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# Activated Carbon Assisted Fenton-Like Treatment of Acid Red G Containing Wastewater

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**Abstract:** Fenton reaction as an effective advanced oxidation technology has been widely used in wastewater treatment for its stable effluent quality, simple operation, mild condition, and higher organic degradation with non-selectivity. However, the traditional Fenton reaction is limited by the sluggish regeneration of $Fe^{2+}$, resulting in a slower reaction rate, and it is necessary to further increase the dosage of $Fe^{2+}$, which will increase the production of iron sludge. Activated carbon (AC) has a strong adsorption property, and it can not be ignored that it also can reduce $Fe^{3+}$. In this study, the degradation of acid red G (ARG) by adding AC to the $Fe^{3+}/H_2O_2$ system, the role of reducing ability, and the reason why AC can reduce $Fe^{3+}$ were studied. By adding three kinds of ACs, including coconut shell activated carbon (CSPAC), wood activated carbon (WPAC), and coal activated carbon (CPAC), the ability of ACs to assist $Fe^{3+}/H_2O_2$ Fenton-like system to degrade ARG was clarified. Through the final treatment effect and the ability to reduce $Fe^{3+}$, the type of AC with the best promotion effect was selected as CSPAC. The different influence factors of particle size, and concentration of CSPAC, concentration of $H_2O_2$, concentration of $Fe^{3+}$, and pH value were further observed. The best reaction conditions were determined as CSPAC powder with a particle size of 75μm and dosage of 0.6 g/L, initial $H_2O_2$ concentration of 0.4 mmol/L, $Fe^{3+}$ concentration of 0.1 mmol/L, and pH = 3. By reducing the adsorption effect of CSPAC, it was further observed that CSPAC could accelerate the early reaction rate of the degradation process of ARG by the $Fe^{3+}/H_2O_2$ system. FT-IR and XPS confirmed that the C-O-H group on the surface of CSPAC could reduce $Fe^{3+}$ to $Fe^{2+}$. This study can improve the understanding and role of AC in the Fenton reaction, and further promote the application of the Fenton reaction in sewage treatment.

**Keywords:** Fenton reaction; activated carbon; reduction of $Fe^{3+}$; adsorption; acid red G (ARG)

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## 1. Introduction

Fenton reaction as one of the effective advanced oxidation technologies (AOPs) has been widely used in wastewater treatment for its stable effluent quality, simple operation, higher organic loading and mild condition [1–3]. For instance, the Fenton process can dispose of wastewater with a large chemical oxygen demand (COD) ranging from 100,000 to 150,000 mg/L [4,5]. Meanwhile, Fenton reaction can degrade not only conventional organic pollutants but also bioaccumulated and refractory pollutants, such as high concentration nitrogenous dye [6–10], estrogens and Antibiotics. Fenton process can also be applied to soil remediation [11–13], biomedicine [14] and treating deep bacteria-infected diseases[15] in addition to water treatment for its lower side effects and lack of equipment restrictions.

However, Fenton reaction mainly relies on the core reaction between $Fe^{2+}$ and $H_2O_2$ at low pH conditions (pH of 2–4) to generate hydroxyl radicals (•OH) for efficient degradation of organic matters in water with non-selectivity [16,17]. In reaction process, $Fe^{2+}$ is oxidized to $Fe^{3+}$. Although, the generated $Fe^{3+}$ can be reduced by $H_2O_2$ to reproduce $Fe^{2+}$, the reaction rate is much lower than that of the oxidation rate of $Fe^{2+}$ to $Fe^{3+}$ [18–23]. The further reduces the overall oxidation efficiency and requires continuous addition of $Fe^{2+}$ salts [24], which results in large amount of iron sludge to be disposed of [25].This will result in the increase the treatment cost of Fenton reaction and potentially generate secondary pollution, which limits the application of homogeneous Fenton reaction in water treatment [25,26].

In recent years, many methods have been used to improve the treatment effect of Fenton reaction. The one strategy is to combine Fenton reaction with other technologies, such as the introduction of light, electricity, microwave, ultrasound and other technologies to named as photo-Fenton, electro-Fenton, photo-electro-Fenton and microwave-driven Fenton, etc. [11,27–31]. This strategy can be widening the pH range at Fenton process and reduce amount of iron sludge [11,32]. Another strategy is to develop heterogeneous Fenton oxidation technology which is to load iron element on electron-rich material, such as metal oxide [7], Metal-organic frameworks(MOFs) [33,34], graphene [35], carbon nanotube [25], activated carbon [36,37], fullerene [38], Carbon Nitride ($C_3N_4$) [39], etc. The iron source is uniformly supported or immobilized on such materials as small aggregates or clusters to enhance $Fe^{3+}/Fe^{2+}$ cycle and Fenton reaction efficiency[30,40]. The third strategy is to employ various reducing agents into the traditional homogeneous Fenton system to promote the reduction of $Fe^{3+}$ to $Fe^{2+}$. Most of the reducing agents such as hydroxylamine [41], quinone hydroquinone [42], organic acid [43], boron [44] and activated carbon [45], are also electron rich materials which can provide electrons to promote the conversion of $Fe^{3+}$ to $Fe^{2+}$. However, these methods also have drawbacks. It is cost sensitive and complex equipment system for the Fenton reaction combined with other technologies [46]. Meanwhile, the heterogeneous Fenton reaction only suitable for the treatment of low concentration pollutants [47,48]. Even when the concentration of organic matter considered in the heterogeneous catalytic study is very high ($C_0$ = 500 mg/L of methylene blue) [47], which is far less than the maximum concentration of organic matters(COD > 100,000 mg/L) that can be treated by the homogeneous Fenton reaction [5]. Adding hydroxylamine or boron into the homogeneous phase will lead to secondary pollution, and the addition of quinone hydroquinone or organic acids will increase the COD value in the water [42,44,49–51]. Therefore, a non-toxic and stable material that can convert $Fe^{3+}$ to $Fe^{2+}$ in homogeneous Fenton reaction and further improve the treatment effect of Fenton reaction should be adopted. In this way, the problem of increasing $Fe^{2+}$ dosage due to $Fe^{2+}$ oxidation can be improved, and the cost and the production of iron sludge can be reduced.

Activated carbon (AC) is one of carbonaceous materials with a large specific surface area, which can provide adequate dispersion and isolation of the catalytic sites and favors the interfacial contact of the substrate with the activated centers [52]. Therefore, AC has been widely used in adsorption and catalysis. In the application of Fenton reaction, the adsorption effect of activated carbon can assist the removal of pollutants. At the same time, AC can also act as an electron donor or/and electron shuttle to promote the reduction of low-cost Cr(VI) and Fe(III) [14,53,54]. This provides a theoretical basis for AC to promote $Fe^{3+}/Fe^{2+}$ cycling in homogeneous Fenton reaction. In the study of the assistance effect of activated carbon on $Fe^{3+}/H_2O_2$ system, the adsorption and reduction properties of activated carbon and the effect of the comprehensive performance of activated carbon on the degradation of pollutants in $Fe^{3+}/H_2O_2$ system will be ignored. In fact, it is meaningful to select the best activated carbon through the treatment effect and the ability to reduce $Fe^{3+}$, study the influence of different influencing factors on the treatment effect of $Fe^{3+}/H_2O_2$/AC system, obtain the conditions with the best treatment effect, and further study the promoting effect of reducing power of AC on $Fe^{3+}/H_2O_2$ and the reduction mechanism.

In this study, coconut shell activated carbon (CSPAC), wood activated carbon (WPAC), and coal activated carbon (CPAC) were introduced into the $Fe^{3+}/H_2O_2$ system to study the positive effect of ACs in Fenton and Fenton-like reactions. The best activated carbon CSPAC was selected, and the effects of CSPAC dosage, initial $H_2O_2$ concentration, initial $Fe^{3+}$ concentration and pH on ARG degradation were investigated. The positive roles of CSPAC in improving the efficiency of ARG degradation and reduction efficiency of $Fe^{3+}$ to $Fe^{2+}$ in $Fe^{3+}/H_2O_2$ reaction system were also studied to boost the application of Fenton or Fenton-like process with ACs in the degradation of organic pollutions from wastewater.

## 2. Materials and Methods

### *2.1. Materials*

Chemicals used in this study including ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$), hydrogen peroxide ($H_2O_2$), sodium hydroxide (NaOH), hydrochloric acid (HCl), potassium dichromate ($K_2Cr_2O_7$), silver sulfate ($Ag_2SO_4$), mercury sulfate ($HgSO_4$), glacial acetic acid, sodium acetate, hydroxylamine hydrochloride, potassium permanganate, methanol were purchased from Sinopharm Chemical Reagent Co., Ltd. , activated carbon (AC) was from Suzhou Carbon Cyclone Activated Carbon Co., Ltd., Acid red G (ARG) was from Tianjin Fine Chemical Co., Ltd., and 1,10-Phenanthroline from Sahn Chemical Technology (Shanghai) Co., Ltd. All chemicals were of reagent grade and used as received except the AC. ACs were acid-washed to remove impurities on the surface, and then immersed in hydrochloric acid solution (10% *v*/*v*) for 24 h, filtered and washed several times with deionized water. the obtained solids were dried at 110 °C for 6 h [55]. Meanwhile, ACs were milled and sieved through different meshes to obtain activated carbon powder with particle sizes of 1000 μm, 500 μm, 250 μm, 100 μm, 75 μm and 50 μm respectively for the experiment. All the solutions were prepared in ultrapure water.

### *2.2. Characterization*

The specific surface area (SSA) of the ACs were determined on a SSA analyzer (SSA-4300, Beijing Builder Electronic Technology Co., Ltd., Beijing, China) using nitrogen adsorption-desorption method at 77 K (Brunauer–Emmett–Teller method), and the pore volumes were calculated by Barrett–Joyner–Halenda method offered by the equipment. Fourier transform infrared spectroscopy (FT-IR) was used to characterize the chemical groups in the samples, and the FT-IR spectra in this study were acquired on a Bruker Tensor 37 infrared spectrometer (Bruker TENSOR 37 FT-IR) in the region from 400–4000 $cm^{-1}$ by the KBr pellet method. The X-ray photoelectron spectroscopy (XPS, Thermo Scientific EscaLab 250Xi) with the emission source of Al K$\alpha$ (1486.71 eV) was used to analyze the composition of the surface elements of the ACs and the valence state of the samples. The C 1s electron binding energy (284.8 eV) was used as the standard to correct all the binding energies (BEs) [56].

### *2.3. Experimental Procedures*

All experiments were conducted in a 250 mL glass beaker. The reaction was initiated with the addition of desired dosages of 200 mL of 100 mg/L Acid Red G (ARG ), 0.01 mol/L $FeCl_3$, AC, and 0.1 mol/L $H_2O_2$. The beaker was placed in a constant temperature water bath controlled at 25 ± 1 °C. At each time interval, 2 mL sample was withdrawn using a 2.5 mL syringe and filtered immediately using by the cellulose acetate membrane with pore diameter of 0.45 μm, and quenched by the addition of methanol. The desired initial pH was adjusted with 0.1 mol/L NaOH and 0.1 mol/L HCl before the reaction.

### *2.4. Analytical Methods*

The characteristic wavelength of UV absorption (UV2600A, Unico, Shanghai, China) at 506 nm was used to detect the concentration of ARG [56]. The concentration of $H_2O_2$ was determined by titanium salt spectrophotometry. $Fe^{2+}$ and $Fe^{3+}$ were determined by 1,10-Phenanthroline spectrophotometry [55,57]. The chemical oxygen demand (COD) detector (Multi-direct, Lovibond) was employed to detect COD [58].

According to the test data, ARG removal rate ($\eta_{COLOR}\%$) and COD removal rate ($\eta_{COD}\%$) were analyzed, and the calculation by Formulae (1) and (2) [3,58]:

$$\eta_{COLOR}\%=\frac{(A_0\text{-}A_t)}{A_0}\times 100\% \tag{1}$$

$$\eta_{COD}\%=\frac{(COD_0\text{-}COD_t)}{COD_0}\times 100\% \tag{2}$$

where $A_0$ and $A_t$ are the absorbance of ARG at the initial moment and the time of t, respectively, $COD_0$ (mg/L) and $COD_t$ (mg/L) are COD concentration in water at the initial time and time t.

## 3. Results and Discussion

### *3.1. Promotion of Fenton-Like Reaction by Different Kinds of ACs*

The degradation of ARG by the $Fe^{3+}/H_2O_2$ system, introduced commercially available coconut shell activated carbon (CSPAC), wood activated carbon (WPAC), and coal activated carbon (CPAC) respectively, was investigated. Through characterization, it is observed that the three kinds of ACs have different pore size distribution, specific surface area, pore volume and average pore size (Figure S1 and Table S1). It can be seen from Figure 1a that ARG in the $Fe^{3+}/H_2O_2$ system without AC was slowly degraded in the early stage of the reaction, and only a decolorization rate of 30% was achieved in the first 10 min, and a decolorization rate of 63% was achieved within 60 min. Nevertheless, when AC was added, the degradation rate of ARG was significantly increased in the early stage. The decolorization rates of 84%, 65%, and 57% could be achieved in $Fe^{3+}/H_2O_2$/CSPAC, $Fe^{3+}/H_2O_2$/WPAC, and $Fe^{3+}/H_2O_2$/CPAC systems within 10 min, respectively, The final decolorization rates of 90%, 73%, and 73% could be achieved in the three reaction systems, indicating that the addition of AC can improve the initial decolorization rate of $Fe^{3+}/H_2O_2$ system and the final decolorization. At the same time, the removal rate of COD after the addition of AC was also observed and shown in Figure 1b. The addition of AC also improved the COD removal efficiency in the system to varying degrees. The promoting effect of AC may be due to its adsorption effect, which can improve the removal effect of ARG, and it is worth noting that AC may also interact with $Fe^{3+}$ to promote the formation of $Fe^{2+}$ to increase the decolorization rate of ARG. To further illustrate this speculation, adsorption experiments were performed on the three kinds of ACs, as well as the determination of $Fe^{2+}$ concentration in the $Fe^{3+}$/AC system (Figure 2). It can be seen from Figure 2a that all three kinds of ACs have the ability to adsorb ARG 61%, 21%, and 15% decolorization rates at first 10 min, and 74%, 25%, and 17% decolorization rates within 60 min were achieved in CSPAC, WPAC, and CPAC systems, respectively, by adsorption. It is shown in Figure 2b that the three kinds of ACs were also able to reduce $Fe^{3+}$ to $Fe^{2+}$. At 5 min, the concentration of $Fe^{2+}$ in the solution including CSPAC, WPAC, and CPAC were 0.05 mmol/L, 0.01 mmol/L, and 0.005 mmol/L, respectively, which indicates that AC can improve the treatment effect of ARG by using its adsorption and reduction properties. By comparison, the adsorption capacity, the ability to reduce $Fe^{3+}$, and the final degradation effect of CSPAC were the best, so CSPAC was chosen as the object of study in the subsequent experiments. To avoid the affection of leaching iron ions on the experimental results, the concentration of iron ions in the solution after the addition of AC treated and untreated by acid solution was studied (Figure S2). The results illustrate that the acid treatment is conducive to avoiding interference caused by iron ion dissolution from AC.

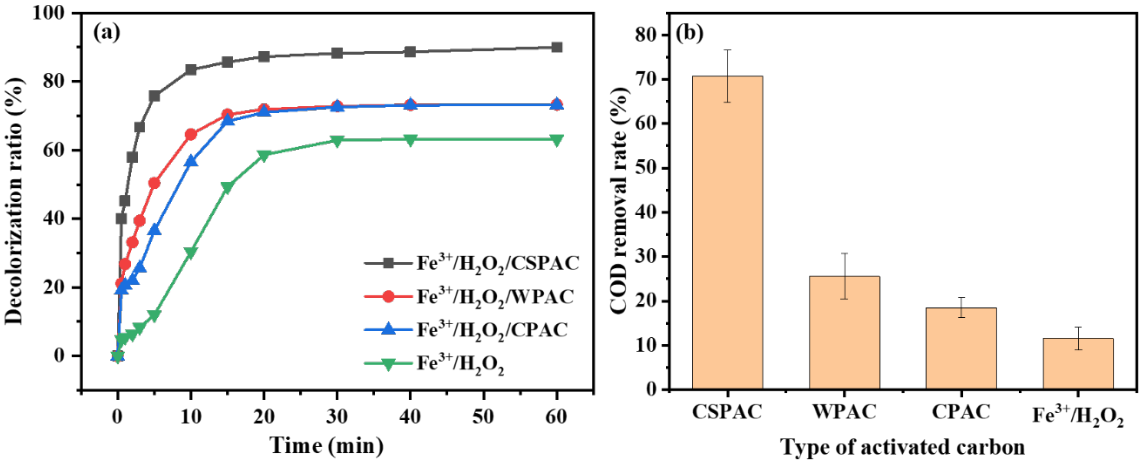

**Figure 1.** (**a**) Decolorization rate and (**b**) COD removal rate of ARG degradation in $Fe^{3+}/H_2O_2$/CSPAC, $Fe^{3+}/H_2O_2$/WPAC, $Fe^{3+}/H_2O_2$/CPAC and $Fe^{3+}/H_2O_2$ systems (conditions: 0.1mmol/L$^{-1}$ $FeCl_3$, 0.2 mmol/L$^{-1}$ $H_2O_2$, 100 mg/L ARG, 0.4g/L PAC (75 μm of particle size), pH = 3).

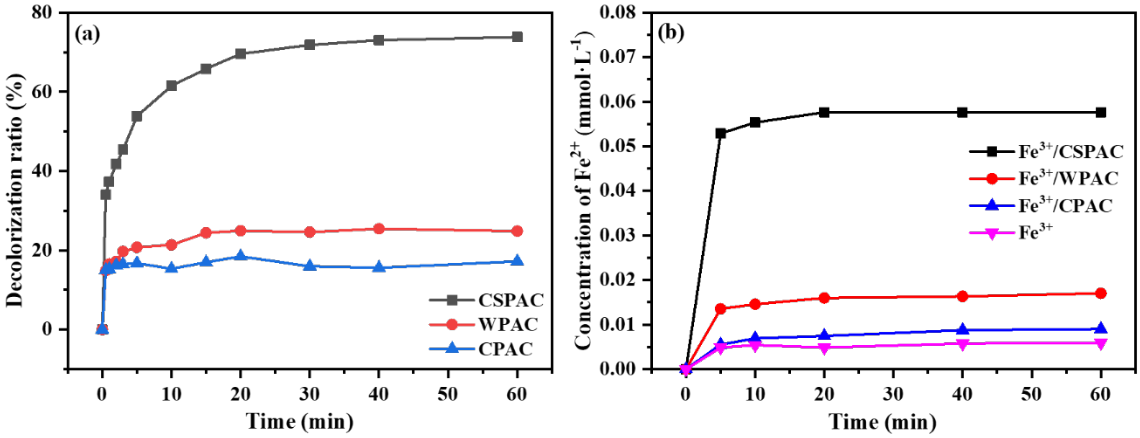

**Figure 2.** (**a**) Decolorization rate of ARG adsorption by CSPAC, WPAC, and CPAC (100 mg/L ARG, 0.4 g/L PAC (75 μm of particle size), pH = 3) (**b**) Concentration of $Fe^{2+}$ generation in $Fe^{3+}$/CSPAC, $Fe^{3+}$/WPAC, and $Fe^{3+}$/CPAC systems ( 0.1 mmol/L $FeCl_3$, 0.4 g/L PAC (75 μm of particle size), pH = 3).

### *3.2. Influencing Factors of $Fe^{3+}/H_2O_2$/CSPAC System*

The different particle sizes and concentrations of CSPAC affect the adsorption and reduction properties of CSPAC, which will have the effect of CSPAC on Fenton-like reaction. As the oxidant and the source of hydroxyl radical in the reaction, the concentration of $H_2O_2$ will affect the efficiency of Fenton and Fenton-like reaction. The different concentrations of $Fe^{3+}$ affect the decomposition rate of $H_2O_2$, so the concentration of $Fe^{3+}$ is also a factor affecting the efficiency of Fenton and Fenton-like reaction. The value of pH is also an important factor in Fenton and Fenton-like reactions. So the effects of particle size and dosages of CSPAC, $H_2O_2$ concentration, $Fe^{3+}$ concentration, and pH on the degradation of ARG were systematically investigated.

Figure 3 shows decolorization of ARG, COD removal rate and $Fe^{3+}$ reduction performance in $Fe^{3+}/H_2O_2$/CSPAC system under different CSPAC particle sizes. As can be seen in Figure 3a, the decolorization rate of ARG had been accelerated in the early stage than that of the $Fe^{3+}/H_2O_2$ system with the decrease of particle size, and the overall treatment efficiency was also improved. The COD removal rate also increased with the decrease of CSPAC particle size (Figure 3b). This is because the adsorption performance of CSPAC increases as the particle size decrease. while the reduction performance of Fe$^{3+}$ was also increased (Figure 3c). However, when the particle size of CSPAC was too small, the improvement of decolorization rate and COD removal were not obvious, and the ability to reduce ferric ions would be slightly reduced, which may be because the particle size is too small to float on water when stirring, and it is not easy to stir evenly and the reaction is not sufficient. At the same time, the small particle size of activated carbon is not conducive to the settlement after the reaction and will increase the operation cost. Therefore, 75 μm was selected as the best CSPAC particle size for the subsequent study.

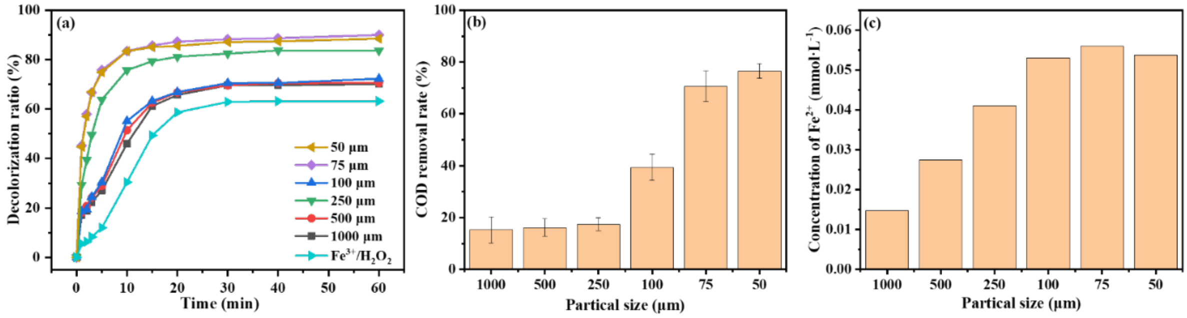

**Figure 3.** Effect of different CSPAC particle sizes on the (**a**) decolorization rate of ARG, (**b**) COD removal rate in Fe$^{3+}$/H$_2$O$_2$/CSPAC system (0.1 mmol/L$^{-1}$ FeCl$_3$, 0.2 mmol/L$^{-1}$ H$_2$O$_2$, 100 mg/L ARG, 0.4 g/L CSPAC (50–1000 μm), pH = 3) and (**c**) generation of Fe$^{2+}$ in Fe$^{3+}$/CSPAC system (0.1 mmol/L FeCl$_3$, 0.4 g/L CSPAC (50–1000 μm), pH = 3).

The decolorization of ARG and COD removal rate in the Fe$^{3+}$/H$_2$O$_2$/CSPAC system at different CSPAC concentrations and the reduction of Fe$^{3+}$ at different CSPAC concentrations were depicted in Figure 4. It can be seen that in the range of CSPAC concentration 0–0.6 g/L, the adsorption of ARG and reduction of Fe$^{3+}$ can be promoted by the increase of CSPAC concentration, which further enhanced both the decolorization rate and COD removal rate. When the CSPAC concentration exceeded 0.6g/L and increased to 0.8g/L, the COD removal rate decreased. Therefore, 0.6 g/L was chosen as the optimum concentration of CSPAC for the subsequent experiments. Therefore, 0.6 g/L was chosen as the optimum concentration of CSPAC for the subsequent experiments.

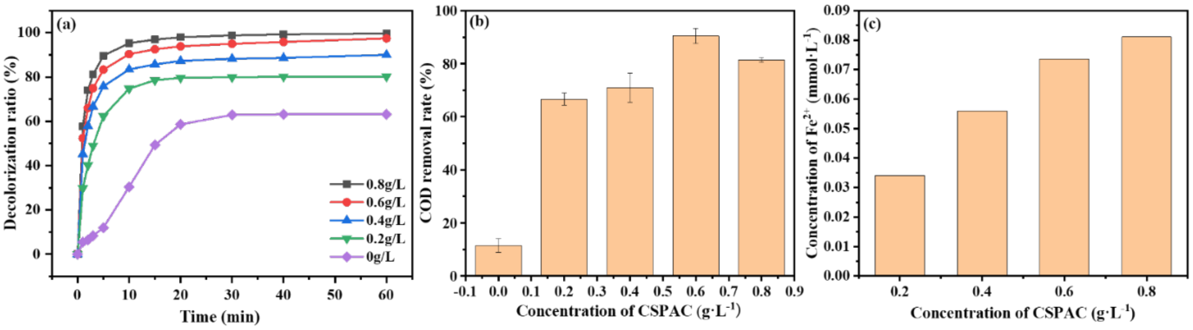

**Figure 4.** Effect of different CSPAC concentrations on the (**a**) decolorization rate of ARG, (**b**)COD removal rate in Fe$^{3+}$/H$_2$O$_2$/CSPAC system (0.1 mmol/L$^{-1}$ FeCl$_3$, 0.2 mmol/L$^{-1}$ H$_2$O$_2$, 100 mg/L ARG, 0–0.8 g/L CSPAC(75 μm of particle size), pH = 3) and (**c**) generation of Fe$^{2+}$ in Fe$^{3+}$/CSPAC system (0.1 mmol/L FeCl$_3$, 0–0.8 g/L CSPAC (75 μm of particle size), pH = 3).

The ARG decolorization and the COD removal rate in the Fe$^{3+}$/H$_2$O$_2$/CSPAC system at different H$_2$O$_2$ concentrations were depicted in Figure 5. It can be seen that the COD removal rates at different H$_2$O$_2$ concentrations are all high, which is because the adsorption performance of CSPAC can improve the COD removal and maintain the COD removal even at very low $H_2O_2$ concentrations. However, too low $H_2O_2$ concentration would reduce the decolorization rate of ARG. When the $H_2O_2$ concentration was over 0.4 mmol/L, the decolorization rate of ARG did not increase much when increasing $H_2O_2$ concentration. Therefore, 0.4 mmol/L was selected as the optimal $H_2O_2$ concentration for the subsequent experiments in terms of the ARG decolorization rate, COD removal rate and economy.

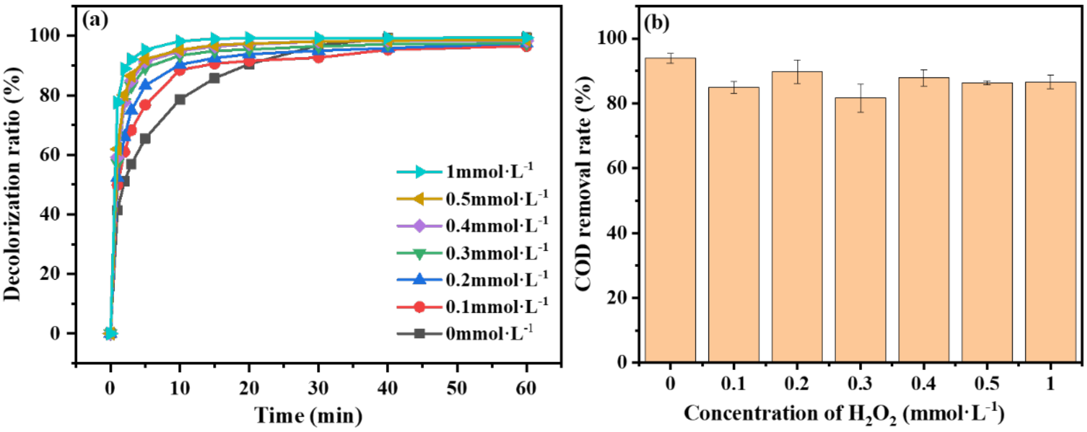

**Figure 5.** Effect of different $H_2O_2$ concentrations on the (**a**) decolorization rate of ARG, (**b**) COD removal rate in $Fe^{3+}/H_2O_2$/CSPAC system (0.1 mmol/L$^{-1}$ $FeCl_3$, 0–1 mmol/L$^{-1}$ $H_2O_2$, 100 mg/L ARG, 0.6 g/L CSPAC (75 μm of particle size), pH = 3).

The ARG decolorization and the COD removal rate in the $Fe^{3+}/H_2O_2$/CSPAC system at different $Fe^{3+}$ concentrations were depicted in Figure 6. It can be seen in Figure 6, after the addition of $Fe^{3+}$, the decolorization rate is improved to a certain extent, but the COD removal rate is decreased, compared with the situation where the adsorption capacity of activated carbon is used to remove pollutants without $Fe^{3+}$, indicating that the addition of Fenton oxidation does not promote the degradation of COD. With the increase of $Fe^{3+}$ concentration, the oxidation capacity was enhanced, and the decolorization rate and COD began to increase. When the concentration of $Fe^{3+}$ rose to 0.1 mmol/L, the decolorization rate and COD removal rate did not change significantly with the increase of the concentration of $Fe^{3+}$, which may be due to the limitation of hydrogen peroxide. Considering the decolorization rate, COD removal rate and economic benefits, 0.1 mmol/L was selected as the optimal $Fe^{3+}$ concentration for subsequent experiments.

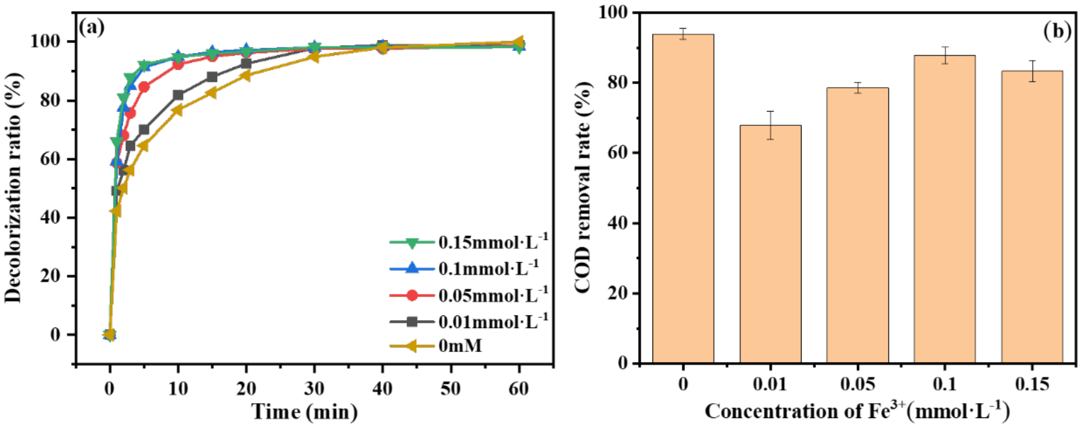

**Figure 6.** Effect of different $Fe^{3+}$ concentrations on the (**a**) decolorization rate of ARG, (**b**) COD removal rate in $Fe^{3+}/H_2O_2$/CSPAC system (0–0.15 mmol/L$^{-1}$ $FeCl_3$, 0.4 mmol/L$^{-1}$ $H_2O_2$, 100 mg/L ARG, 0.6 g/L CSPAC(75 μm of particle size), pH = 3).

The ARG decolorization rate and the COD removal rate in the $Fe^{3+}/H_2O_2$/CSPAC system at different pH conditions were depicted in Figure 7. It can be seen that the decolorization rate and COD removal rate at pH 2.5 are smaller than those at pH 3, because the lower the pH, overmuch H+ in solution destroyed the balance between $Fe^{2+}$ and $Fe^{3+}$, affecting the generation of the hydroxyl radicals, thereby reducing the oxidation ability of Fenton reaction, and affect the removal of pollutants by $Fe^{3+}/H_2O_2$/CSPAC system [59,60]. When $pH > 3$, promoted $Fe^{2+}$ and $Fe^{3+}$ to convert to hydrogenate precipitation or complex. The oxidation properties of the Fenton reaction will be reduced [59,60], so the decolorization rate will decrease. But the adsorption capacity of CSPAC is strong, the COD removal rate remains very high. Because $pH > 3$ is not conducive to the subsequent study of Fenton reaction in the system, so $pH = 3$ is finally selected as the best condition for subsequent experiments.

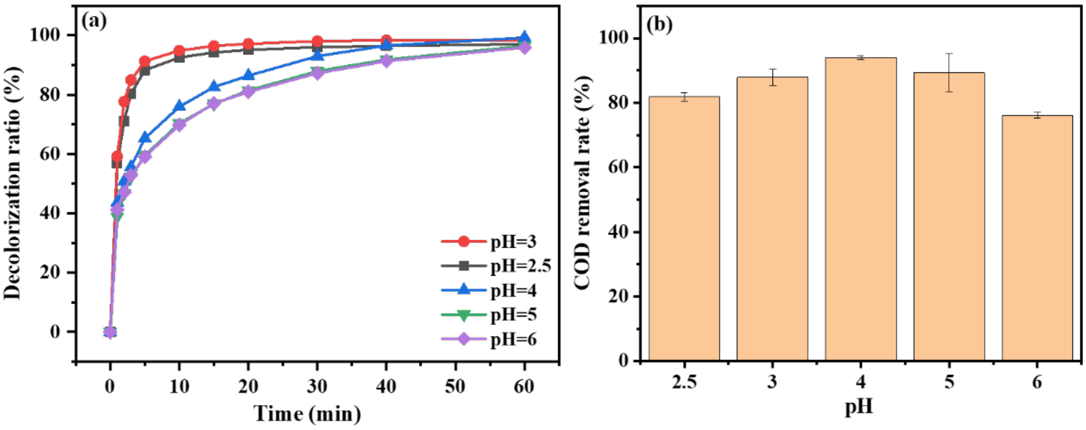

**Figure 7.** Effect of different pH on the (**a**) decolorization rate of ARG, (**b**) COD removal rate in $Fe^{3+}/H_2O_2$/CSPAC system (0.1 mmol/L$^{-1}$ $FeCl_3$, 0.4 mmol/L$^{-1}$ $H_2O_2$, 100 mg/L AR, 0.6 g/L CSPAC(75 μm of particle size), pH = 2.5–6).

### 3.3. *Performance of CSPAC Enhanced $Fe^{3+}/H_2O_2$ Oxidation*

To further understand the oxidation performance enhancement of the $Fe^{3+}/H_2O_2$ system by the addition of CSPAC, the degradation of ARG in the single CSPAC system, $Fe^{3+}$/CSPAC, $H_2O_2$/CSPAC, $Fe^{3+}/H_2O_2$, and $Fe^{3+}/H_2O_2$/CSPAC systems were investigated, respectively. As shown in Figure 8a, only about 77% of the decolorization rate was achieved in the $Fe^{3+}/H_2O_2$ system, but the reaction rate was slow in the early stage. However, the decolorization rate of ARG in the single CSPAC system, $Fe^{3+}$/CSPAC and $H_2O_2$/CSPAC system could reach 99% after adding CSPAC, which is due to the strong adsorption ability of CSPAC. It can be seen from Figure 8a that the treatment effects of CSPAC, $Fe^{3+}$/CSPAC, and $H_2O_2$/CSPAC systems are the same, indicating that adding $Fe^{3+}$ and $H_2O_2$ systems alone to CSPAC does not promote the removal of pollutants. Since the strong adsorption performance of CSPAC would mask other effects of CSPAC, the decolorization in $Fe^{3+}/H_2O_2$ and $Fe^{3+}/H_2O_2$/CSPAC systems was investigated after reducing the adsorption performance of CSPAC. As shown in Figure 8b, it can be seen that a decolorization rate of 61.8% was achieved at the first 5 min in $Fe^{3+}/H_2O_2$/CSPAC system, which is much greater than that of $Fe^{3+}/H_2O_2$ system (only 26.0%) and single CSPAC adsorption (only 21.7%), indicating that the addition of CSPAC exhibits a certain degree of acceleration of the $Fe^{3+}/H_2O_2$ system decolorization rate of ARG in the early reaction stage. Then the final decolorization effect is basically the same due to the limited hydrogen peroxide. And it can be seen from the Figure 8, the CSPAC with reduced adsorption properties and untreated CSPAC were added to the $Fe^{3+}/H_2O_2$ system. Through the contrast of the decolorization curves, it can be seen untreated CSPAC in initial stage have a faster decolorization rate, a better decolorization effect. This indicates that the adsorption property of

CSPAC can promote the decolorization rate of ARG at the initial stage, and can improve the decolorization effect of ARG in $Fe^{3+}/H_2O_2$/CSPAC system.

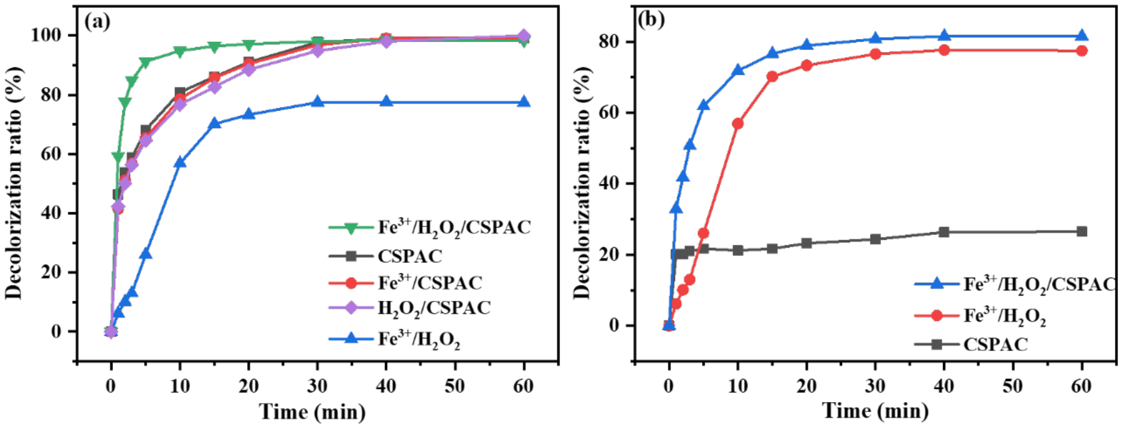

**Figure 8.** Decolorization rate of ARG in different systems under (**a**) untreated and (**b**) adsorbed saturated CSPAC conditions (0.1 mmol/L $FeCl_3$, 0.4 mmol/L $H_2O_2$, 100 mg/L ARG, 0.6 g/L CSPAC (75 μm of particle size), pH = 3).

To further study the performance of CSPAC to accelerate the degradation of ARG in $Fe^{3+}/H_2O_2$/CSPAC system, $Fe^{2+}$ and $H_2O_2$ were monitored during the reaction. From Figure 9a, it can be seen that the final concentration of $Fe^{2+}$ in the $Fe^{3+}/H_2O_2$ system was 0.007 mmol/L, and the final concentration of $Fe^{2+}$ in the $Fe^{3+}$/CSPAC system increased to 0.076 mmol/L, up to nearly 10 times, which illustrates the ability of CSPAC reduce $Fe^{3+}$ to $Fe^{2+}$. After the addition of CSPAC to the $Fe^{3+}/H_2O_2$ system, the concentration of $Fe^{2+}$ decreased rapidly compared with the $Fe^{3+}$/CSPAC system due to the rapid reaction between $H_2O_2$ and the generated $Fe^{2+}$. To verify this, the different systems were compared in terms of their ability to degrade $H_2O_2$. From Figure 9b, only about 8% of $H_2O_2$ was consumed in $Fe^{3+}/H_2O_2$ system, and about 35% of $H_2O_2$ was degraded in $H_2O_2$/CSPAC system, while the $H_2O_2$ consumption in $Fe^{3+}/H_2O_2$/CSPAC system was significantly increased more than 95%. It can also be observed that the concentration of $Fe^{2+}$ started to increase after 20 min in $Fe^{3+}/H_2O_2$/CSPAC system (Figure 9a) when $H_2O_2$ concentration in the system almost reduced to zero (Figure 9b). These results indicate the positive role of activated carbon in Fenton reaction and Fenton-like reaction.

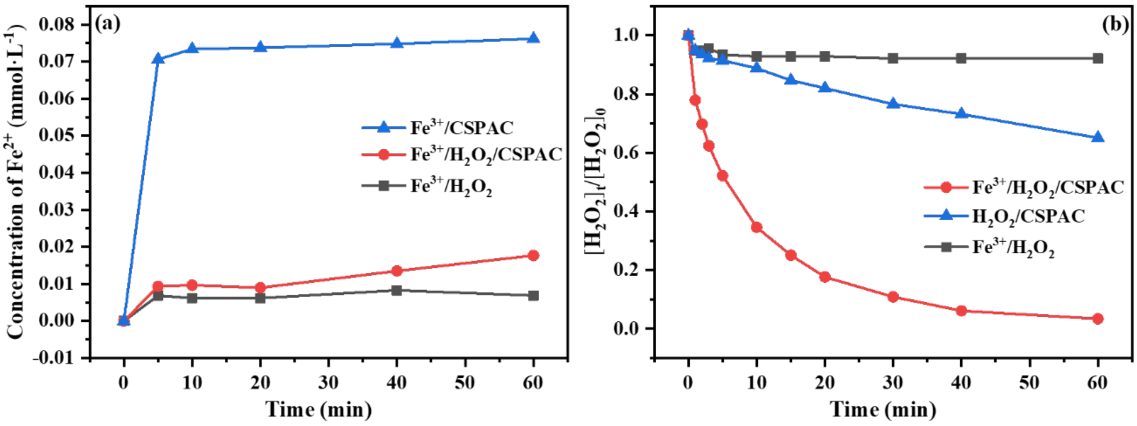

**Figure 9.** (**a**) Generation of $Fe^{2+}$ and (**b**) degradation of $H_2O_2$ in different systems (0.1 mmol/L $FeCl_3$, 0.4 mmol/L $H_2O_2$, 0.6 g/L CSPAC (75 μm of particle size), pH = 3).

### *3.4. The Catalytic Process of CSPAC during the Reaction*

The changes of CSPAC surface groups before and after the reaction of different systems were observed by FT-IR and XPS to reveal the mechanism of the reduction of $Fe^{3+}$ by CSPAC during the Fenton reaction. Figure 10 shows the FT-IR spectra of CSPAC before and after the reaction in $Fe^{3+}/H_2O_2$/CSPAC system as well as after the reaction in $Fe^{3+}$/CSPAC system. The peak appearing near 3400 $cm^{-1}$ corresponds to the stretching band of the hydroxyl functional group O-H [61], the peak at 1737 $cm^{-1}$ corresponds to COOH [62], the peak at 1600-1400 $cm^{-1}$ corresponds to the C=C bond of the aromatic ring in AC structure [63], the peak at 1088 $cm^{-1}$ corresponds to the C-O stretching[63,64]. The CSPAC before the reaction contains O-H as well as C-O functional groups, while the peak at 1737 $cm^{-1}$ shows very weak and almost absent, while after the reaction, a more obvious peak at 1737 $cm^{-1}$ appears, which indicates that CSPAC was oxidized and carboxyl groups are produced during the reaction. To further investigate the role of $Fe^{3+}$ in the reaction process, the FT-IR spectrum of CSPAC after degradation of ARG in the $Fe^{3+}$/CSPAC system was also tested, and it can be seen that CSPAC also showed a more obvious peak at 1737 $cm^{-1}$ after the reaction, which indicates that $Fe^{3+}$ can oxidize a portion of organic groups on CSPAC surface during the reaction. So that a portion of carbons on the surface of CSPAC were oxidized to form carbonyl groups by $Fe^{3+}$ and thus $Fe^{3+}$ was reduced to $Fe^{2+}$ in the same time.

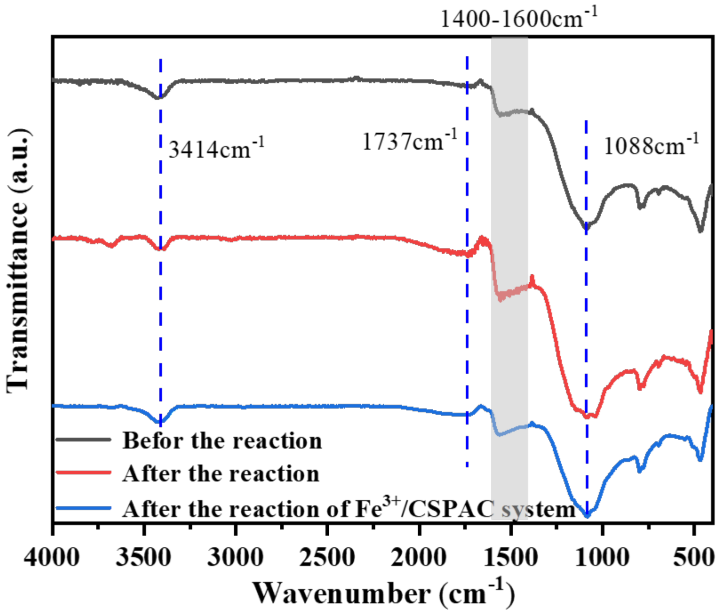

**Figure 10.** FT-IR spectra of CSPAC before and after the reaction in $Fe^{3+}/H_2O_2$/CSPAC system, and after the reaction in $Fe^{3+}$/CSPAC system.

The chemical states of C and O elements in CSPAC were further analyzed using X-ray photoelectron spectroscopy. By comparing the full scan spectra of CSPAC before and after reaction (Figure S3), the percentage of O 1s increased from 15.8% to 17.4%, while the percentage of C 1s decreased from 84.2% to 82.6% due to the oxidation of the system, and the Fe species did not appear in CSPAC. And it could be seen from Figure S4 that CSPAC did not adsorb $Fe^{3+}$ and $Fe^{2+}$, which indicated that CSPAC had almost no chelation with $Fe^{3+}$ or $Fe^{2+}$. Figure 11 shows high-resolution C1s spectra of CSPAC before and after the reaction, and after the reaction in the $Fe^{3+}$/CSPAC system. 284.0 eV, 284.8 eV, 286 eV, and 288.9 eV, represent C=C, C-C, C-O, and C=O in the presence of carboxylate structure, respectively [65,66]. Figure 12 shows the High-resolution O1s spectra of CSPAC before and after the reaction, and after the reaction in the $Fe^{3+}$/CSPAC system. 532.3 eV, 533.5 eV, and

534.7 eV represent O-H in the hydroxyl group, C-O and C=O in the carboxyl group, respectively [65]. The results illustrate that the surface of CSPAC before the reaction contains C-O as well as O-H functional groups, which is consistent with the FT-IR characterization, and the presence of C=O in the carboxyl structure after the reaction indicates that CSPAC was oxidized after the reaction, which further indicates that CSPAC can reduce $Fe^{3+}$ to $Fe^{2+}$ while the reducing functional groups on the surface of CSPAC were oxidized to generate carboxyl groups.

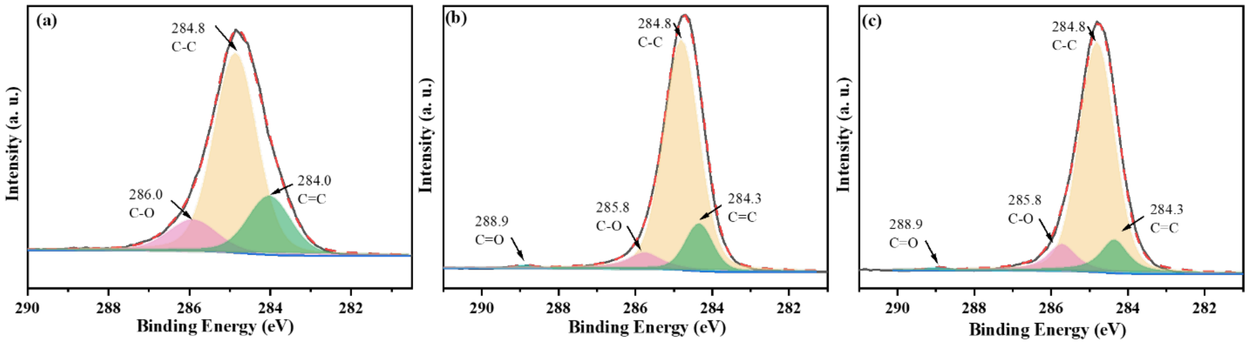

**Figure 11.** High-resolution C1s spectra in CSPAC (**a**) before and (**b**) after the reaction in $Fe^{3+}$/CSPAC/$H_2O_2$ system, and (**c**) after the reaction in $Fe^{3+}$/CSPAC system.

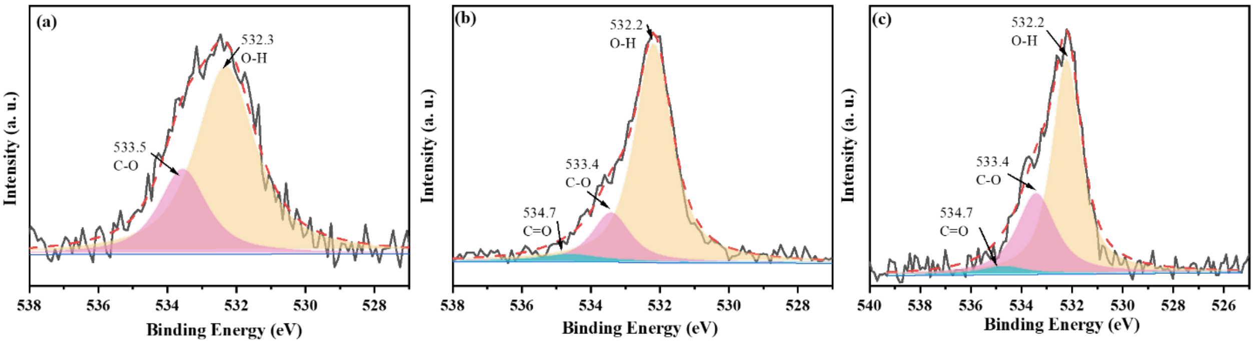

**Figure 12.** High-resolution O1s spectra in CSPAC (**a**) before and (**b**) after the reaction in $Fe^{3+}$/CSPAC/$H_2O_2$ system, and (**c**) after the reaction in $Fe^{3+}$/CSPAC system.

Through the above characterization, it was observed that CSPAC has O-H functional group, and it is speculated that the C-O-H group on the surface of CSPAC transfers electrons to $Fe^{3+}$ and is oxidized to form the carboxyl group. To further prove that it was the C-O-H functional group on the surface of CSPAC reduced $Fe^{3+}$, CSPAC was treated with 1 mol/L NaOH at 60 °C to increase the O-H on its surface. The reduction ability of CSPAC was compared with that of untreated CSPAC, and the results were shown in Figure 13. It can be seen from FT-IR spectra that, after NaOH treatment, O-H content on CSPAC increased, which proved that O-H functional groups were successfully added on the surface of NaOH-CSPAC. Then, the $Fe^{3+}$ reduction ability of the two CSPACs with or without NaOH treatment was compared, and the results were shown in Figure 13b. NaOH-CSPAC can generate 0.086 mM of $Fe^{2+}$, which is higher than that of untreated CSPAC, 0.076mM, indicating that the C-O-H group on the surface of CSPAC can reduce $Fe^{3+}$ to $Fe^{2+}$and and itself was oxidized into carboxyl group.

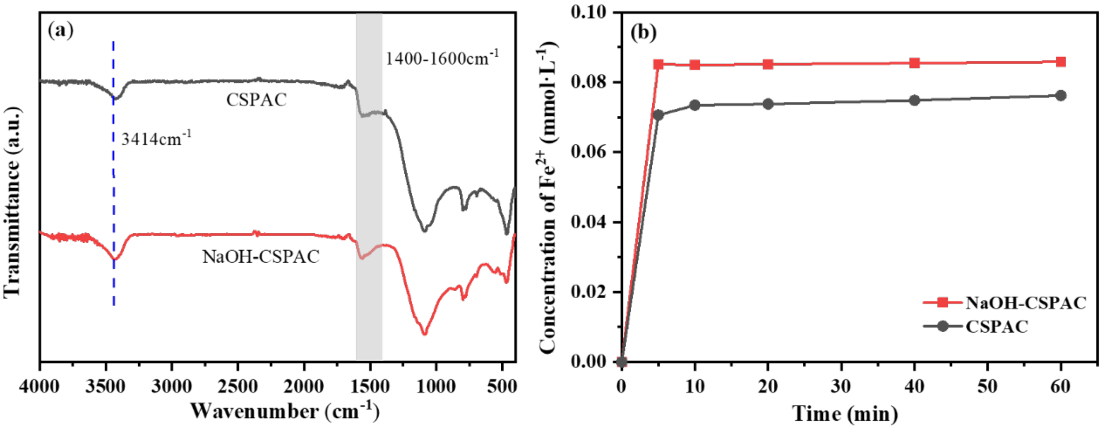

**Figure 13.** FT-IR spectra of NaOH-CSPAC and CSPAC (**a**) and concentrations of $Fe^{2+}$ generated by NaOH-CSPAC and CSPAC in $Fe^{3+}$/CSPAC system (**b**).

## 4. Conclusions

In this study, ACs were employed to the $Fe^{3+}/H_2O_2$ system, and the adsorption and reduction properties of ACs were used to significantly improve the removal of ARG in water. The results show that adding different types of ACs (coconut shell activated carbon (CSPAC), wood activated carbon (WPAC), and coal activated carbon (CPAC) to the $Fe^{3+}/H_2O_2$ system can improve the removal effect of ARG, and also confirm that AC has the ability to reduce $Fe^{3+}$, while different types of ACs have different treatment effects due to their different adsorption properties and ability to reduce $Fe^{3+}$. CSPAC exhibited the best performance in reducing $Fe^{3+}$ to $Fe^{2+}$ in $Fe^{3+}/H_2O_2$ system. Different particle sizes and different concentration of CSPAC, different concentrations of $H_2O_2$, different concentrations of $Fe^{3+}$, and different pH can affect the reaction efficiency of $Fe^{3+}/H_2O_2$ system with CSPAC. CSPAC can reduce $Fe^{3+}$ to $Fe^{2+}$ and accelerate the consumption of $H_2O_2$， increasing the early stage of the reaction rate. The C-O-H on the surface of CSPAC is responsible for the reduction of $Fe^{3+}$ to $Fe^{2+}$ in water. This finding will provide useful information for understanding the chemistry of Fenton-like systems interacting with active carbon. In addition, the interaction between the adsorption and reduction properties of activated carbon in $Fe^{3+}/H_2O_2$/ CSPAC system, the interaction between the adsorption and oxidation in the $Fe^{3+}/H_2O_2$/CSPAC system, and the subsequent reuse of AC in iron mud are also worthy of further study.

**Supplementary Materials:** The following supporting information can be downloaded at: www.mdpi.com/xxx/s1, Figure S1. $N_2$ adsorption-desorption isotherm of CSPAC (a), WPAC (c) and CPAC (e); and pore diameter distribution of CSPAC (b), WPAC (d) and CPAC (f); Table S1: The specific surface area, pore size and pore volume of three kinds of ACs; Figure S2: Total iron ion concentration in solution (a) before and (b) after acid treatment; Figure S3: Full-scan XPS spectra of CSPAC before and after the reaction in $Fe^{3+}$/CSPAC/$H_2O_2$ system; Figure S4: Adsorption of (a) $Fe^{3+}$ and (b) $Fe^{2+}$ by CSPAC.

**Author Contributions:** Conceptualization, J.F.; investigation, X.Y. and H.L.; writing—original draft preparation, X.Y. and J.F.; writing—review and editing, J.F., B.H., M.Z. and W.Y. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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