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Degradation of ion exchange resin using Fenton's reagent

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ABSTRACT

The ion-exchange resin is commonly used in the cooling water purification of nuclear reactors, for removing radioactive elements. As the resin is used for long periods of time inside the reactor system, it becomes radioactive. After the useful life of the resins is over, its reutilization becomes inappropriate, and for that reason, the resin is considered radioactive waste. To ensure environment security, the direct solidification of spent ion exchange resin by cementation is currently the main immobilization process, decreasing its release to the environment. This immobilization consists in a mixture of water, cement and radioactive waste. Because of its characteristic of contraction and expansion, the incorporation of resin is limited in 10%, causing high costs in its direct immobilization. Therefore, it is recommended the utilization of a pre-treatment, capable of reducing the resins volume, degrading them, and increasing 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), Brazil, using the Fenton's reagent (hydrogen peroxide and a catalyst). Three forms of the resin were used: cationic (IR 120P), anionic (IRA 410) and a mixture of both resins. The reactions were conducted by varying the amounts of catalyst, hydrogen peroxide and temperature. 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. The experiments showed two good different types of method to degrade the resin. One of them is used for cationic or anionic resin and, the other, was used for a mixture of them. Both of these methods will be described in this work with their respective results.

1. INTRODUCTION

Radioactive waste is defined by Brazilian Nuclear Commission as "any material resulting from human activities that contains radionuclides in quantities higher than the exemption levels established in the standard CNEN-NE-6.02 – Licensing of Radioactive Installations" [1]. Many types of waste are generated which can be classified according to the phase, origin, activity, lifetime, disposal requirements etc. Nuclear power reactors generate among others, ion exchange resins used to purify the cooling water of primary circuit. After its useful time in a long period inside the reactor, the spent ion exchange resin is considered radioactive waste and must be conveniently treated.

The most common method to treat the resins is the immobilization in Portland cement. Despite of the low cost, the process increases the final volume of the waste due to the low immobilization capacity of the cement.

There are many methods of pre-treatment described in the literature like pyrolysis [2] and incineration [3], but the most promissory one is the Advanced Oxidative Process (AOP), because of its moderate operating conditions and significant volume reduction [2], a pre-treatment discussed in this paper using the Fenton's reagent (H_2O_2 / Fe^{+2}), in which high reactive hydroxyl radicals are capable to destroy many organic compounds [4].

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), Brazil, using the Fenton's reagent (hydrogen peroxide and a catalyst).

2. MATERIALS AND METHODS

Three forms of the resin were used: cationic (IR 120P), anionic (IRA 410) and a mixture of both resins. The reactions were conducted by varying the amounts of catalyst, hydrogen peroxide and temperature. The resin degradation was confirmed by the presence of $CaCO_3$ as a white precipitate resulting from the reaction between the $Ca(OH)_2$ (Merck) and the CO_2 released from the resin degradation.

The difference between cationic and anionic resins is the functional group, in cationic is a SO_3H and in anionic is a $CH_2N^+R_4Cl^-$ group. The results of the resin decomposition are as follows:

$$C_8H_8SO_3 + 20H_2O_2 \rightarrow 8CO_2 + 23H_2O + H_2SO_4 \quad (1)$$

$$C_{12}H_{19}NO + 31H_2O_2 \rightarrow 12CO_2 + NH_4OH + 38H_2O \quad (2)$$

$$C_{10}H_{10} + 25H_2O_2 \rightarrow 10CO_2 + 30H_2O \quad (3)$$

$$C_8H_8 + H_2O_2 \rightarrow 8CO_2 + 24H_2O \quad (4)$$

[2]

Figure 1 shows cationic resins (IR 120P) without any treatment:

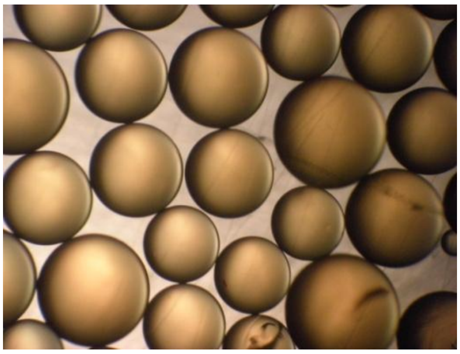

Figure 1. Non-degraded cationic resins under an optical microscope (10x).

The oxidation experiments of the resins were conducted with 1 g of non-radioactive resins, 50 ml of catalyst solution, prepared with 1 g of ferrous sulphate (Merck) and distilled water. The hydrogen peroxide (Sigma - Aldrich) (50% for mixture and 30% for anionic or cationic) and the catalyst solution were slowly dropped in the solution using peristaltic pumps (Model Pump P1, Pharmacia Biotech) and the oxidation reaction was conducted under agitation under inert atmosphere. Two concentrations of hydrogen peroxide were adopted because it is more difficult to degrade a mixture of resins compared with cationic or anionic only. The off-gas released by reaction was bubbled in calcium hydroxide solution, approximately 4 liters, as shown in Figure 2. Since the reaction is exothermic, the temperature was controlled by the flow rates of the reactants at approximately 70 ºC. The reaction was kept between 1h30min to 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, Fanem), and weighed.

Figure 2. 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, Fisatom).

3. RESULTS AND DISCUSSION

In Figure 3, we can observe resins after degradation process using Fenton’s reagent.

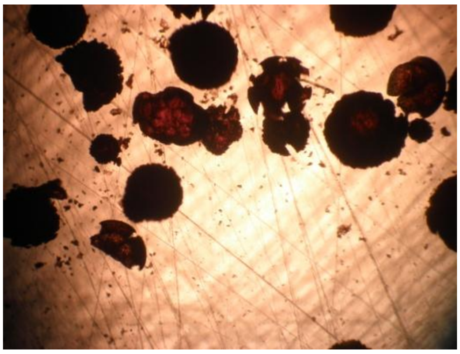

Figure 3. Degraded resins after one hour and thirty minutes of reaction time under an optical microscope (10x).

The flow rate of the catalyst solution and hydrogen peroxide was controlled according to the temperature of the reaction, kept at approximately 70-80°C. Above 80ºC it was observed foam formation which could decrease the efficiency of degradation due to the segregation of the resins. The degradation of the resins was evaluated by calcium carbonate and resin remaining masses. Table 1 shows these results.

Table 1. Some oxidation experiments with their respective results.

Resin	Ferrous sulphate (g)	Hydrogen peroxide concentration (%)	Calcium carbonate (g)	Degrade resin (%)
Cationic	0.56	30	0.9686 $\pm$ 0.0109	99.79
Anionic	0.56	30	0.8402 $\pm$ 0.0038	98.46
Mixture	1.14	50	1.0249 $\pm$ 0.0074	99.88

The cationic resin is easier to be degraded than anionic resin because its functional group attracts hydroxyl radicals. The percentages of resin degradation were close to 100%, showing that the method was efficient. The amount of calcium carbonate precipitated was different for the three types of samples and it was not possible to correlate with the degradation process. For this reason, the remaining solution will be analyzed to determine the Total Organic Carbon (TOC).

4. CONCLUSIONS

The degradation of ion exchange resin with Fenton's Reagent (H_2O_2 / Fe^{2+}) with the right flow rate of catalyst solution and hydrogen peroxide seems to be efficient and we may conclude that:

- Hydrogen peroxide 50% is more efficient in mixture degradation than hydrogen peroxide 30% due the difficult to maintain the best rate for temperature.
- It is more difficult to maintain the best reaction rate in the beginning of the reaction due the low volume water.
- The quantities of resins remaining after the reaction are insignificant compared to the initials one.

5. REFERENCES

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