

Dissolution and Degradation of Spent Radioactive Cation Exchange Resin by Fenton Oxidation Combining Microwave

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Received: 27 February 2020; Accepted: 19 May 2020

Abstract: This study introduced a significantly effective approach called the microwave-enhanced Fenton method to degrade spent radioactive cation exchange resin. Compared with the Fenton (99% after 180 min) and photo-Fenton (90% after 198 min) reactions, this unique microwave-enhanced Fenton reaction has the highest degradation rate for spent radioactive cation exchange resin degradation (98.55% after 60 min). Carbon dioxide, sulfate and small molecular compounds were produced in the degradation of cation exchange resin, as determined by XRD and FT-IR. A model for the microwave-enhanced Fenton degradation mechanism of cation exchange resin was constructed. Microwaves were implemented to boost the concentration of hydroxyl radicals in the Fenton reaction so that the cation resin infiltrated and formed a channel to facilitate entrance of hydroxyl groups into the interior of the resin. This paper provides a method for accelerating the treatment of spent radioactive ion exchange resin, which could exert a significant influence on the degradation pathway for radioactive organic matter.

Keywords: Spent radioactive exchange resin; microwave irradiation; fenton oxidation process

1 Introduction

In the nuclear industry, granular and powdery ion exchange resins are widely used in equipment such as condensate demineralizers, condensate filter demineralizer systems, reactor water purification systems and effluent treatment systems. In terms of the chemical properties of spent radioactive resins, swelling causes failure even though the resins are directly treated with cement [1]. Disposal of spent radioactive resins has become one of the concerns of many researchers. At present, many nuclear power plants temporarily store a large number of spent radioactive resins that need to be processed in stainless steel barrels. Therefore, it is imperative to identify a safe, economical and efficient way to address this challenge. To resolve these problems, various methods have been used to treat spent radioactive resins, such as acid digestion [2], hot super compaction [3], cold glass vitrification [4], incineration [5], and supercritical water oxidation [6]. However, all of these methods treat the resin in a two-step process. The first step is



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dissolution and mineralization. The second step is solidification of the dissolved and mineralized resins with cement. It is obvious that Fenton oxidation, an advanced oxidation technology, is considered a powerful tool for resin dissolution and mineralization.

Recently, many attempts have been made to degrade spent radioactive resins by Fenton-like reactions. Zhong et al. [7] used a Fenton reagent to react with resin for three hours, and the chemical oxygen demand (COD) removal rate was 99%. It has been reported that introducing photochemical conditions is helpful for increasing the degradation of resins by the Fenton process. Srinivas et al. [8] degraded resins within 3.3 hours by the photo-Fenton method, resulting in a COD removal rate of 90%. However, these methods do not seem to be as efficient or economical as expected. They suffer from low degradation efficiency, long reaction time and high reaction cost, which limit the pace of industrial production. Therefore, selecting an appropriate way to enhance the efficiency of the Fenton process is the key to improving the degradation efficiency.

Microwaves are a part of the electromagnetic spectrum in the frequency region between infrared and radio waves [9]. Increasing attention has been paid to microwaves due to their “magic” effects in chemical reactions. The special electromagnetic field effect and heating effect of microwaves result in abrasive heating of chemical reaction systems and cause necessary changes in molecular energy levels. In the microwave environment, it is easier for the Fenton reagent to generate hydroxyl groups so that the organic matter is rapidly degraded [10–12]. The combination of these two options seems to be a promising measure.

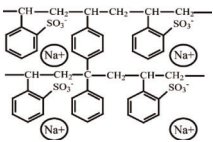
Inspired by this, the Fenton reaction and microwaves were combined to degrade cation exchange resins to improve the degradation efficiency of the resins. The results confirmed that the degradation rate of the cation exchange resin reached an optimal 98.55% in 60 min. The liquid component after degradation was simple and easy to handle. Therefore, it is obvious that the microwave-assisted Fenton reaction is better than other Fenton methods for degrading spent radioactive resins. Undoubtedly, the microwave-assisted Fenton process for degrading spent radioactive resins will be one of the candidates for efficient and economical disposal of spent radioactive resins in the nuclear industry.

2 Materials and Methods

2.1 Reagents

The cation exchange resins used were strong acid styrene-divinylbenzene copolymers (732), made by Shanghai Nankai Resin Co., Ltd. Tab. 1 shows the characteristics and performance of the cation exchange resins used in this project.

Table 1: The characteristics and performance of the cation exchange resins

| Parameter | Cation exchange resin |
|-------------------------------|--|
| Structure |  |
| Appearance | Brown globular particles |
| Complete exchange capacity | ≥4.5 meq/g |
| Particle size | 0.45–0.6 mm |
| Wet density | 1.23–1.27 g/mL |
| Water content | 46–52% |
| Apparent humidity density | 0.75–0.85 g/mL |
| Active group | -SO ₃ H |
| Maximum operating temperature | ≠100 |

H_2O_2 (30% v/v in water), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, H_2SO_4 , NaOH and all other reagents used in this work were of analytical purity and purchased from Chengdu Kelong Chemical Reagent Institute Co., Ltd. Deionized water was used.

2.2 Experimental Procedure

The setup of the microwave-enhanced Fenton reaction is depicted in Fig. 1. Experiments were conducted in a 250 mL three-necked round-bottom flask. The reactor was immersed in a power-tunable microwave generator. An exhaust gas absorption device was attached to the end of the reactor. Fifteen grams of cation exchange resin and catalyst ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were mixed with H_2O_2 (30%) in the reactor. The pH value was adjusted by H_2SO_4 solution. The temperature was recorded. A 1 mL aliquot of sample was taken with a pipette and diluted 50 times. The diluted sample was used for subsequent analysis and testing.

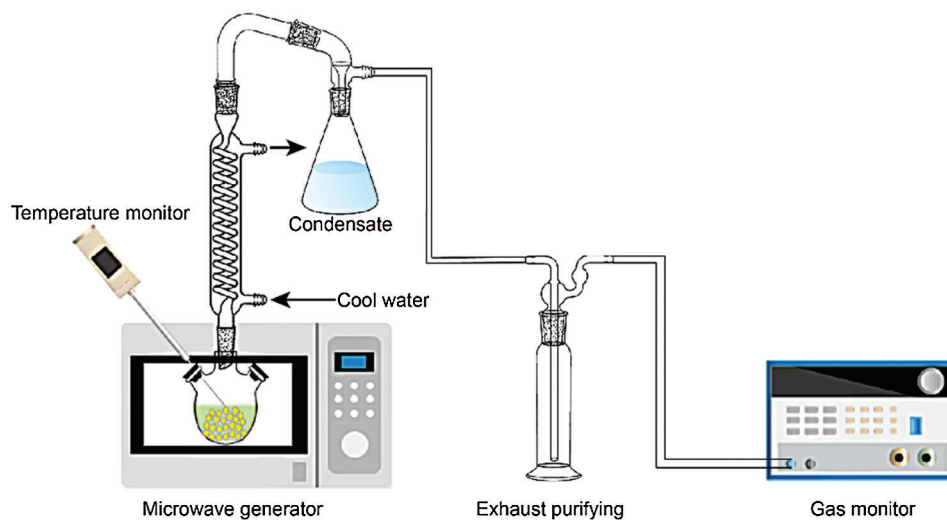


Figure 1: Setup of the microwave-enhanced Fenton reaction

The initial COD value of the resin directly affects the evaluation of the resin oxidative degradation efficiency. In this work, the resin was a granular solid. The initial COD value of the resin could not be directly measured with laboratory instruments. Therefore, the initial COD value of the resin was obtained by theoretical calculation. The cation exchange resin was a styrene-type strong acid resin, the matrix was divinylbenzene cross-linked polystyrene, and the exchangeable functional group was a sulfonic acid group. Therefore, the resin could be regarded as consisting of three parts: (1) a styrene structural unit with an exchangeable functional group; (2) a styrene structural unit without an exchangeable functional group; and (3) a crosslinking agent attached to a structural unit without an exchange functional group. The reaction formulas describing the complete oxidization of the three parts can be expressed as follows [13]:



The content of the first 1 g of dry resin can be calculated as 0.82 g based on exchange capacity, the content of the third part can be calculated as 0.08 g based on cross-linking degree, and the content of the

second part is the residual mass, which is 0.1 g. The mass of oxygen required for the complete oxidation of 1 g of the resin was calculated to be 3.96 g; that is, the initial COD value of the resin was 3.96 g/g. The COD removal rate can be expressed as follows:

$$\text{The COD removal rate} = \frac{\text{the initial COD} - \text{the final COD}}{\text{the initial COD}} \times 100\% \quad (4)$$

2.3 Analytical Methods

The chemical oxygen demand (COD) of the dissolved resin solution was measured with QCOD-3F from Shenzhen Chanhong Technology Co., Ltd. The pH value was measured by PHS-3C from Shanghai Yoke Instrument Co., Ltd.

Scanning electron microscopy (SEM) images were obtained on a Zeiss Ultra 55 SEM instrument operating at 10 kV. X-ray diffraction (XRD) patterns were recorded on a Panalytical X'Pert PRO X-ray diffractometer (Panalytical, Netherlands). Reflectance measurements were conducted on an FT-IR instrument. The infrared spectra were collected using a Bruker VER spectrophotometer (Bruker, Germany). The actual FT-IR measurement ranged from 4000 to 400 cm^{-1} . The fluorescence spectra of 2-hydroxyterephthalic acid were measured on an LS-55 fluorescence spectrophotometer (PerkinElmer, USA). The main components of the exhaust gas were determined by a NOVA PLUS flue gas analyzer (MRU, Germany).

3 Results and Discussion

3.1 Effects of Catalyst Type, Microwave Power, Fe^{2+} Dose, H_2O_2 Dose and pH

In the microwave-enhanced Fenton reaction, the majority of metal ions could react with H_2O_2 . The effects of Mg^{2+} , Mn^{2+} , Ag^+ , Cu^+ , Cu^{2+} and Fe^{2+} ions as catalysts on degradation by the microwave-enhanced Fenton reaction are shown in Fig. 2. When Mg^{2+} , Mn^{2+} and Ag^+ were used as catalysts, a large amount of unreacted cation exchange resin was left. In contrast, when Cu^+ , Cu^{2+} or Fe^{2+} was used, all of the cation exchange resins were dissolved in the liquid. In the initial stage, many bubbles were generated while the cation exchange resin disappeared, moving up and down in the solution. When the resin completely disappeared, the solution changed from colorless to brown. As the reaction progressed, the

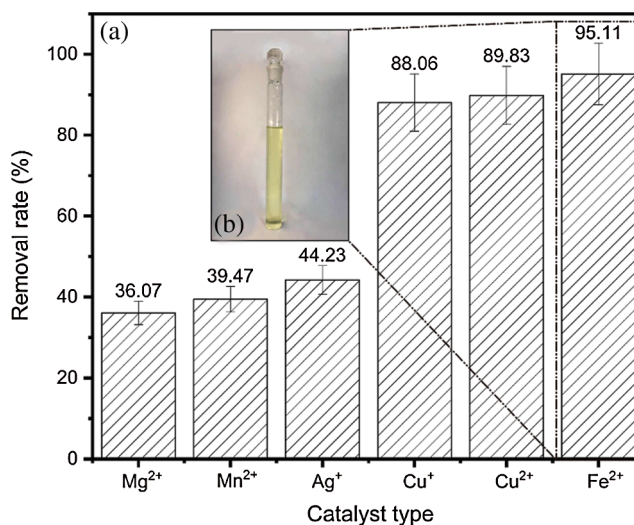


Figure 2: The effect of different catalysts on the degradation of cation exchange resins. ([a] 100 mL 30% H_2O_2 , 50 mL 0.02 M [catalyst], microwave power = 120 W, time = 60 min, pH = 2, $T_0 = 97 \pm 2^\circ\text{C}$; [b] the solution after degradation by the Fe^{2+} -catalyzed Fenton process under the enhancement of microwaves)

solution eventually became a yellow-green clear liquid, as shown in Fig. 2b. The volume and composition of the gas produced during the process was also monitored, and approximately 10.410 L of end gas was collected by drainage over 60 min. The end gas contained a large amount of O₂ and CO₂, and the gas monitoring system detected SO_x. This observation is consistent with the work of Taylor [14].

When Cu²⁺, Cu⁺ and Fe²⁺ were used as catalysts, the degradation effect was better than that of other ions. The degradation effect using Cu²⁺ or Cu⁺ had a substantial effect, and the removal rates were 89.83% and 88.06%, respectively. When Fe²⁺ was used, the degradation effect was significantly changed, and the removal rate was 95.11%. When using different ions as the catalyst, the removal rates can be ordered as Fe²⁺ > Cu²⁺ > Cu⁺ > Ag⁺ > Mn²⁺ > Mg²⁺. The Fe²⁺ ion had a stronger catalytic ability than other ions and improved the efficiency of degrading the cation exchange resin. Therefore, Fe²⁺ was selected as the best catalyst for the degradation of cation exchange resin by the microwave-enhanced Fenton process.

Fig. 3a shows the resin degradation rates as a function of microwave power. Compared with the traditional Fenton process, microwave heating enables the reactants to reach the optimal reaction temperature quickly in a short time. The introduction of microwaves greatly increases the removal rate of the cation exchange resin and increases the degradation rate by 18.83%. Interestingly, it was found that as the microwave power increased, the removal rate no longer increased significantly. Hameed et al. [15] suggested that high-temperature conditions are favorable for accelerating the dissociation of H₂O₂ to form hydroxyl radicals (•OH), further increasing the probability of contact between pollutant molecules and •OH. Therefore, the increase in microwave power in the initial reaction stage (0–20 min) has a promoting effect on the mineralization process of the resin in the system. However, when the temperature tends to be stable (45–60 min), microwave power enhancement does not significantly alter the mineralization effect of the resin. Some degradation inhibition occurs even when the microwave power is higher than 120 W. The reason for this finding might be the intense molecular motion of the reaction system at high microwave power, forcing the free radicals to terminate the reaction. It can be concluded that microwaves play a dual role in the oxidant degradation of cation exchange resins during microwave-enhanced Fenton oxidation. A lower microwave power can achieve rapid degradation of cation exchange resin, which is an advantageous reaction condition. The optimal microwave power was determined to be 120 W.

Fig. 3b shows the results of resin degradation rates with different doses of Fe²⁺. The experiments were carried out at Fe²⁺ doses of 6×10^{-4} , 8×10^{-4} , 1×10^{-3} , 1.2×10^{-3} and 1.4×10^{-3} mol. It can be seen that as the Fe²⁺ dosage increases, the removal rate of the system gradually increases. In a certain period, the dose of Fe²⁺ has a linear relationship with the removal rate. However, as the reaction progresses, the dose of Fe²⁺ has little effect on the rate of degradation. In the initial stage of the reaction, the Fe²⁺ dose (6×10^{-4} or 8×10^{-4} mol) significantly reduces the degradation rate when compared to other doses because the low Fe²⁺ dose was unable to trigger the Fenton chain reaction, resulting in the inability to produce high enough concentrations of •OH. At a reaction time of 40 min, very similar degradation rates were observed for Fe²⁺ quantities of 1.2×10^{-3} and 1.4×10^{-3} mol. When the dose of Fe²⁺ is above a certain level, hydroxyl radicals are unexpectedly produced in a short time. The quenching effect of hydroxyl radicals causes the molecular decomposition rate to remain approximately the same.

H₂O₂, an oxidant in the microwave-assisted Fenton reaction, is the source of hydroxyl radicals. The dose of H₂O₂ will directly affect the degradation efficiency of cation resins, and there is an optimal dose of H₂O₂. Fig. 3c shows the effect of H₂O₂ on degradation. The results show that the removal rate was the lowest when 1.06 mol H₂O₂ was used. However, there is an optimal value for the dose of hydrogen peroxide. When the dose of hydrogen peroxide is lower than the optimal value, increasing the dose of hydrogen peroxide will improve the degradation rate. Otherwise, the degradation efficiency will be reduced.

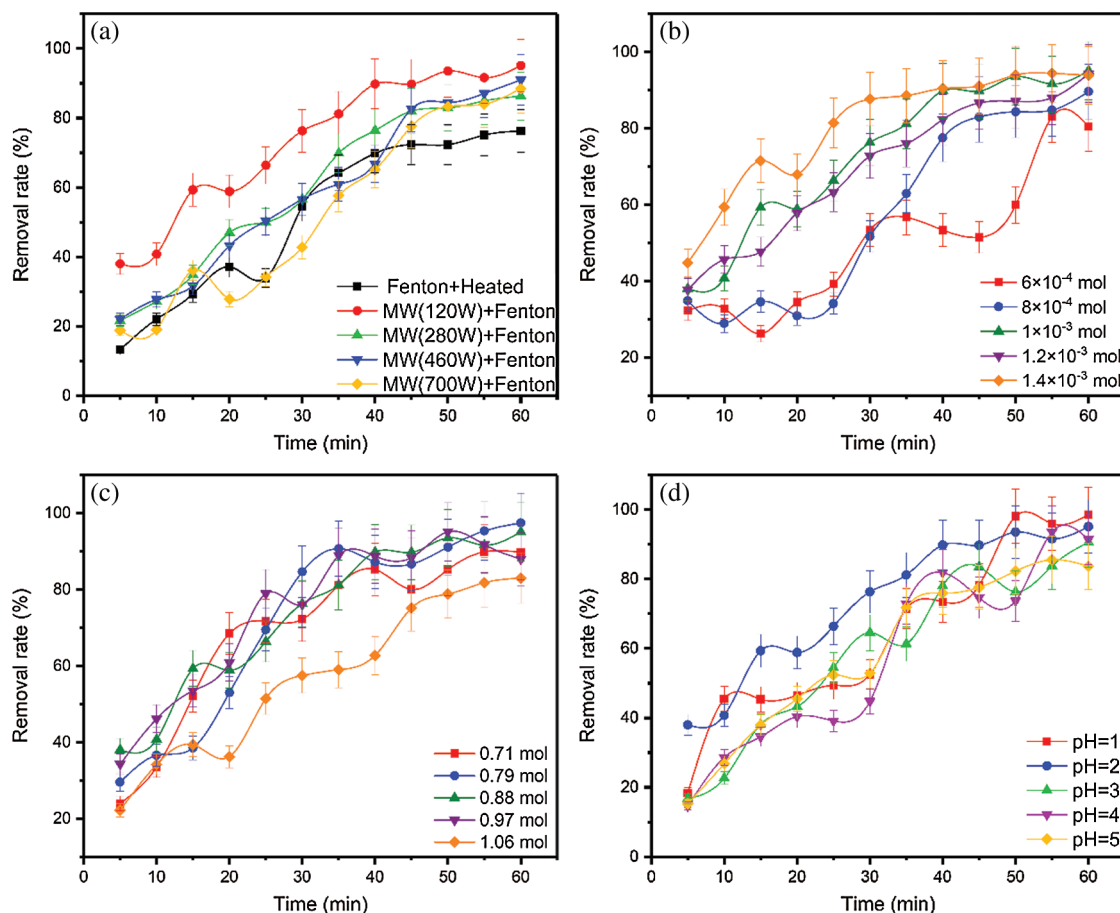


Figure 3: The effect of a single parameter on the degradation of cation exchange resin. (a: microwave power (1×10^{-3} mol $[\text{Fe}^{2+}]$, 0.88 mol H_2O_2 , pH = 2, $T_0 = 97 \pm 2^\circ\text{C}$); b: Fe^{2+} dose (0.88 mol H_2O_2 , pH = 2.0, microwave power = 120 W, $T_0 = 97 \pm 2^\circ\text{C}$); c: H_2O_2 dose (1×10^{-3} mol $[\text{Fe}^{2+}]$, pH = 2, microwave power = 120 W, $T_0 = 97 \pm 2^\circ\text{C}$); d: initial pH (0.88 mol H_2O_2 , 1×10^{-3} mol $[\text{Fe}^{2+}]$, microwave power = 120 W, $T_0 = 97 \pm 2^\circ\text{C}$))

When the dose of hydrogen peroxide is lower than the optimal value (i.e., the dose of hydrogen peroxide is 0.71–1.06 mol), the dose of hydrogen peroxide is insufficient, and Fe^{2+} is not converted into Fe^{3+} because of the oxidation of hydrogen peroxide. At this time, the yield of hydroxyl radicals will increase with increasing hydrogen peroxide dose; that is, the removal rate will increase with increasing hydrogen peroxide dose. When the dose of hydrogen peroxide is higher than the optimal value (i.e., the dose of hydrogen peroxide is 0.88–1.06 mol), the reaction of hydrogen peroxide without oxidation forms Fe^{3+} with Fe^{2+} , and the excessive hydrogen peroxide may occupy the partial complexation site of Fe^{3+} , forming the inner dihydroxy complex ($[\text{Fe}^{\text{III}}(\text{HO}_2)]^{2+}$, $[\text{Fe}^{\text{III}}(\text{OH})(\text{HO}_2)]^+$) [16,17], which affects the progress of the Fenton chain reaction and reduces the yield of hydroxyl radicals, thus reducing the probability of resin molecules being attacked by $\cdot\text{OH}$. On the other hand, the reaction temperature reaches approximately 100°C , resulting in decomposition of a small amount of H_2O_2 , and with an increase in the amount of H_2O_2 , the foaming amount in the device will also increase. In practical applications, the increase in foaming volume will cause extreme safety problems.

In this section, the effect of pH value was investigated, as shown in Fig. 3d. The Fenton reagent has an excellent treatment effect when a large amount of $\cdot\text{OH}$ is generated under acidic conditions (pH = 1.0), and

the system has the best degradation effect, with a removal rate of 98.55%. When the initial pH of the system is 3~5, the removal rate in the solution decreases from 90.62% to 83.70 %. When the pH value is low (pH = 1~2), Fe^{2+} still exists in ionic form, which stimulates the chain reaction of H_2O_2 to generate hydroxyl radicals, which play a leading role in the degradation of the cation resin. When the pH value is high (pH = 3~5), the hydroxyl radicals participating in the complex coordination reaction of iron ions in the solution increase, the competition between the cation resin and hydroxyl radicals decreases, and Fe^{2+} mainly reacts with the hydroxyl radicals. When the pH value changes from 1 to 3.5, the concentration of $\text{Fe}(\text{OH})^{2+}$ in the solution gradually reaches a peak, indicating that when the pH value of the degradation system changes from 2 to 3, the ability of hydroxyl radicals to compete for Fe^{2+} will greatly increase [18]. When the pH value is higher (pH = 3.5~5), continuing to increase the pH value will increase the concentration of hydroxyl radicals in the solution, and $\text{Fe}(\text{OH})_3$ will precipitate, further reducing the ability of hydroxyl radicals to attack organic matter.

3.2 Morphological Change of Resins and the Oxidation Product

To further investigate why the microwave-enhanced Fenton oxidation degradation method for the degradation of cation exchange resins is more effective than traditional methods, statistics of the micromorphology and oxidation products were determined.

Fig. 4 shows the SEM images of the fresh resin (Fig. 4a), the resin at the primary stage (5–10 min, Figs. 4b and 4c), the resin at the breaking stage (15–20 min, Figs. 4d and 4e) and the resin at the mineralization stage (25 min, Fig. 4f). Clearly, the resin has undergone significant morphological changes in the primary stage, forming severe cracks on its surface. According to the analysis of the SEM images, the disintegration of the resin may be attributed to three reactions. First, the microwaves accumulate on the surface of the resin, and the temperature rapidly rises to form a “hot spot.” Hamza et al. [19] also demonstrated that the formation of plasma occurs because of electromagnetic hot spots arising from the cooperative interplay of Mie resonating in the spheres. At the same time, hydroxyl radicals force the surface to collapse, as shown in Fig. 5b.

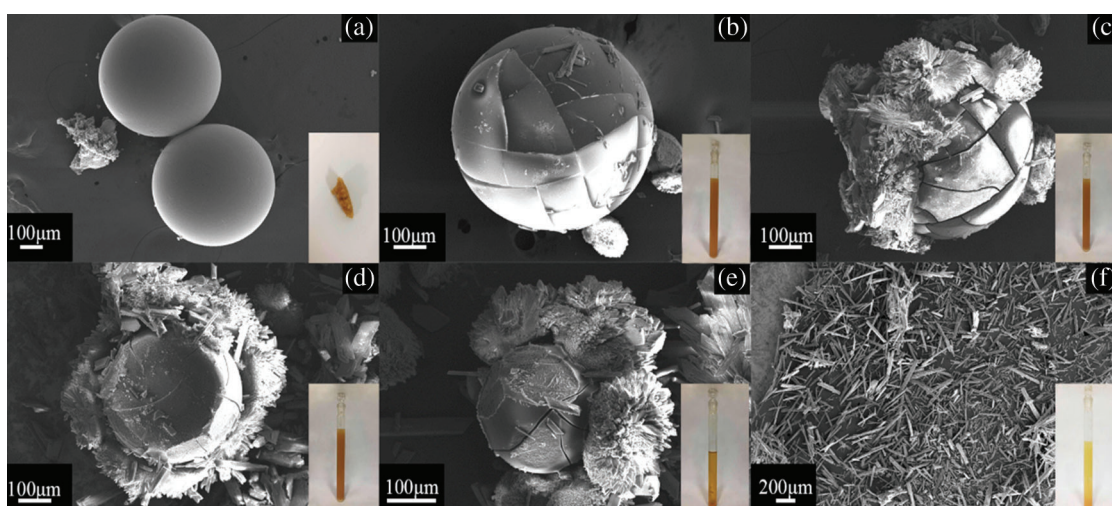


Figure 4: Photographs and morphology changes of resin at different reaction times: (a) fresh resin (0 min); (b) 5 min; (c) 10 min; (d) 15 min; (e) 20 min; (f) 25 min (50 mL 0.02 M $[\text{Fe}^{2+}]$, 100 mL 30 % H_2O_2 , pH = 2, microwave power = 120 W, $T_0 = 97 \pm 2^\circ\text{C}$)

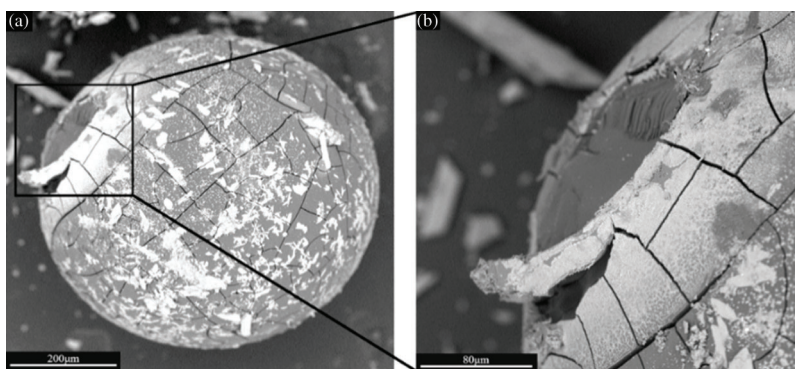


Figure 5: Morphology of resin spalling: (a) primary stage, (b) partial enlargement of (a). (50 mL 0.02 M $[\text{Fe}^{2+}]$, 100 mL 30% H_2O_2 , pH = 2, microwave power = 120 W, $T_0 = 97 \pm 2^\circ\text{C}$)

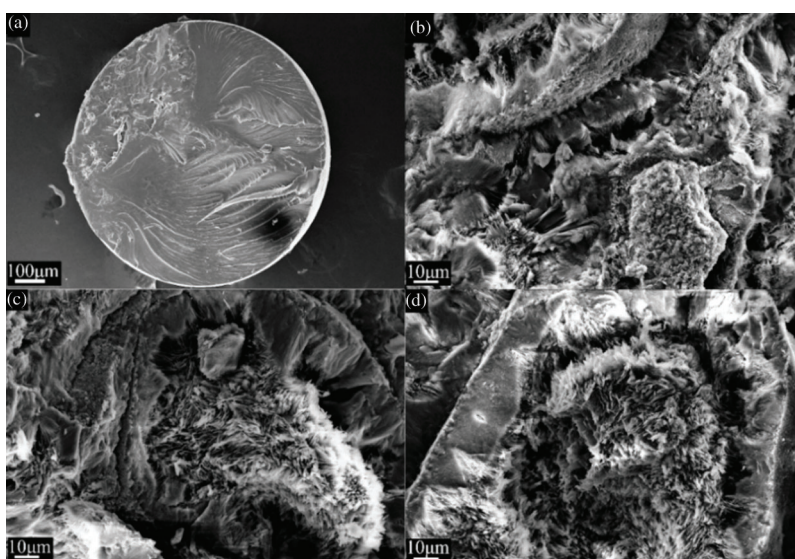


Figure 6: The morphology of the cross-sectional resin: (a) fresh resin and (b–d) primary stage. (50 mL 0.02 M $[\text{Fe}^{2+}]$, 100 mL 30% H_2O_2 , pH = 2, microwave power = 120 W, $T_0 = 97 \pm 2^\circ\text{C}$)

Second, due to the formation of high-temperature surface sites and the disintegration of hydroxyl radicals, the resin channels are expanded. Hydroxyl radicals easily enter the interior of the resin and react with the resin internally, as shown in Figs. 6b–6d. The penetration effect of the microwave accelerates the cracking of the resin, and the basic condition that the hydroxyl group ($\bullet\text{OH}$) enters the insert of the resin through the crack of the resin surface is constructed.

Finally, the hydroxyl radical ($\bullet\text{OH}$) simultaneously erodes the external organic molecule and the internal resin particle. The large amount of gas generated in the process also forces the resin to rupture from the inside to the outside. Herein, the resin rupture process is attributed to the oxidation of hydroxyl radicals, the osmosis of microwaves and the cracking of the resin caused by gases. This is why cation exchange resins are more effectively degraded by microwave-enhanced Fenton oxidation processes than by conventional methods. Figs. 5 and 6 offer additional favorable evidence for this view.

Zahoroda et al. [20] mentioned that particles remained spherical during the dissolution process, confirming the importance of surface reactions. Nevertheless, on the basis of these results, we conclude

that during the dissolution process, the surface of the resin reacts simultaneously with the interior due to the penetration of microwave radiation. Observation of the microscopic morphology showed the difference between the microwave system and the degradation process of other systems [21–23]. The microwave system showed a unique and fascinating advantage.

Fig. 7 shows the XRD pattern of the oxidized product after freeze-drying. The pattern agrees with a standard pattern of Na_2SO_3 , Na_2SO_4 , FeSO_4 and Fe_2O_3 . The pattern for 32.7° has a number of peaks that can be well indexed to Na_2SO_3 , and the X-ray diffraction pattern shows peaks at 22.4° , which are characteristic of (101) Na_2SO_4 . Peaks appearing at 20.2° , 23.2° , 26.1° , 34.0° , 37.1° , 45.2° and 49.5° can be indexed to FeSO_4 . Those at 32.3° , 35.2° , 49.6° , 54.0° and 57.2° can be indexed to Fe_2O_3 . It must also be mentioned that Na comes from the material itself.

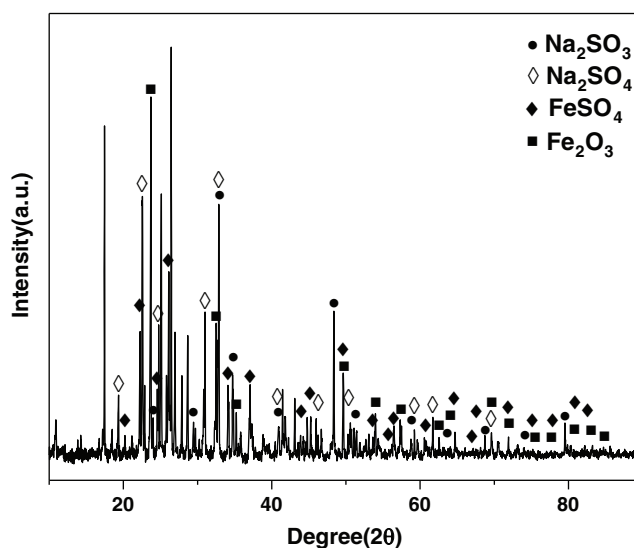


Figure 7: XRD of the oxidized product after freeze-drying (50 mL 0.02 M $[\text{Fe}^{2+}]$, 100 mL 30% H_2O_2 , pH = 2, microwave power = 120 W, microwave irradiation time = 60 min, $T_0 = 97 \pm 2^\circ\text{C}$)

The structural performance of the fresh resin and its oxidized product after freeze-drying were tested using Fourier transform infrared (FTIR) spectroscopy. The structural difference between these samples is shown in Fig. 8 and listed in Tab. 2. After the reaction, the characteristic peaks at 1452 cm^{-1} , due to the stretching vibrations of the molecular frame and the stretching vibrations of the $-\text{CH}_3$ bond, respectively, shifted to the right. Furthermore, several new peaks were generated, such as at 2604 , 1731 , 1289 , 1206 , 1176 , 1070 and 1007 cm^{-1} , which were attributed to S-H stretching, C=O stretching of the carbonyl group, C-H stretching of alkenes, C-O-C stretching of the ether group, C-C stretching of alkanes, C-O-C stretching of the ether group, and C-H stretching of alkenes, respectively. The increased absorption in the region from 3100 to 3500 cm^{-1} suggests the formation of intermediates containing hydroxyl groups (such as hydroxyl adducts and carboxylic acids). It can be concluded that some oxidation products are formed after degradation. Identical conclusions were obtained in the studies by Xu, in which the intermediate products were oxalic and formic acids [24].

3.3 Mechanism Discussion

The concentration of $\bullet\text{OH}$ produced by the Fenton reaction in different environments was studied using a previously described method. It is known that $\bullet\text{OH}$ reacts with terephthalic acid (TA) in basic solution to generate 2-hydroxyterephthalic acid (TAOH), which emits a unique fluorescence signal with a peak

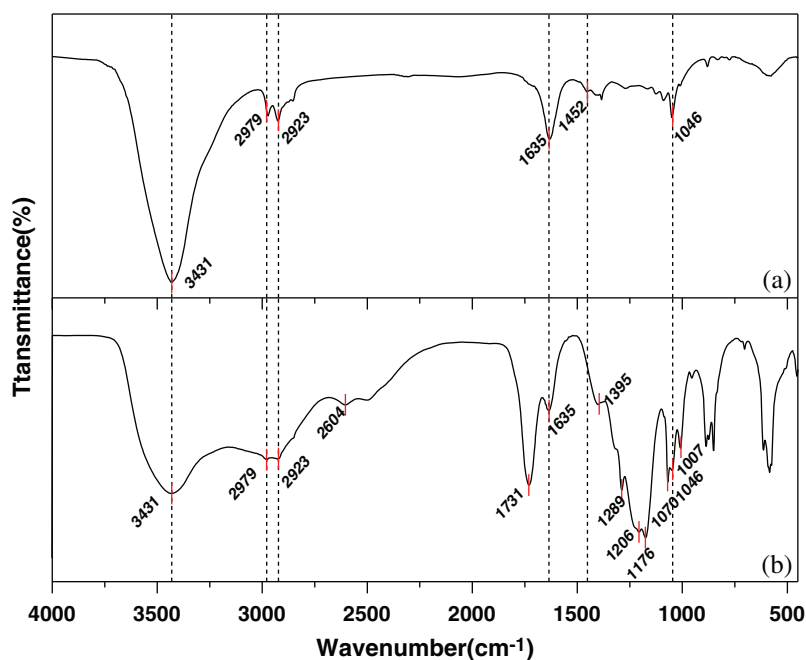


Figure 8: Changes in the FTIR spectrum of resin during the oxidation process: (a) fresh resin; (b) oxidized product after freeze-drying (50 mL 0.02 M $[\text{Fe}^{2+}]$, 100 mL 30% H_2O_2 , pH = 2, microwave power = 120 W, microwave irradiation time = 60 min, $T_0 = 97 \pm 2^\circ\text{C}$)

Table 2: Summary of FTIR bands and tentative assignments of the resin

| Assignment | Before oxidation | After oxidation |
|----------------------------------|------------------|-----------------|
| | Band position | |
| O-H stretching (hydrogen-bonded) | 3431 | 3431 |
| -CH ₃ stretching | 2979 | 2979 |
| -CH ₂ stretching | 2923 | 2923 |
| S-H stretching | | 2604 |
| C=O stretching, carbonyl group | | 1731 |
| C=C stretching, alkene | 1635 | 1635 |
| -CH ₃ stretching | 1452 | 1395 |
| C-H stretching, alkene | | 1289 |
| C-O-C stretching, ether | | 1206 |
| C-C stretching, alkane | | 1176 |
| C-O-C stretching, ether | | 1070 |
| S=O stretching | 1046 | 1046 |
| C-H stretching, alkene | | 1007 |

centered at approximately 426 nm [25,26]. The differences in the peak intensity of TAOH in the H_2O_2 process, the heated Fenton process, the unheated Fenton process, and the microwave-enhanced Fenton process were compared in this section, as shown in Fig. 9. The fluorescence intensity of TAOH in the

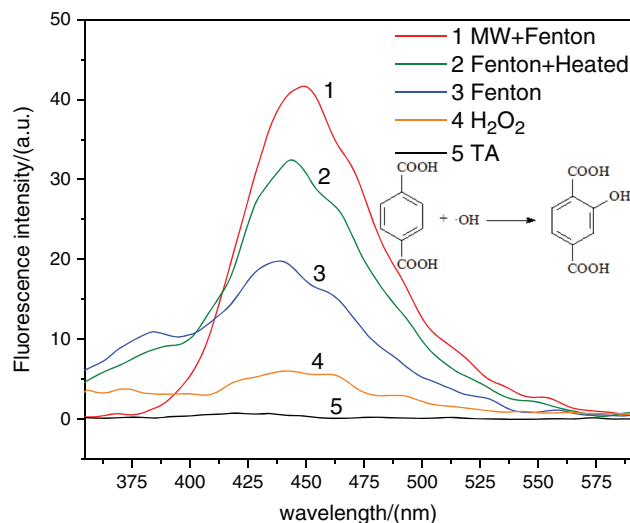


Figure 9: Fluorescence spectra of $\bullet\text{OH}$ generated in different processes (0.1 M H_2O_2 , 2 mM FeSO_4 , microwave power = 120 W, microwave irradiation time = 90 s, heat time = 6 min, $T_0 = 97 \pm 2^\circ\text{C}$)

microwave-enhanced Fenton process was highest, and the lowest value was observed for TA without any additional reagent. Furthermore, the fluorescence intensity of the H_2O_2 process was higher than that of TA because H_2O_2 can produce a small amount of $\bullet\text{OH}$. The Fenton reaction produced a large amount of $\bullet\text{OH}$ only at a certain temperature. Therefore, microwaves are an indispensable condition for increasing the concentration of $\bullet\text{OH}$. Li et al. [27] also found that microwaves can promote the Fenton reaction.

On the basis of the above experimental results, a possible reaction mechanism model was proposed, as presented in Fig. 10. The Fenton process rapidly produced a large amount of $\bullet\text{OH}$ under microwave irradiation. $\bullet\text{OH}$ surrounds the surface of the resin, and as described above, under microwave irradiation, the pores of the resin expand, and $\bullet\text{OH}$ enters the inside of the resin. Finally, the resin is broken and

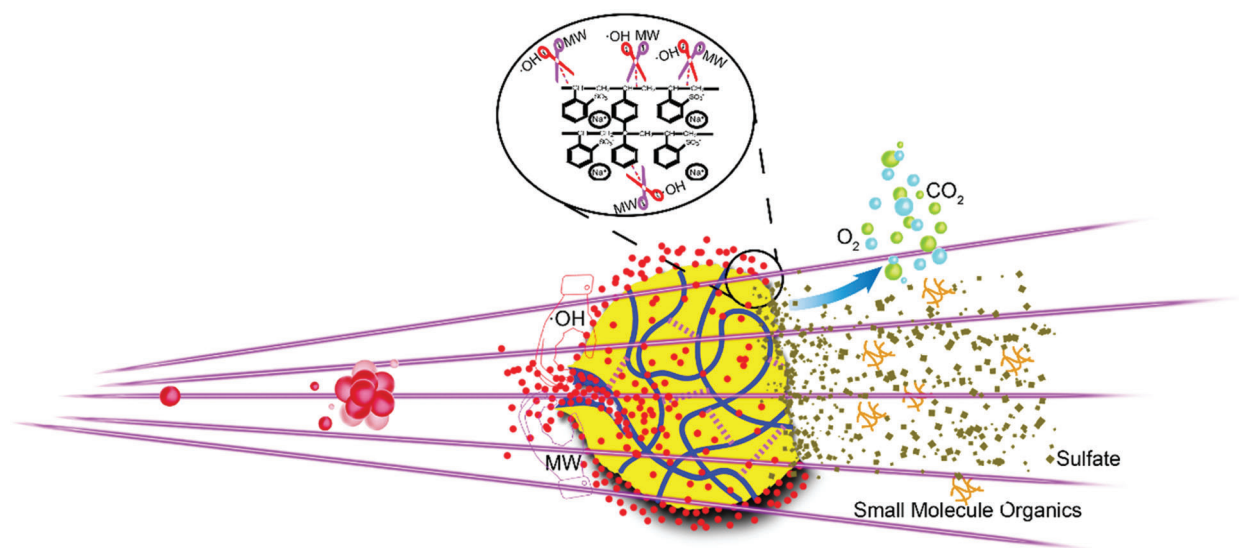


Figure 10: Schematic illustration of the degradation of cation exchange resin by the microwave-enhanced Fenton reaction

decomposed. Furthermore, these radicals react along three reaction channels: hydrogen abstraction, electrophilic addition to π -systems and electron transfer. Once the polystyrene chains are broken into shorter, extra water-soluble fragments, their further degradation and mineralization can proceed. Finally, the polymer (resin) under the action of microwaves and the Fenton processes became a gas, small organic molecules, and sulfate. Notably, the study of radioisotope distribution is of great significance for the practical application of this method. Therefore, the simulated radioactive element Sr is used to simulate the real process. A certain concentration of Sr^{2+} (the concentration of Sr in the resin is $0.1 \text{ g}\cdot\text{L}^{-1}$) was added to the resin in the microwave-assisted Fenton reagent degradation reactor. In the degradation process, the tail gas was washed in ultrapure water to determine the strontium content in the gas. After acidification of the condensate and tail gas washing liquid, ICP-MS analysis was carried out. The results show that the content of Sr in the condensate was $3.345 \mu\text{g}\cdot\text{L}^{-1}$, and no Sr was detected in the tail gas washing solution. Analysis shows that during the experiment, due to a large amount of liquid evaporation and gas emissions, nuclides mainly stayed in the degradation solution and did not escape.

4 Conclusions

In this work, microwave and Fenton processes were combined to degrade cation exchange resins. The optimum degradation conditions were determined to be a pH value of 1.0, an Fe^{2+} dose of 50 mL (20 mM), a H_2O_2 (30%) dose of 100 mL, a microwave power of 120.0 W and an irradiation time of 60 min. This method has a high cation resin removal rate (98.55%). The advantages of the combination of microwave and Fenton processes are as follows: First, the microwave environment allows the reaction system to reach the optimum reaction temperature in a very short time. Second, microwaves increase the concentration of hydroxyl groups produced by the Fenton process. At the same time, the microwaves form a high-temperature site on the surface of the resin, facilitating the movement of the hydroxyl groups into the interior of the resin. Moreover, the resin formed carbon dioxide, sulfate and small molecular compounds after degradation, which are easier to handle. In addition, this method for the disposal of radioactive organics opens up new avenues of research.

Funding Statement: The research was supported by Sichuan Science and Technology Program (Nos. 2018jy0449, 2018129). The authors would also like to thank the Scientific Research Found of Sichuan Provincial Education Department (No. 17cz0037).

Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

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