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Kinetic study and optimization of electro-Fenton process for dissolution and mineralization of ion exchange resins

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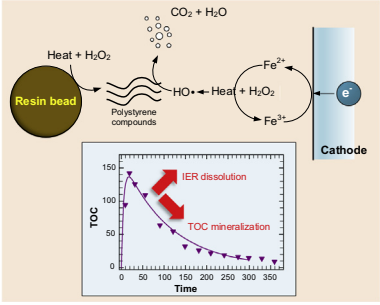
HIGHLIGHTS

- An effective E-Fenton process was developed to completely mineralize resins.
- A mechanistic kinetic model was derived to assess the removal of TOC.
- Strong acid and concentration of H_2O_2 predominated the dissolution of resin beads.
- Reaction rate of TOC removal was strongly influenced by applied current and pH.
- Iron catalyst could be recycled for repeating the treatment of resin.

GRAPHICAL ABSTRACT



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ABSTRACT

Spent ion exchange resins have become a crucial radioactive solid waste from the nuclear industry. Developing effective and safe disposal methods as alternatives to the present cementation method remains challenging. This investigation demonstrates the treatment of a mixed resin (sulfonated and quaternary ammonium polystyrene beads with a weight ratio of 40%:60%) by the electro-Fenton process. Mesh-type titanium metal that was coated with IrO_2/RuO_2 (Ti-DSA) was used as the anode and a stainless steel net was used as the cathode. The conversion of resins to soluble fragments and the removal of total organic carbon reached 92% and 99.4%, respectively, under conditions of solid loading = 40g L^{-1}, pH 2, applied current = 2 A, H_2O_2 flow rate = 1.2 mL min^{-1}, $FeSO_4$ = 20 mM at 85 °C. A pseudo first-order kinetic model of consecutive reactions specified that the efficacy of the electro-Fenton depended strongly on the slowly generated styrene in the aqueous phase by H_2O_2 and strong acid, which was rapidly mineralized by the hydroxyl radicals. The electro-Fenton process with reused iron catalyst was effective for treating ion exchange resin for at least for three runs, greatly reducing the volume of waste resin liquid.

1. Introduction

Ion exchange resins (IERs) have been extensively utilized in various processes, such as the separation of pollutants, the purification of wastewaters, drug delivery, extraction and organic catalysis [1,2]. One of the uses of IERs is to remove radioactive contaminants (neutron activation and fission products that leak from fuel elements) from the demineralized water at nuclear facilities [3]. Spent IERs, as important radioactive low-level wastes (LLW), were used to take up ^{90}Sr, ^{60}Co, ^{137}Cs, ^{235}U, ^{238}U and other elements. The common treatment of resins is immobilization, which involves cementation, bituminization and plastic solidification. Cementation includes chemical fixation and mechanical sealing, and is widely accepted in the treatment of spent resins [4]. However, internal stress is established between the packing

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material and dehydrated resins when the resins swell upon the adsorption of water, causing the leaking of radioactive nuclides [5]. The volume of cement may be six times larger than that of the original waste resins [6]. Incineration and pyrolysis can efficiently reduce the volume of resins, but generate secondary waste [7]. Chemical oxidation before solidification effectively reduces potential risks by removing the organic substances and converting resin particulates into inorganic liquid [8,9].

To deal with this problem, advanced oxidation processes (AOPs) have been recognized as promising chemical oxidation methods for the degradation of recalcitrant pollutants. AOPs generate a very powerful oxidizing agent, hydroxyl radicals (·OH) in solution, which are effective in the total mineralization of a variety of organic compounds [10]. The ·OH is formed under heterogeneous and homogeneous photocatalysis using near-UV or visible solar irradiation, O_3, Fenton's reagent, ultrasound, or wet (hot) oxidation [11,12]. Fenton's reagent has attracted widespread interest for use in the oxidation of toxic organics since 1960s. The major mechanism of the Fenton process creates hydroxyl radicals by the classical Fenton's reaction, [13]

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {\cdot}OH + OH^- \quad k = 63\ M^{-1}\ s^{-1} \tag{1}$$

where Fe^{2+} plays a role of catalyst when the solution pH is controlled below 3.0 (to prevent the precipitation of Fe^{3+}), but the reduction of Fe^{3+} (so called Fenton-like reaction) is relatively slow.

$$Fe^{3+} + H_2O_2 = \left[Fe^{III}(HO_2)\right]^{2+} + H^+ \quad K = 3.1 \times 10^{-3} \tag{2}$$

$$\left[Fe^{III}(HO_2)\right]^{2+} \rightarrow Fe^{2+} + HO_2^{\cdot} \quad k = 2.7 \times 10^{-3}\ s^{-1} \tag{3}$$

Hydroperoxy radicals ($HO_2^{\cdot}$) are much less reactive with organic compounds than hydroxyl radicals (·OH) [14]. The efficiency of the Fenton's reagent is influenced by various factors such as temperature, pH, H_2O_2, and concentration of ferrous ions, which affects the control of Fe^{2+} regeneration from Fe^{3+} that is produced in the process. The Fenton reaction is normally optimized at pH ~ 3 because this pH value maximizes the availability of Fe^{2+} in the reaction medium [15]. At pH > 5.0, Fe(III) precipitates as $Fe(OH)_3$ and the H_2O_2 decays into O_2 and H_2O, reducing the amount of catalyst in the solution [16]. To improve the slow catalytic kinetics of Fe^{3+} in a regular Fenton reaction, the electro-Fenton process (E-Fenton) is utilized via different routes: (1) H_2O_2 and Fe^{2+} are generated by the reduction of oxygen that is sparged on the cathode and dissolved from a sacrificial anode, respectively [17–19]; (2) H_2O_2 can be added and Fe^{2+} is regenerated on an active cathode following the production of ·OH (Eq. (1)) [20,21].

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad E^0 = 0.77\ V\ vs.\ NHE \tag{4}$$

To the author's experience, a controlled digestion of polystyrene-based IERs by H_2O_2 and the mineralization of the derivatives (intermediates in the formation of total organic carbons) by ·OH, catalyzed by transition metals (in Fenton or Fenton-like reactions for example) have been proposed but not yet fully explored [3,22]. After dewatering, the quantity of iron oxides generated from Fenton process is sometimes very large depending on the scale of treatment system. Such byproduct is normally treated as the municipal solid waste after decontaminating wastewaters. However, it is difficult to deal with industrial byproduct containing radioactive nuclides. The E-Fenton can be the primary alternative that minimizes the production of waste iron oxides by recycling Fe(II)/Fe(III) in an electrolytic cell. The present work investigates in detail the oxidative treatment of IERs in solutions by an effective E-Fenton process. The weight ratio of cationic and anionic resins of IER sample herein was 2–3, consistent with that of spent IER from the Institute of Nuclear Energy Research, Taiwan, who was implementing the decommissioning of power plant. The kinetics of the degradation of IERs into carbon dioxide and inorganic salts (SO_4^{2-}, NH_4^+) were elucidated using a rate model of consecutive reactions. Experimental parameters include IER loading, pH, flow rate of H_2O_2, and current density, which were varied to optimize the E-Fenton treatment of IERs.

2. Materials and methods

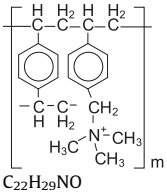
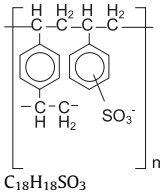
2.1. Chemicals

The mixed ion exchange resins (Purolite 37SC) were in a bead form with a weight ratio of cation- to anion-type resin of 40:60. The cationic resin was consisted of protonated sulfonated polystyrene cross-linked with divinylbenzene ($C_{18}H_{18}SO_3$, 66.50% C, 18.91% S, 14.59% O) and the anionic resin was consisted of protonated Type 1 quaternary ammonium polystyrene cross-linked with divinylbenzene ($C_{22}H_{29}NO$, 84.65% C, 8.41% N, 6.94% O). Properties of selected IERs were as listed in Table 1. Fenton reagents included hydrogen peroxide (H_2O_2, 50%, Chang Chun Group) and ferrous sulfate hepta-hydrated ($FeSO_4{\cdot}7H_2O$, Merck) were of analytical grade and used without further purification. The solution pH was conditioned by sulfuric acid (H_2SO_4, Merck, 95–97%). The waters for all chemicals were doubly deionized using a laboratory-grade RO-ultrapure water system (resistance > 18.3 MΩ).

2.2. Experimental procedure

A semi-batch reactor used to perform the electro-Fenton process is as depicted in Fig. 1. The cylinder-shaped anode and cathode were made of titanium metal coated with IrO_2/RuO_2 (Ti-DSA, 176 cm^2) mesh and stainless steel net (274 cm^2), respectively, and were mounted into a four-neck flask of one liter capacity. The distance between anode and cathode was 1.5 cm (the setup of E-Fenton apparatus is demonstrated in the Supporting information). Ti-DSA is one of dimensionally stable anodes, which have several merits, including insolubility, long service life and cost-effectiveness (compared with noble metal/metal oxide, for instance, Pt). The stainless steel net could provide high surface area to efficiently reduce Fe(III), and have proven to be an effective cathode for E-Fenton process [23,24]. A known concentration of $FeSO_4$ (as the catalyst) and IERs particles were prepared within 500 ml of reaction solution and mixed by stirring at 250 rpm. H_2O_2 (50%) was continuously introduced into the reactor at a constant flow rate using an automatic titrator. E-Fenton reaction was initiated by turning on the power supply at constant current mode. Due to the exothermic dissolution of IERs the temperature of solution

Table 1
Properties of commercial cationic and anionic exchange resins (NRW37SC, Purolite Ltd., Unit Kingdom) used in this work.

Properties	Anion exchange resin	Cation exchange resin
Appearance	Light-brown granular	Dark-brown granular
Volume ratio	60%	40%
Specific gravity	1.06	1.2
Molecular structure		
Molecular formula	$C_{22}H_{29}NO$	$C_{18}H_{18}SO_3$
Molecular weight	323	314
Total carbon	81.7%	68.8%
Ion exchange capacity	1100 meq L^{-1}	1800 meq L^{-1}
Particle size	0.425–1.2 mm	