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Treatment of spent radioactive anionic exchange resins using Fenton-like oxidation process

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HIGHLIGHTS

- The spent radioactive resins could be degraded by Fenton-like oxidation.
- The operational conditions for resin oxidation were optimized.
- Chemical oxygen demand (COD) reduction rate was more than 90%.
- The resin morphological change during oxidation was observed using SEM.

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ABSTRACT

The treatment and disposal of spent radioactive ion exchange resins produced during the operation of the nuclear facilities is of great importance to minimize their potential hazard to the environments. In this paper, the degradation and disintegration of spent anionic resins was carried out using the Fenton-like oxidation process to reduce their volume and weight. The influencing factors, such as temperature, initial concentration of Cu(II), pH value were determined. The experimental results showed that the degradation efficiency (in term of COD removal rate), weight and volume reduction percentage was 97%, 68%, 75%, respectively, when pH was 3, Cu(II) concentration was 0.5 M and temperature was 95 ± 2 °C. The SEM observation indicated the process of resin disintegration and dissolution. The Raman and FTIR spectrum provided the information of functional groups change of resins during oxidation process, which is useful for further studying the intermediate products of resin degradation. The possible mechanism of anionic resins degradation was proposed to explain why they were difficult to degrade. Fenton-like oxidation process was a potential and promising method for significant volume reduction of spent radioactive resins.

1. Introduction

Ion–exchange resins (IERs) are kind of large molecular polymer, composing of three dimension mesh structures based on styrene monomer (C_8H_8) and cross-linked with divinylbenzene ($C_{10}H_{10}$), functional group and the opposite charges on the group. They can be divided into cationic exchange resins and anionic exchange resins according to their functional groups. The functional group of the anionic ion exchange resins is quaternary amine. The molecular formula ($C_{12}H_{19}NO$) was used to represent the anionic exchange resins.

Ion exchange resins are widely used in pure water preparation [1], treatment of wastewater, biochemical products extraction and organic catalyzing [2]. The spent resins are important wastes in the nuclear facility operation [3], which is used for purification of radioactive wastewater, recycling of nuclear fuel and so on. Resins suffered from agents oxidizing, high temperature, catalytic effect of metal ions, adsorbed species [4] and mechanical destruction, which could lead to deterioration of the structure of resins [5].

The spent radioactive ion exchange resins have been produced during the operation of the nuclear facilities in the nuclear industry. The resins loaded with radioactive nuclides could not be regenerated and reused in nuclear power plant because the regeneration of the resins loaded with radionuclides can cause another problem, that is, to produce the radioactive liquid waste, which also needs further treatment. Therefore the treatment and disposal of the spent radioactive resins is a very important to minimize their potential hazard to the human health and ecological environments [6].

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The common treatment of resins is immobilization, such as cementation [8–14], bituminization and plastic solidification [15]. However, those methods will cause the volume increase, leading to the high expense of transportation and management. Several volume reduction methods, *e.g.* incineration [16] and pyrolysis [17] can get high percentage of volume reduction. However, secondary waste will be produced in these processes. The wet oxidation can deal with these problems, such as supercritical water oxidation (SCWO) [18], plasma technology [19] and Fenton-like oxidation [1,3]. The first two have high requirements for the facility materials and the treatment cost is also high. The treatment of cationic resins using Fenton-like oxidation has been reported since 1980s [20]. In 1989, the Institute of Nuclear Power in Japan reported that combination of Fe(II/III) and Cu(II) were effective for oxidation of mixture of cationic and anionic resins [21]. In 1990s, Central Electricity Generating Board (CEGB) in England verified mixture of Fe(II) and Cu(II) were effective for degradation of anionic resins [22,23]. Our research group has studied the feasibility of degradation of resins with Fenton process since 1993. Jian et al. [7] studied the Fenton-like degradation of cationic and anionic resins without acidifier. Percentage of weight reduction of anionic resins was found to be 60%. In most cases, they used total organic carbon (TOC) as the evaluation index. To find out the nuclide distribution in the system, "hot test" was carried out with spent radioactive mixed resins from "Factory 821" in Sichuan Province, China. The results showed that degradation performance of the real radioactive mixed reins was similar to that of the fresh resins and almost all of radionuclides were left in the residual liquid. No radionuclides were detected in off gas [7].

Fenton-like process is an advanced oxidation process, which is initiated by hydroxyl radicals ($HO^{\cdot}$) produced by reaction of catalyst and H_2O_2 [24] (reaction (1)). The generated Cu(I) are converted to Cu(II) through reactions (2). There is also peroxide radicals ($HOO^{\cdot}$) produced during this process (reaction (3)). It can lead to a series of chain reactions (reaction (4)). The organic compounds can react with $HO^{\cdot}$ and $HOO^{\cdot}$. In the end, the organics are decomposed into small molecular organics (reactions (5) and (6)). Reactions (7) and (8) represent the reaction of styrene monomer and divinyl benzene with H_2O_2

$$M^{(n-1)+} + H_2O_2 \rightarrow M^{n+} + OH^- + HO^{\cdot} \ (M = Fe, Cu...) \quad (1)$$

$$M^{n+} + H_2O_2 \rightarrow M^{(n-1)+} + H^+ + HOO^{\cdot} \quad (2)$$

$$HO^{\cdot} + H_2O_2 \rightarrow H_2O + HOO^{\cdot} \quad (3)$$

$$HOO^{\cdot} + H_2O_2 \rightarrow H_2O + O_2 + HO^{\cdot} \quad (4)$$

$$HO^{\cdot} + RH \rightarrow H_2O + R^{\cdot} \quad (5)$$

$$C_{12}H_{19}NO + 3H_2O_2 \rightarrow 38H_2O + 12CO_2 + NH_4OH \quad (6)$$

$$C_8H_8 + 20H_2O_2 \rightarrow 8C_2O + 24H_2O \quad (7)$$

$$C_{10}H_{10} + 25H_2O_2 \rightarrow 10C_2O + 30H_2O \quad (8)$$

According to the study of Walling et al. [25], during the Fenton process, the reaction (5) can be divided into three parts, that is, reactions (9–11). Free radicals R_1, R_2 and R_3 have different effects during the Fenton process. Taking catalyst Fe as sample, as shown in reaction (12), $R_1^{\cdot}$ can reduce Fe^{3+} into Fe^{2+}. However, $R_2^{\cdot}$ is hardly oxidized by Fe^{3+}, and the catalyst can even be oxidized by $R_3^{\cdot}$ (reaction (13)). This may be the reason why some organics cannot be oxidized in the Fenton process

$$HO^{\cdot} + R_1H \rightarrow H_2O + R_1^{\cdot} \quad (9)$$

$$HO^{\cdot} + R_2H \rightarrow H_2O + R_2^{\cdot} \quad (10)$$

$$HO^{\cdot} + R_3H \rightarrow H_2O + R_3^{\cdot} \quad (11)$$

$$R_1^{\cdot} + Fe^{3+} \rightarrow R_1^+ + Fe^{2+} \quad (12)$$

$$R_3^{\cdot} + Fe^{2+} \rightarrow Fe^{3+} + R_3^- \xrightarrow{H_2O} R_3H \quad (13)$$

Walling et al. found that Cu(II) was effective oxidant to the alkane radical which can transfer reactions (10–11) into reaction (9). Thus Cu(II) can facilitate the Fenton process.

The degradation of resins with the Fenton process are mainly focused on the cationic resins using Fe(II) as the catalyst [1,2]. For example, we studied the disintegration and dissolution of spent cationic resins by Fenton-like process [26], and found that the COD removal rate was achieved by 99% at pH < 1, [Fe(II)] = 0.2 M, and $T = 97 \pm 2$ °C.

Anionic resins with quaternary amine are difficult to bind with catalyst than cationic resins. For degradation effect of fresh resins and used radioactive mixed resins is similar. Thus, in this work, we carried out the experiments with anionic resins. The effects of catalyst types and initial pH on anionic resin dissolution were investigated. We also studied the process of dissolution with electron scanning microscope (SEM), Raman spectra and infrared spectra which can provide the important information for understanding the degradation process of spent resins. Through scanning electron microscopy, the degree of resin degradation in different time was observed. Raman spectra and infrared spectra were used to study the change of resin chemical bond information during this process. At last, the mechanism of degradation was analyzed.

2. Materials and methods

2.1. Resins

The IERs used in this study are strong alkali styrene-divinylbenzene copolymer (Amberlite INR78), made by ROHM & HAAS. Fig. 1 presents the structure of anionic exchange resin.

Table 1 listed the characteristics of anionic exchange resins used in this study.

H_2O_2 (30% v/v in water), $FeSO_4{\cdot}7H_2O$, H_2SO_4, $CuSO_4{\cdot}5H_2O$, NaOH, Na_2CO_3, citric acid and all other reagents used in this study were of analytical purity, purchased from Beijing Chemical Plant. Deionized water was used.

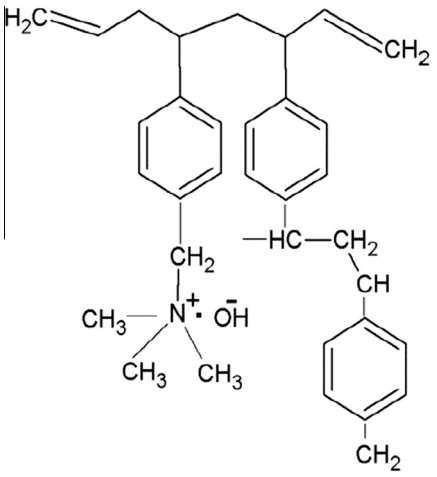

Fig. 1. Structure of anionic exchange resin.