Evaluation of the resin oxidation process using Fenton's reagent

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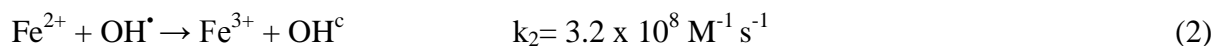05508-000 São Paulo, SP
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ABSTRACT

The ion exchange resin is considered radioactive waste after its final useful life in nuclear reactors. Usually, this type of waste is treated with the immobilization in cement Portland, in order to form a solid monolithic matrix, reducing the possibility of radionuclides release in to environment. Because of the characteristic of expansion and contraction of the resins in presence of water, its incorporation in the common Portland cement is limited in 10% in direct immobilization, causing high costs in the final product. A pre-treatment would be able to reduce the volume, degrading the resins and increasing the load capacity of this material. This paper is about a method of degradation of ion spent resins from the nuclear research reactor of Nuclear and Energy Research Institute (IPEN/CNEN-SP), Brazil, using the Fenton's reagent. The resin evaluated was a mixture of cationic and anionic resins. The reactions were conducted by varying the concentration of the catalyst (25 to 80 mM), with and without external heat. The time of reaction was two hours. The concentration of 50 mM of catalyst was the most effective in degrading approximately 99%. The resin degradation was confirmed by the presence of $CaCO_3$ as a white precipitate resulting from the reaction between the $Ca(OH)_2$ and the CO_2 from the resin degradation. It was possible to degrade the resins without external heating. The calcium carbonates showed no correlation with the residual resin mass.
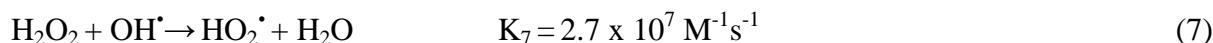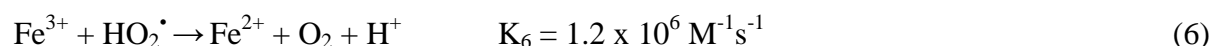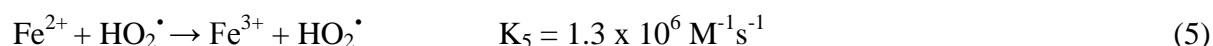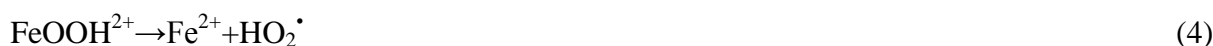
1. INTRODUCTION

One of the most common radioactive wastes generated from nuclear reactors is the ion exchange resin. It is used in the cooling water of primary circuit, maintaining low the level of impurities inside the reactor. When the end of useful life is reached, the resin is considered radioactive waste and must be treated according to specific regulations. Usually, these wastes are immobilized with Portland cement, because of its good mechanical properties, low cost and extensive knowledge of this material in the literature [1-2], reducing the possibility of radionuclides release into the environment. However, the incorporation of the resins in the cement is limited in 10%, because of the resin characteristic of expansion and contraction. Due to this problem, there are many methods described in the literature aiming the degradation of the resins, increasing its incorporation and decreasing costs compared to the direct immobilization. The common methods are the pyrolysis [3,4], incineration [4,5], acid digestion [6] and the Advanced Oxidation Process (AOP) [7-9]. The AOP utilization is applicable due the unnecessary utilization of high temperatures (<100ºC) and pressure control [9,10]. The AOP uses high reactive hydroxyl radicals, capable to destroy many organic

compounds [10]. The Fenton's reaction, considered as AOP, is one of most used because of its low cost and easy operation [11]. This reaction is described in literature [12-15] and the reactions are shown in equations 1-7.

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^{\bullet} \text{ (radical)} \qquad k_1 = 76 M^{-1}s^{-1} \qquad (1)$$

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^c \qquad k_2 = 3.2 \times 10^8 \ M^{-1}s^{-1} \qquad (2)$$

$$Fe^{2+} \text{ and } Fe^{3+} \text{ exist as aqueous-complexes.}$$

$$Fe^{3+} + H_2O_2 \rightleftharpoons FeOOH^{2+} + H^+ \qquad K_3 = 0.001 - 0.01 \ M^{-1}s^{-1} \qquad (3)$$

$$FeOOH^{2+} \rightarrow Fe^{2+} + HO_2^{\bullet} \qquad (4)$$

$$Fe^{2+} + HO_2^{\bullet} \rightarrow Fe^{3+} + HO_2^{\bullet} \qquad K_5 = 1.3 \times 10^6 \ M^{-1}s^{-1} \qquad (5)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+ \qquad K_6 = 1.2 \times 10^6 \ M^{-1}s^{-1} \qquad (6)$$

$$H_2O_2 + OH^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \qquad K_7 = 2.7 \times 10^7 \ M^{-1}s^{-1} \qquad (7)$$
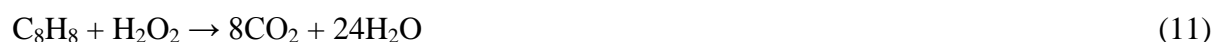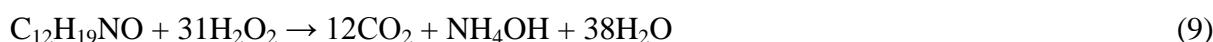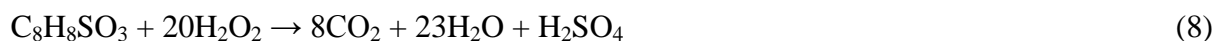
This work aims to conduct exploratory tests to degrade ion exchange resins from the nuclear research reactor of Nuclear and Energy Research Institute (IPEN/CNEN-SP), Brazil using the Fenton's reagent (hydrogen peroxide and ferrous sulphate as catalyst).

2. METHOD

Two types of resins were used, cationic (IR 120P) and anionic (IRA 410), as well a mixture of both resins. The difference between these resins is the functional group. Cationic has a SO_3H and anionic one has a $CH_2N^+R_4Cl^-$ group.

It was evaluated the catalyst concentration and the necessity of external heating. To verify the efficiency of degradation, the CO_2 released from the resin degradation was precipitated as calcium carbonate in a $Ca(OH)_2$ solution.

The equations of the resin decomposition are as follows [1]:

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

$$C_{12}H_{19}NO + 31H_2O_2 \rightarrow 12CO_2 + NH_4OH + 38H_2O \qquad (9)$$

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

$$C_8H_8 + H_2O_2 \rightarrow 8CO_2 + 24H_2O \qquad (11)$$

The oxidation experiments were conducted with 1 g of wet non-radioactive resins, distilled water and 50 mL of catalyst solution. The $Fe_2SO_4.7H_2O$ catalyst concentration varied from

20 to 80 mM. It was also evaluated the $CoCl_2$, with 100 mM and a mixture of $Cu(NO_3)_2$ and $Fe_2SO_4.7H_2O$ (40 mM each one). The hydrogen peroxide (Sigma - Aldrich) (25 to 30%) and the catalyst solution were slowly dropped in the solution using peristaltic pumps (Model Pump P-1) and the oxidation reaction was conducted under agitation and inert atmosphere. Two concentrations of hydrogen peroxide were adopted. The off-gas released by reaction was bubbled in calcium hydroxide solution, approximately 4 liters, as shown in Figure 1. Since the reaction is exothermic, the temperature was controlled or by the external heating under 50ºC or by the flow rates of the reactants at approximately 70 ºC. The reaction was kept about 2h. The experiments were carried out in duplicate.

After the reaction, the precipitated calcium carbonate was vacuum filtrated, stove-dried for 24 hours at 70ºC, and weighed in an analytical balance. In the same way, the resins remained were filtrated using a sieve, stove-dried (Model 315 SE), and weighed. Three types of catalyst were evaluated. The Fe^{2+}, the mixture of Fe^{2+}/Cu^{2+} (40:40 mM) and the Co^{2+} (100 mM). According to the literature (16), the mixture of Fe^{2+}/Cu^{2+} was the most efficient to degrade mix resins, and the Co^{2+}, is one of the radionuclides existent in the radioactive waste. The surface of the resins pre and post-treatment was studied using Scanning Electron Microscopy (SEM).

Figure 1: Experimental apparatus used in degradation experiments for a mixture of cationic and anionic resins. 1. Liquid nitrogen. 2 and 3. Peristaltic pumps. 4. Solution of hydrogen peroxide 50%. 5. Solution of catalyst. 6. Resin (anionic + cationic). 7. Solution of calcium hydroxide. 8. Magnetic stirrer (Model 753A).

3. RESULTS AND DISCUSSION

The results obtained with 20 mM $FeSO_4.7H_2O$ solutions are shown in Table 1.

Table 1 – Percentages of resins degradation with 20 mM $FeSO_4.7H_2O$ solutions.

Resin	% degradation
Cationic*	99
Anionic*	99
Cationic	98
Anionic	70
Mixture (1:1)	16

* Experiments conducted under external heating

There was degradation of about 99% of cationic and anionic resins, under external heating. In the reactions conducted without the external heating, the degradation was less efficient in anionic and mixed resins, about 70 and 16%, respectively. However, the cationic resin without heating showed degradation about 98%. According to the literature [16], this behavior occurs because is more difficult to degrade anionic and mixed than cationic resins. The reasons presented by the authors are: (1) The S atom, from cationic resins, releases electrons, while the hydroxyl attracts electrons. This makes them approach and react easily. The SO_3H group separates from benzene, forming the sulfuric acid, degrading the benzene and making the resulted liquid free of aromatic compounds in cationic resins. The N^+ radical of the anionic resin attract electrons and it has stable benzyl radical, becoming more difficult to react with hydroxyl radicals; (2) In the decomposition of anionic resins are produced complex agents for metallic ions, prejudicing the catalyst efficiency; (3) Decomposition of the quaternary amines is difficult due to theirs slow oxidation reaction.

It was also conducted experiments varying concentration of the $FeSO_4.7H_2O$ solutions. The results of these experiments are shown in Table 2. Under heating, it was observed degradation percentages of about 70, 85 and 97, with 20, 35 and 80 mM Fe_2SO_4 solutions, respectively.

It was observed degradation percentages of about 99, with 50, 70 and 80 mM $Fe_2SO_4.7H_2O$ solutions without heating. Therefore, it was observed higher efficiency using high concentrations of catalyst. The molarity of 50 mM was considered the most efficient because it was the lower catalyst concentration in comparison with the others, degrading the same percentage.

Table 2 – Residual resin masses from oxidation reactions

Resin	Dry initial mass (g)	$FeSO_4.7H_2O$ concentration (mM)	Residual resin mass (g)**
Mixed*	0.56	20	0.17 ± 0.03
		35	0.08 ± 0.03
		80	0.02 ± 0.01
Mixed	0.56	50	0.01 ± 0.01
		70	0.02 ± 0.01
		80	0.01 ± 0.01

* Experiments under external heating at 70ºC.
** $\bar{X} \pm S$ (average $\pm$ standard deviation) of the residual resin masses by semi- analytical balance.

The standard deviations, showed in Table 2, were similar or even equals to the average values, because some final residual resin masses were closed to the minimum value of measurement (semi-analytical balance).

Different catalysts were evaluated. The concentrations used and the residual resin masses are shown in Table 3.

Table 3 – Residual resin masses obtained in oxidation reactions with different catalysts

Dry initial mass (g)	Catalyst	Concentration (mM)	Residual resin mass (g) **
0.56	Ferrous sulphate	80	0.01 ± 0.01
0.56	Ferrous sulphate and copper nitrate	40*	0.04
0.56	Cobalt chloride	100	Not reacted

* The catalyst solutions used in this experiment were composed of 40 mM of $FeSO_4.7H_2O$ and 40 mM for $Cu(NO_3)_2$.
** $\bar{X} \pm S$ (average $\pm$ standard deviation) of residual resin masses measured by semi-analytical balance.

The mixture of Fe^{2+}/Cu^{2+} was so efficient as the Fe^{+2} in resin degradation, reaching 92%. This result is similar to [16], which more than 85% of resin was degraded in a study with 25 grams of mixed resins 2:1 (cationic: anionic) with Fe^{2+}/Cu^{2+} and external heating.

The calcium carbonate masses are resulting of the reaction of carbon dioxide, released from reaction, with the calcium hydroxide solution. The calcium dioxide was monitored to evaluate the mass balance of the process. The obtained masses are shown in Table 4.

Table 4 – Carbonate masses obtained and residual resin mass of the oxidation reactions

Experiments	Initial resin mass (g)	Residual resin mass (g) **	Carbonate mass (g)**
Cationic	0.56	<0.01	1.03 ± 0.11
Anionic	0.56	0.12 ± <0.01	0.87 ± <0.01
Mixture	0.56	0.02 ± <0.01	0.98 ± 0.04
Mixture *	0.56	0.03 ± <0.01	0.85 ± 0.02

* The carbon dioxide was captured with sodium hydroxide.
** $\bar{X} \pm S$ (average ± standard deviation) of the residual resin masses and carbonate measured by semi-analytical balance.

The quantified carbonate masses showed in Table 4 were similar and no correlation with the residual resin mass was observed. These values are lower than the theoretical masses calculated from the chemical equations, about 3 g. The inefficiency of the gas dissolution in the sodium hydroxide solution was probably the cause of these low values, about 30% of the theoretical value. In a similar work [17], the authors did not also obtain the expected theoretical mass, with about 15% of the calculate value. It could indicate that this method is inefficient to monitor the reaction.

Morphologic Analysis

The surface of the resins pre and post-treatment was studied. Samples of resins were analyzed by Scanning Electron Microscopy (SEM). The micrograph images are shown in Figure 2. The Figure 2c shows the residual resin (1% of initial resin).
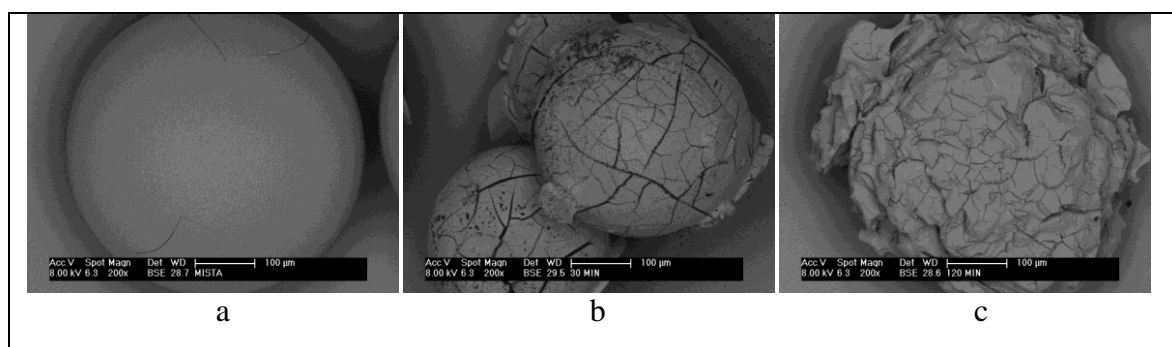

Figure 2 a: Resins without treatment. b and c: Resins after 30 and 120 minutes, respectively (100mM Fe$_2$SO$_4$).

It is possible to see in Figure 2 that there are cracks on the surface in 30 min. In 120 min, it is possible to observe the detachment of the resin surface.

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