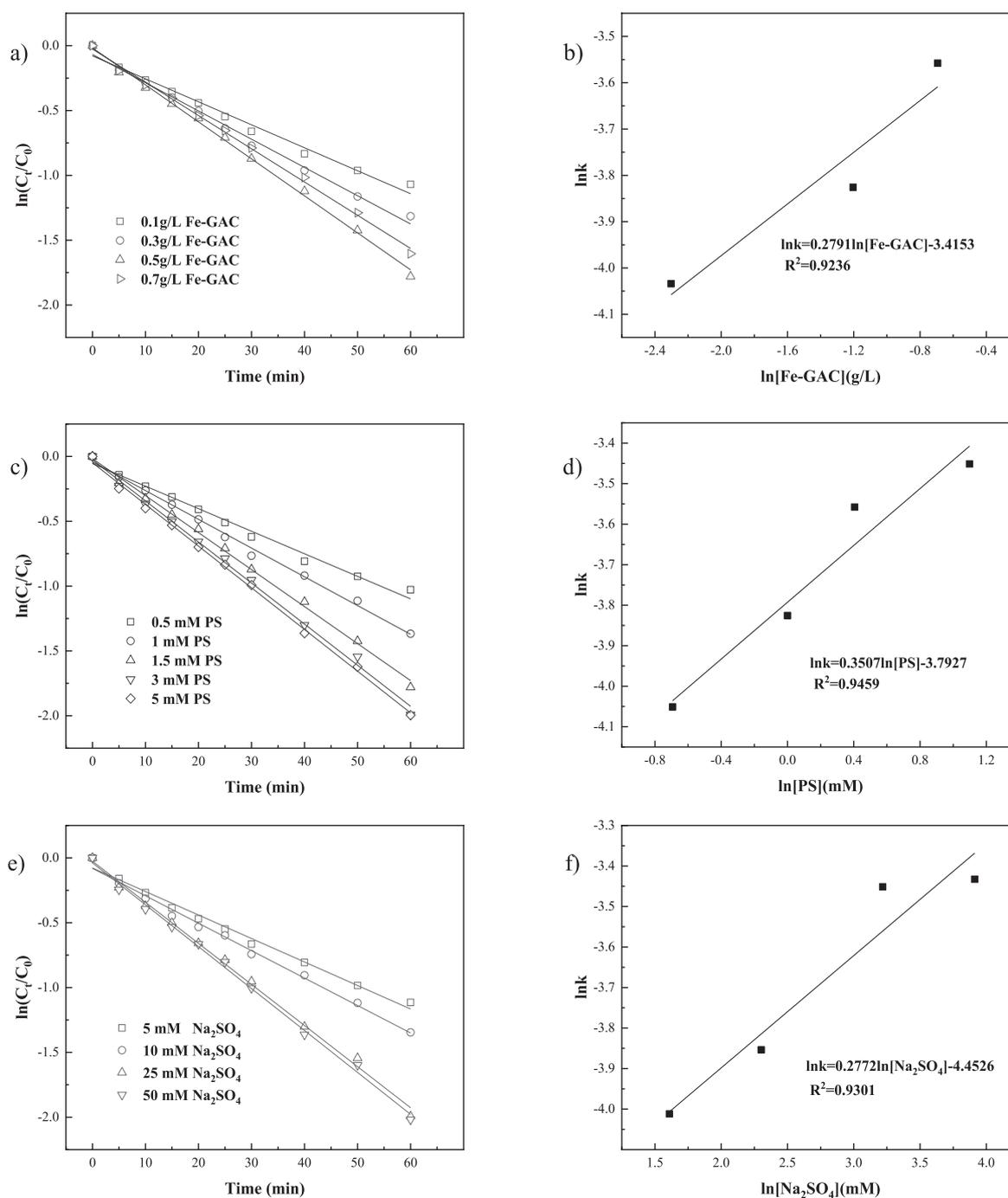


Fig. 5. Effect of Fe-GAC a), PS c) and  $\text{Na}_2\text{SO}_4$  e) at varying concentrations on TCH decomposition and plot of  $\ln k$  vs  $\ln[\text{Fe-GAC}]$  b),  $\ln k$  vs  $\ln[\text{PS}]$  d),  $\ln k$  vs  $\ln[\text{Na}_2\text{SO}_4]$  f).

process under EC/Fe-GAC/PS system is as follows: part of TCH is adsorbed by Fe-GAC and oxidized into small molecular compounds by electric field. The PS was activated to produce  $\text{SO}_4^{\cdot-}$ , reduced to  $\text{SO}_4^{\cdot-}$  at the cathode. In addition, some of the  $\text{SO}_4^{\cdot-}$  reacted with  $\text{H}_2\text{O}$  or  $\text{OH}^-$  to produce  $\cdot\text{OH}$  and  $\text{H}_2\text{O}$  also produced  $\cdot\text{OH}$  on the anode plate. The introduction of electric field could also regenerate Fe-GAC and reduce  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  on the surface, continuing to activate PS to remove TCH.

### Reaction Kinetics of Degradation TCH in the EC/Fe-GAC/PS System

The reaction kinetics of the EC/Fe-GAC/PS system was accorded with the first-order kinetic equation according to the linear relationship between TCH concentration and time. The reaction efficiency constant of  $k$  is affected by several factors, such as  $[\text{Fe-GAC}]$ ,  $[\text{PS}]$ ,  $[\text{Na}_2\text{SO}_4]$ ,  $[\text{current density}]$  and  $[\text{plate spacing}]$  under the condition of TCH initial concentration of 20 mg/L and initial pH = 3.0.

Then that could be expressed as Equation (6):

$$\begin{aligned} k &= k_1[\text{Fe-GAC}]^a && \text{or} \\ k &= k_2[\text{PS}]^b && \text{or} \\ k &= k_3[\text{Na}_2\text{SO}_4]^c && \text{or} \\ k &= k_4[\text{current density}]^d && \text{or} \\ k &= k_5[\text{plate spacing}]^e && (6) \end{aligned}$$

where  $k_1, k_2, k_3, k_4, k_5, a, b, c, d$  and  $e$  are constant. In order to obtain these constant, data analysis was conducted. As can be seen from Fig. 5a) and 5b),  $k = 0.0329 [\text{Fe-GAC}]^{0.2791}$  when other factors were same. Likewise,  $k = 0.0225[\text{PS}]^{0.3507}$  as can be seen from Fig. 5c) and 5d),  $k = 0.0116 [\text{Na}_2\text{SO}_4]^{0.2772}$  as can be seen from Fig. 5e) and 5f),  $k = 0.0106 [\text{current density}]^{0.4022}$  as can be seen from Fig. 6a) and 6b), and  $k = 0.0005 [\text{plate spacing}]^{0.7928}$  as can be seen from Fig. 6c) and 6d) under certain conditions separately.

From the above equation, the order of the factors affecting the reaction efficiency from strong to weak is as follows: Plate spacing, current density, PS concentration, Fe-GAC concentration,  $\text{Na}_2\text{SO}_4$  concentration.

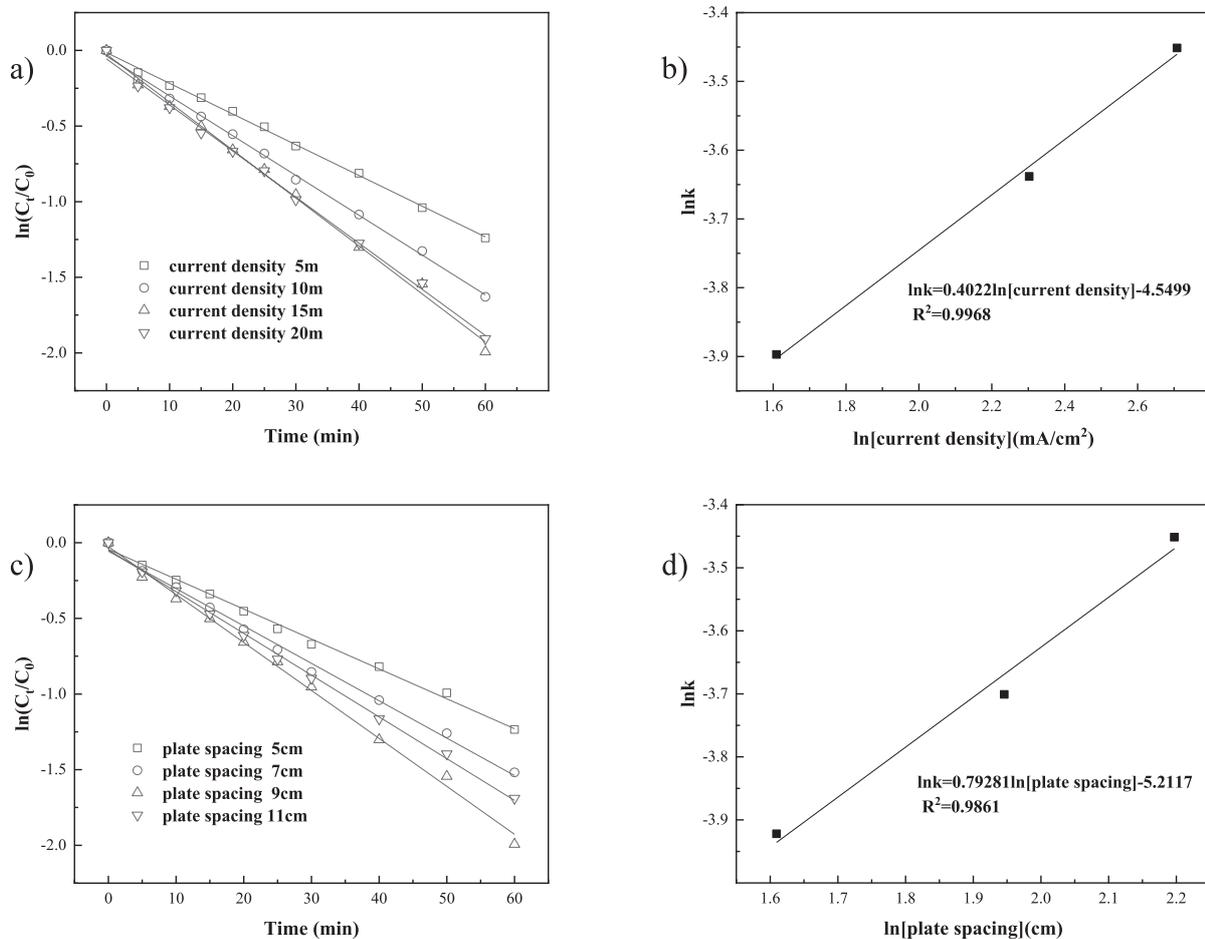


Fig. 6. Effect of current density a) and plate spacing c) at varying concentrations on TCH decomposition and plot of  $\ln k$  vs.  $\ln[\text{current density}]$  b), and  $\ln k$  vs.  $\ln[\text{plate spacing}]$  d).

### Comparison with Previous Similar Studies

Zhidan studied the removal of tetracycline in water by anodic electrochemical oxidation of titanium-based tin-antimony [42]. The method used in the above study has a higher removal rate than the method used in this study, but the preparation of the electrode plates is more complicated.

Arif Chowdhury used Ni-Co-S nanoparticle-loaded activated carbon to degrade antibiotics in wastewater [43]. The method used in this study has a lower degradation efficiency of antibiotics than the above methods, but the loading methods and materials used in the above methods are more expensive and less economical.

### Conclusions

Ferrous ion-supported granular activated carbon materials were prepared by infiltration method. Activated carbon supported metal catalyst and electrochemistry were used to activate persulfate to degrade tetracycline hydrochloride. The effects of different reaction factors on the removal of tetracycline hydrochloride were investigated. Through experiments, the removal rate of tetracycline hydrochloride was 86.12%. This study preliminarily explored the oxidation reaction mechanism of tetracycline hydrochloride. By analyzing the reaction kinetics, the linear relationship between the reaction system and the degradation of tetracycline hydrochloride was good. This new treatment method has great promise.

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### Conflict of Interest

The authors declare no conflict of interest.

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