Evaluation of Resin Dissolution Using an Advanced Oxidation Process – 13241

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ABSTRACT

The ion-exchange resin is widely used in nuclear reactors, in cooling water purification and removing radioactive elements. Because of the long periods of time inside the reactor system, the resin becomes radioactive. When the useful life of them is over, its reutilization becomes inappropriate, and for this reason, the resin is considered radioactive waste. The most common method of treatment is the immobilization of spent ion exchange resin in cement in order to form a solid monolithic matrix, which reduces the radionuclides release into the environment. However, the characteristic of contraction and expansion of the resin limits its incorporation in 10%, resulting in high cost in its direct immobilization. Therefore, it is recommended the utilization of a pre-treatment, capable of reducing the volume and degrading the resin, which would increase the load capacity in the immobilization. This work aims to develop 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 Advanced Oxidative Process (AOP) with Fenton's reagent (hydrogen peroxide and ferrous sulphate as catalyst). The resin evaluated was a mixture of cationic (IR 120P) and anionic (IRA 410) resins. The reactions were conducted by varying the concentration of the catalyst (25, 50, 100 e 150 mM) and the volume of the hydrogen peroxide, at three different temperatures, 50, 60 and 70°C. The time of reaction was three hours. Total organic carbon content was determined periodically in order to evaluate the degradation as a function of time. The concentration of 50 mM of catalyst was the most effective in degrading approximately 99%, using up to 330 mL of hydrogen peroxide. The most effective temperature was about 60ºC, because of the decomposition of hydrogen peroxide in higher temperatures. TOC content was influenced by the concentration of the catalyst, interfering in the beginning of the degradation process. It was possible to correlate it with the final amount of non-degraded resins. These results show that these conditions were favorable to destroy the resins, indicating to be the AOP an effective technique to reduce the volume of the waste.

INTRODUCTION

Many types of radioactive wastes are generated from nuclear technology applications. One of them is the ion exchange resins used in nuclear power reactors to purify the cooling water of

primary circuit. After its useful time, the resin is considered radioactive waste and must be treated according to the Brazilian Nuclear Commission regulations.

As the waste must be safely stored, it is usually adopted the immobilization with Portland cement, because it is a simple and low cost method and provide a product with good mechanical properties [1-2]. However, swelling characteristic of the resin limits its incorporation in cement, increasing considerably the final volume of the waste.

New techniques capable to destroy completely the resin and increase its incorporation in the cement matrix have been developed. These techniques have a target to decrease volume and cost compared to direct immobilization. There are several methods of pre-treatment described in the literature such as pyrolysis [3], incineration [4,5], acid digestion [6] and the Advanced Oxidative Process (AOP)[7,8,9]. Special attention must be given to AOP, especially for not requiring high temperatures (between 60°C to 100ºC) through a process that operates near ambient temperature and pressure [10]. Used as a pre-treatment, AOP is capable to destroy many organic compounds with high reactive hydroxyl radicals [11]. There are many combinations of methods considered AOP, but the Fenton's reaction (H_2O_2 / Fe^{+2}) is one of the most used due its low cost and easy operation [12].

This work aims to develop 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 Advanced Oxidative Process (AOP) with Fenton's reagent (hydrogen peroxide and ferrous sulphate as catalyst).

MATERIALS AND METHODS

The resin evaluated was a mixture of cationic (Amberlite® IR 120P) and anionic (Amberlite® IRA 410) resins, both provided by Sigma-Aldrich. The oxidation reactions with Fenton's reagent were conducted by varying the amounts of catalyst (ferrous sulphate), hydrogen peroxide and temperature.

The experiments were conducted with 10 g of non-radioactive resins in a glass reactor, under agitation. Ferrous sulphate solution was added as catalyst into two parts, first, 200mL to saturate the exchange sites of the resin for 15 minutes and, second, 120 mL were dropped during the reaction. The concentration of the catalyst solutions were 25, 50, 100 and 150 mM, prepared with $Fe_2SO_4.7H_2O$ (GR) and distilled water. All solutions were acidified with 2 mL of 1M H_2SO_4 solution to avoid air oxidation. A 25% (w/w) H_2O_2 solution was slowly dropped using a peristaltic pump, in a flow rate of approximately 2 mL/min, in order to control the reaction. The volume of the H_2O_2 solution ranged from 350 to 500 mL. As the oxidation process is an exothermic reaction, it was not used an external heater, being the temperature controlled by the flow rates of the H_2O_2 and catalyst solutions. The reactions were conducted at three different

2

temperatures, 50, 60 and 70 °C, controlled with a multimeter and using only the 50 mM $FeSO_4 7H_2O$ concentration. All reactions were conducted in triplicate, for 180 minutes. Table I shows the main experimental conditions.

Table I – Experimental conditions in 10 g resins oxidation process

H_2O_2 concentration (%)	H_2O_2 volume (mL)	$FeSO_4 7H_2O$ concentration (mM)
25	480	25
25	335	50
25	350	100
25	340	150

The degradation efficiency was determined by the Total Organic Carbon (TOC) analyzer and residual resins. TOC content was measured periodically (15, 30, 45, 60, 120 and 180 minutes) in order to evaluate the degradation as a function of time. The Fig. 1, indicates the experimental conditions used in this work.
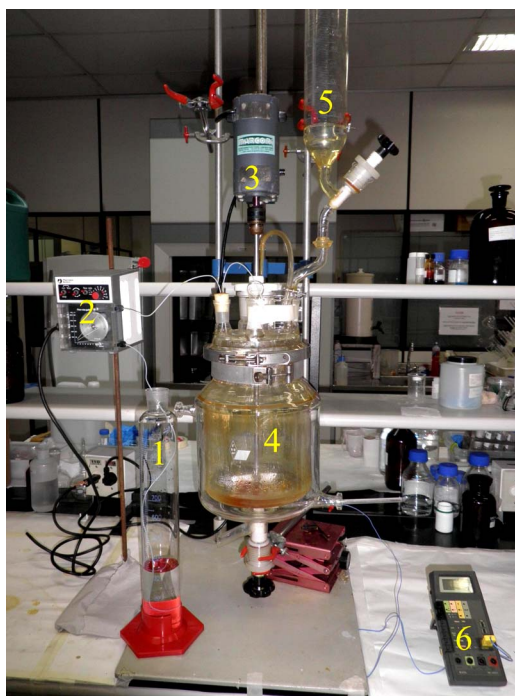
Fig. 1. Apparatus for the degradation of 10 g of ion exchange resins. 1. Hydrogen peroxide. 2. Peristaltic pump. 3. Stirrer. 4. Glass reactor. 5. Catalyst solution. 6. Multimeter.

RESULTS AND DISCUSSION

The residual resin mass and temperatures are shown in Table II.

Table II – Residual resin mass in different temperatures

Temperature (ºC)	Residual resins mass (g)
48.1 ± 4.1	0.47 ± 0.04
58.5 ± 0.9	0.02 ± 0.01
70.8 ± 2.6	0.08 ± 0.01

It was observed that the most efficient temperatures were 60 and 70ºC, with a degradation of 99 and 98.5%, respectively. However, it must be considered that hydrogen peroxide undergoes to

decomposition above 60ºC. The temperature showed an important parameter to degrade the resins.

The residual resin mass was quantified in the end of reactions conducted with different concentrations of $FeSO_4.7H_2O$. The experimental conditions are shown in Table III.

Table III – Residual resins mass for different $FeSO_47H_2O$ concentrations

$FeSO_47H_2O$ concentration (mM)	Temperature (ºC)	H_2O_2 volume (mL)	Residual resin mass (g)
25	41.1 ± 1.0	480 ± 20	1.75 ± 0.32
50	60.4 ± 6.5	323 ± 6	0.01 ± 0.00
100	53.8 ± 0.7	345 ± 26	0.11 ± 0.07
150	54.4 ± 0.5	337 ± 13	0.65 ± 0.07

The concentration of 25 mM $FeSO_47H_2O$ solution was not sufficient to maintain the desired temperature, resulting in a resin degradation of 69%. The 150 mM of $FeSO_47H_2O$ solution showed a lower degradation compared with 50 and 100 mM, indicating that the excess of $FeSO_47H_2O$ can interfere in the process. The concentrations of 50 and 100 mM of $FeSO_47H_2O$ were the most efficient, degrading 99 and 98% of resin, respectively. However, the catalyst concentration that promotes the most effective attack is the 50 mM, considering the mass of ferrous sulphate used.

The Total Organic Carbon (TOC) was studied to evaluate the reaction efficiency. The behavior of TOC content in function of time can be seen in Figure 2.
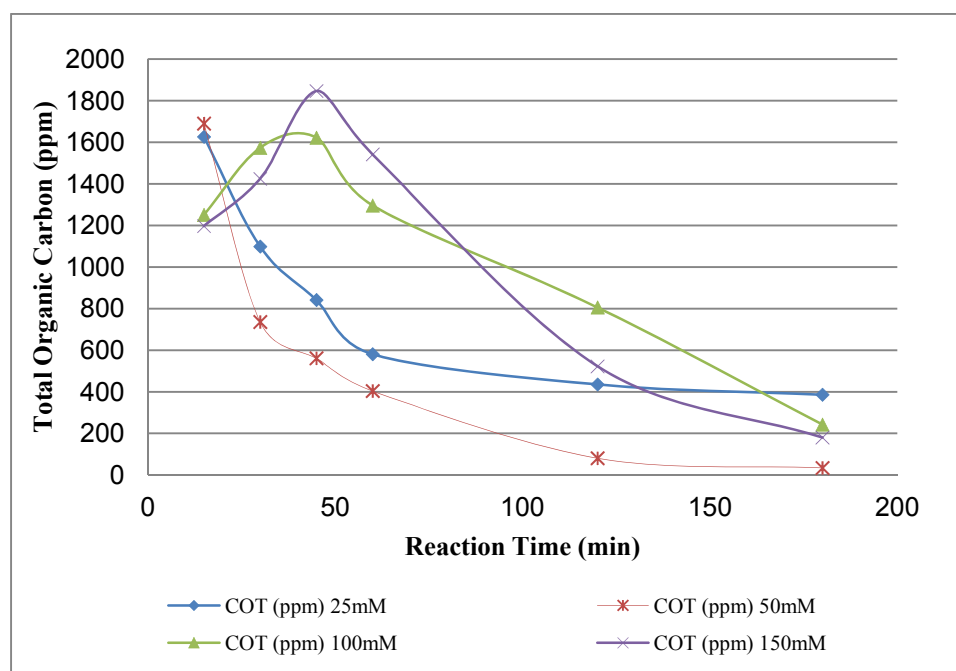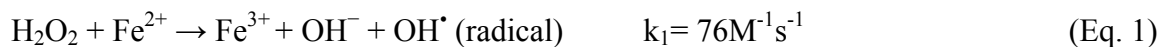
Fig. 2. Total Organic Carbon in function of time.

In Figure 2, it is possible to observe that the behavior of TOC vs. time with smaller amounts of catalyst showed a progressive decrease since the beginning. On the other hand, in larger quantities, it was observed an increase in TOC content in 1 hour of reaction, followed by a decrease until the end. The TOC showed to be influenced by catalyst concentration, interfering with the beginning of the degradation process. According to [12], this behavior can be explained by the excess of Fe^{+2} ions that can act as "scavenger" of the free radicals OH •, presented in Equation (2), reducing the availability of these radicals in the ion exchange resins degradation process, delaying it.

The reaction time of the radicals with the Fe^{+2} is 3.2 x 10^8 L. mol^{-1} s^{-1}, faster than Fenton reaction with 76 L. mol^{-1} s^{-1} [14].

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

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

Besides, according to [13], the ion exchange resin is initially solubilized, increasing the TOC and finally decreased as the soluble organics are oxidized to carbon dioxide gas.

6

The efficiency of the TOC as a parameter of reaction control was evaluated. Its values were compared with final residual resins. The final residual resin and TOC are shown in Table IV. In general, the results were similar, indicating that TOC is an efficient parameter to determine the degradation rates of resins.

Table IV – Final residual resin and Total Organic Carbon **(TOC)** in percentages.

Molarity	Final residual resins (%)	TOC (%)
25	62 - 92	77 - 93
50	87 - 100	94 - 99
100	97 - 100	80 - 98
150	87 - 93	84 - 96

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 3. The Figure 3c shows the non dissolved resin (1% of initial resin).
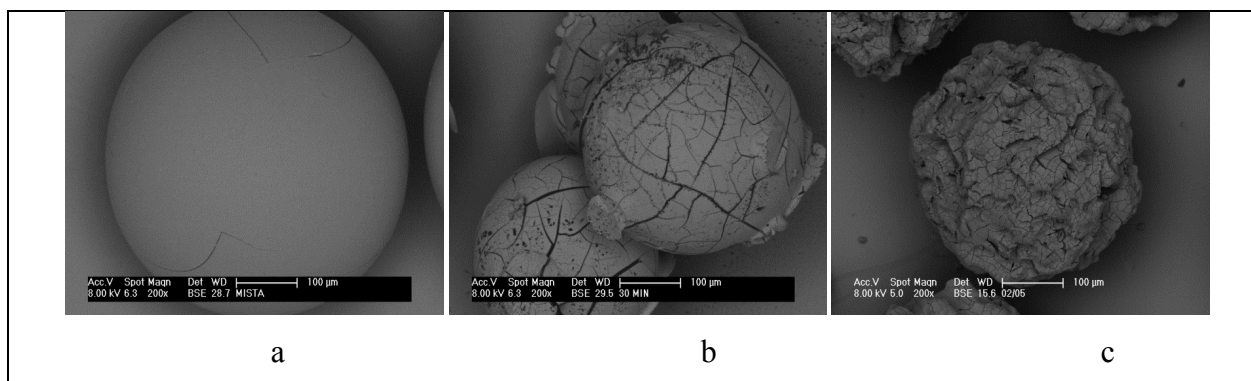

Fig. 3. a: Resins without treatment. b and c: Resins after 30 and 180 minutes, respectively $(100mM\ Fe_2SO_4)$.

It was possible to see in Figure 3 that this attack was not restricted to the surface, but it happened internally too. Initially, it can be seen cracks on the surface, with a several external breaks in 30 min. In 180 min, it is possible to observe a reduction in size of the resin due to the cracking and detachment of the superficial resin attacked.

CONCLUSIONS

Advanced Oxidative Process (AOP) with Fenton's reagent was evaluated to degrade ion spent resins. Temperature, catalyst concentration and the morphologic surface of the resins were the parameters studied. It was possible to conclude that:

• The catalyst concentration affects the oxidation reaction. The most effective concentrations were 50 and 100 mM.

• It is possible to degrade the resins efficiently without external heating. A temperature of 60 º C was effective.

• The best catalyst concentration was 50 mM, because it requires less volume of catalyst compared to 100 mM with the same degradation rate.

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