The Treatment of IRN77/78 Resin Using Fenton Oxidation Process

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Abstract. The degradation and oxidation of IRN77/78 resin using Fenton technique were studied. The oxidation rate of resin for different conditions were researched, and the better conditions for cation and anion resins were also gained. The scale-up experiments were carried out using the better conditions. The research results show that: IRN77/78 resin can be successfully oxidized; the remove of COD can be reached more than 97%.

1. Introduction
Fenton oxidation is a kind of wet oxidation. During the reaction, various short-lived radicals will be formed, such as hydroxyl radical (HO·) and peroxyl hydroxyl radical (HOO·). Hydroxyl radical is one of the strongest oxidant ($E^0 = 2.73$V), and which is twice as active as chlorine, can strongly decompose organics.

Fenton reagent is highly oxidizing, and its oxidability is not selective, so it can be used for the treatment of various kinds of waste water. Therefore, the Fenton reagent has a wide range of applications for the treatment of cyanide, phenol, dye waste water, dye intermediate waste water, pesticide waste water, coking waste water, garbage leachate and other aspects. For example, a professional chemical company producing pharmaceutical intermediates in Yangzhou, Jiangsu Province, uses the Fenton reagent micro-electrolytic process to treat waste water containing a large amount of nitrobenzene products\cite{1}. The Fenton oxidation technology developed by JGC of Japan is used by the US nuclear power plant to process the liquid chemical waste containing EDTA, etc., which has achieved a good treatment result\cite{2}.

Ion exchange resin is organic substances and is widely used in the nuclear industry for nuclear research, operation of nuclear power plants, nuclear fuel cycle facilities, and waste water treatment. Spent radioactive resin (hereinafter abbreviated as spent resin) generally contain a variety of radionuclides, and these radionuclides are usually attached to functional groups of ion exchange resins in the form of ions. These nuclides can establish equilibrium between the solid and liquid phase in water or aqueous solution\cite{3}. The spent resins produced so far are usually treated by cement solidification, but this method has problems such as hardening, swelling, and decomposition of the spent resin. Therefore, complete oxidation of spent resin is an attractive treatment scheme. Spent resin can be treated to inorganic substance with Fenton oxidation technology to convert unstable organic waste into chemically stable inorganic waste. Compared with other processing technologies, Fenton oxidation technology has the following advantages:
(1) The technology can achieve waste volume reduction and can effectively reduce the cost of waste transportation and disposal. Compared with the direct solidification technology, Fenton oxidation and residue solidification can save the total cost of final waste treatment by about 50%\cite{4}.

(2) It can realize the inorganic treatment of spent resin, reduce the swelling of spent resin and the generation of radiolysis gas, improve the safety of temporary storage and long-term disposal\cite{5}.

(3) The conditions of Fenton oxidation process are relatively mild. Fenton reaction occurs in the atmospheric pressure, and the exhaust gas does not contain sulfur and nitrogen oxides. Besides, radionuclides absorbed in the spent resin are almost all concentrated in the residue, and the gas contains almost no radionuclides\cite{6}.

The mixed oxidation system composed of $H_2O_2$ and $Fe^{2+}$ is an inorganic chemical reagent discovered and named by the chemist Fenton H. J. in 1893. It is also called the Fenton oxidation system\cite{7}. Fenton reagent captures hydrogen by attacking organic molecules using $OH\cdot$, which is generated by catalysing and decomposing of $H_2O_2$. It degrades macromolecule organics into small molecular organic compounds or oxidizes to inorganic substances such as $CO_2$ and $H_2O$. The chemical reaction equations are:

$$ Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\cdot $$

$$ OH\cdot + resin \rightarrow \text{linear soluble styrene polymer} + CO_2 + SO_4^{2-}/NH_4^+ + H_2O $$

$$ \text{linear soluble styrene polymer} + OH\cdot \rightarrow CO_2 + H_2O + \text{small molecular organics} $$

Organics are first degraded into small-molecule organics through reactions (2) and (3), and finally oxidized into inorganic substances such as $CO_2$ and $H_2O$. The pH, reaction temperature, $H_2O_2$ concentration and $Fe^{2+}$ concentration of the solution are the main factors affecting the oxidation result. During the reaction, Fenton reagent has an optimal ratio of $H_2O_2$ to $Fe^{2+}$, and excess $H_2O_2$ will react with $OH\cdot$ (reaction (4)). Excess $Fe^{2+}$ will react with $OH\cdot$ (reaction (5)), and the resulting $Fe^{3+}$ may initiate reactions (6) and (7)\cite{8}.

$$ OH\cdot + H_2O_2\rightarrow HO_2\cdot + H_2O $$

$$ Fe^{2+} + OH\cdot \rightarrow Fe^{3+} + OH^- $$

$$ Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2\cdot $$

$$ Fe^{3+} + HO_2\cdot \rightarrow Fe^{2+} + H^+ + O_2 $$

The ideal resin decomposition reaction can be expressed by the following equations:

$$ C_8H_8SO_3+20H_2O_2\rightarrow 8CO_2+23H_2O+H_2SO_4 $$

$$ C_{12}H_{19}NO+31H_2O_2\rightarrow 12CO_2+NH_4OH+38H_2O $$

$$ C_{10}H_{10}+25H_2O_2\rightarrow 10CO_2+30H_2O $$

$$ C_8H_8+20H_2O_2\rightarrow 8CO_2+24H_2O $$

Reactions (8) and (9) are decomposition reactions of resin with functional groups; reaction (10) and reaction (11) are decomposition reactions of the crosslinker and styrene matrix without functional groups.

The objective of this work was to study the decomposition of spent radioactive resins by Fenton process, to determine the influencing factors of resin decomposition.

2. Materials and methods

2.1. Resins and chemicals

The resins used in this study are strong acid and strong alkali styrene–divinylbenzene copolymer which were made by ROHM &HAAS (Amberlite INR77 and IRN78). The characteristics of cation and anionic exchange resins are listed in Table 1.

| Cation | Anion |
|-------|-------|
| Physical form | Spherical amber beads | Yellow spherical beads |
| Functional group | Sulfonic acid | Trimethyl ammonium |
| Ionic form as shipped | $H^+$ | $OH^-$ |
| Particle size | 0.60-0.70 mm | 0.58-0.68 mm |
The chemicals used in this study are of analytical purity, including $\text{H}_2\text{O}_2(30\% \text{ v/v in water}), \text{FeSO}_4\cdot7\text{H}_2\text{O}, \text{H}_2\text{SO}_4, \text{CuSO}_4\cdot5\text{H}_2\text{O}, \text{NaOH}$, which were purchased from Tianjin Kermel Chemical Reagent Co. Ultrapure water was used.

2.2. Experimental set-up and procedures
Experiments were conducted in a 500 ml, three-necked round-bottom flask, with a magnetic stirrer. The reactor was immersed into a water bath controlled at a constant temperature. Ten grams of resins and power catalyst (FeSO$_4$·7H$_2$O or CuSO$_4$·5H$_2$O) were added into reactor. The pH was adjusted by H$_2$SO$_4$ or NaOH solution. The H$_2$O$_2$ was added at different flow rate using peristaltic pump. During this process, the temperature change was recorded. After 2 h, the reaction was stopped and the pH and volume of the dissolved resin solution were measured.

2.3. Analytical methods
The chemical oxygen demand (COD) of the dissolved resin solution was measured with 5B-3A of Lianhua Technology Co., China. The pH value was obtained by Leici PHS-3E, China.

3. Experimental results and discussion

3.1. Oxidation of cation resin (IRN77) using Fenton reagent
According to the results of literature research, there are five factors that affect the degree of oxidation of cation resin: catalyst dosage, oxidant dosage, reaction time, reaction temperature, and pH value. Therefore, single factor tests were conducted for the above five factors.

3.1.1. Effect of catalyst dosage. The resin used in the test was nuclear type IRN77 resin actually used in nuclear power plants. The reaction temperature was first set at 95°C, the initial pH of the reaction system was set to about 2, the oxidant consumption was calculated theoretically, and the reaction time was tentatively set for 150 minutes. The single-factor test of catalyst dosage was performed. From the test results (Figure 1), it can be seen that the COD removal rate increases with the increase of the amount of catalyst. However, when the mass of the catalyst is more than 0.64 g, there is a phenomenon that part of the resin cannot be decomposed, and the mass of the undecomposed resin increases as the mass of the catalyst increases. When the mass of the catalyst was 0.32 g, the COD removal rate reached more than 95%, so the follow-up single factor test used this condition for subsequent tests.

3.1.2. Effect of reaction time. According to the single-factor test results of the catalyst dosage, the reaction temperature was set to 95°C, the initial pH of the reaction system was set to about 2, the oxidant consumption was calculated theoretically, and the mass of the catalyst was 0.32 g. The single-factor test of reaction time was performed. From the test results (Figure 2), it can be seen that the COD removal rate increases with the increase of reaction time. When the reaction time is 120 min, the removal rate of COD reaches more than 95%, and the increase of reaction time has little effect on the COD removal rate. Therefore, considering the period of each batch of the experiment, the reaction time of the subsequent single-factor test is selected. It is 120 minutes.

3.1.3. Influence of initial pH. According to the results of single factor test of catalyst dosage and reaction time, the reaction temperature was set to 95°C, the amount of oxidant used was calculated theoretically, the mass of the catalyst was 0.32 g, and the reaction time was 120 min. The single-factor test of the initial pH was performed. From the test results (Figure 3), it can be seen that the initial pH
has little effect on the removal rate of COD, but when pH = 2.0, the COD removal rate is the highest, so the initial pH value of the subsequent single factor test was selected as 2.0.

3.1.4. Effect of reaction temperature. Based on the above single-factor test results, the mass of the catalyst was set to 0.32 g, the reaction time was 120 min, the amount of oxidant used was calculated theoretically, and the initial pH value of 2.0 was used as the single-factor test of reaction temperature. From the test results (Figure 4), it can be seen that when the initial bath temperature is 30°C and 40°C, the resin is not dissolved after 120 minutes of reaction. When the reaction temperature is greater than 50°C, the removal rate of COD increases with the increase of initial bath temperature. When the water bath temperature is the boiling point of water, the COD removal rate is the highest, which is 97.28%. Therefore, the boiling point of water is selected for the subsequent test.

3.1.5. Effect of oxidant dosage. According to the above single-factor test results, the mass of the catalyst was set to 0.32 g, the reaction time was 120 min, the initial pH was 2.0, and the reaction temperature was 100°C. The single-factor test of the amount of oxidant was performed. From the test results (Figure 5), it can be seen that the removal rate of COD increases with the increase of the oxidant consumption. When the oxidant usage reaches more than 90% of the theoretical amount, the removal rate of COD does not increase significantly. In order to decrease the amount of oxidant, the follow-up tests can be performed using 90% of the theoretical oxidant dosage.

3.1.6. Effect of catalyst type. The catalyst type test was performed based on the superior test conditions obtained by the above single-factor tests. From the test results (Figure 6), it can be seen that under the same conditions, the oxidation effect of Fe powder is best, and the COD removal rate is the highest.
3.2. Oxidation of anion resin (IRN78) using Fenton reagent

3.2.1. Influence of initial pH on COD of reaction system. According to the results of the literature survey, the following conditions were chosen to carry out initial oxidation tests of anion resin: the initial pH values were 1, 2, and 3, and the catalyst was Fe²⁺/Cu²⁺ (molar ratio was 1:1). The total amount of catalyst was 8.9×10⁻⁴ mol, the water bath temperature was 95±2°C, the rate of 30% H₂O₂ adding was 1.00 mL/min, and the total reaction time was 210 min. From the experimental results (Figure 7), it can be seen that the COD value of each system dropped to less than 3000 mg/L when the reaction time was 120 minutes, and the COD value of the systems with initial pH values of 1 and 2 was almost the same, about 2700 mg/L; the system with a pH of 3 was lower than 2000 mg/L, indicating that the degree of oxidation was better. After 150 min of reaction, the COD value of each system dropped below 100 mg/L. As the reaction proceeded, the resin in the system was further degraded.

3.2.2. Effect of catalyst types. The oxidation effects of different catalysts, FeSO₄, CuSO₄, and FeSO₄/CuSO₄ (Fe²⁺:Cu²⁺=1:1), were compared. The initial pH value was 2, the total amount of H₂O₂ was 120 ml. After the reaction, the COD of the residual was measured. From the test results (Figure 8), it can be seen that the catalytic performance of the mixed catalyst is significantly better than that of the single catalyst. Under the condition of the initial pH value of 2, FeSO₄/CuSO₄ had the best catalytic...
effect, followed by FeSO$_4$ and CuSO$_4$ worst. The reason for the good catalytic effect of the mixed catalyst is that the presence of Cu$^{2+}$ improves the catalytic efficiency of Fe$^{2+}$.

3.2.3. Catalytic performance of Fe$^{2+}$/Cu$^{2+}$. The molar ratio of Fe$^{2+}$/Cu$^{2+}$ was 1:1. The amount of mixed catalyst was changed and the COD value of the residual was measured after the reaction was completed. From the test results (Figure 9), it can be seen that the higher the amount of catalyst under the same conditions, the lower the residual liquid COD value and the better the oxidation effect will be. When the amount of catalyst is too large, the residual liquid COD value no longer decreases, there is an increase trend. The reason may be that after the increase of the catalyst, the increase of side reactions causes a large loss of hydroxyl radicals, the decrease of the oxidant utilization rate, and the increase of the residual COD.

3.2.4. Effect of oxidizer adding rate. Based on the above experimental results, the effects of different oxidizer adding rates on the residual COD were studied. From the test results (Fig. 10), it can be seen that the residual COD value increases with the increase of the hydrogen peroxide adding rate, and the COD value of the residual increases significantly when it exceeds 1.0 ml/min. Studies have shown that a lower adding rate enables the use of sufficient hydrogen peroxide to decompose the OH· to make the residual liquid COD value low. When the hydrogen peroxide adding rate is too high, the side reaction accelerates to cause insufficient oxidation and makes residual COD increases. However, an excessively low adding rate may increase the reaction time and reduce the efficiency of the treatment resin per unit time.

3.3. Pilot test
According to the optimal reaction parameters obtained from the tests, a 1 kg cationic and anionic resin pilot tests were performed. From the test results (Figure 11), it can be seen that the COD removal rate
of cationic and anionic resin has reached more than 97%, and the oxidation effect is better. However, the total COD removal rate is not as high as the laboratory test. The reason is due to the fact that the volume of the residual in the pilot test is very large and the dilution effect on the oxidant is significant, thereby reducing the use efficiency of the oxidant.

![Figure 11. Pilot test.](image)

4. Conclusion and outlook
The oxidation of nuclear grade IRN77, 78 ion exchange resins were performed using Fenton reagent. The process conditions of Fenton reagent of cationic and anionic resin were studied preliminarily. The influence of pH, catalyst, oxidant and other reaction conditions on the Fenton oxidation process was investigated and the process parameters were optimized. From the results of laboratory and pilot experiments, it can be seen that the use of Fenton reagent can achieve good oxidation of both anionic and cationic resins, and the COD removal rate can reach over 97%, which laid the foundation for the development of Fenton oxidation treatment technology for the treatment of spent resin.

It is suggested to optimize the process conditions for different kinds of resin in pilot tests, and the optimization of the parameters should be further guided by studying the reaction kinetics. This provides theoretical and experimental support for the engineering application of this technology.

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