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# APPLICATION OF ADVANCED OXIDATIVE PROCESS IN TREATMENT RADIOACTIVE WASTE

**Cátia Kim[1,2], Solange K. Sakata [1,2], Rafael V.P. Ferreira[1], Julio T. Marumo[1]**

[1] Instituto de Pesquisas Energéticas e Nucleares, IPEN - CNEN/SP
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
jtmarumo@ipen.br

[2] Faculdades Oswaldo Cruz,
Rua Brigadeiro Galvão 540
01151-000 São Paulo, SP

## ABSTRACT

The ion exchange resin is used in the water purification system in both nuclear research and power reactors. Combined with active carbon, the resin removes dissolved elements from water when the nuclear reactor is operating. After its consumption, it becomes a special type of radioactive waste. The usual treatment to this type of waste is the immobilization with Portland cement, which is simple and low cost. However, its low capacity of immobilization and the increase volume of waste have been the challenges. The development of new technologies capable of destroying this waste completely by increasing its solidification is the main target due to the possibility of both volume and cost reduction. The objective of this work was to evaluate ion exchange resin degradation by Advanced Oxidative Process using Fenton's Reagent ($H_2O_2$ / $Fe^{+2}$) in different concentration and temperatures. One advantage of this process is that all additional organic compounds or inorganic solids produced are oxidized easily. The degradation experiments were conducted with IRA-400 resin and Fenton's Reagents, varying the $H_2O_2$ concentration (30% e 50%) and heat temperature (25, 60 and 100ºC). The resin degradation was confirmed by the presence of $BaCO_3$ as a white precipitate resulting from the reaction between the $Ba(OH)_2$ and the $CO_2$ from the resin degradation. All experiments run in duplicate. Higher degradation was observed with Fenton's Reagent ($Fe^{+2}$ /$H_2O_2$ 30%) at 100ºC after 2 hours.

## 1. INTRODUCTION

The development of nuclear technology led to high diversity of applications, since nuclear fission to produce electricity until the use of radioisotopes in agriculture, research, medicine and industry. The cost to society that arises from the use of technology is the radioactive waste generation that like any other waste must be treated to guarantee the protection of human health and the environment.

According to International Atomic Energy Agency, the radioactive waste is "the material that contains or is contaminated with radionuclides at concentrations or activities greater than clearance levels as established by the regulatory body". Brazilian Nuclear Commission defines 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 [1-3].

Radioactive waste may be classified according to several criteria depending on the phase, origin, activity, lifetime, disposal requirements etc. Usually, it is adopted a combination of criteria, which will depend on the waste management of the installation. Many types of waste

are generated such as pieces of paper, plastic, glass and equipments. From nuclear power reactors, ion exchange resins[1] used to purify the cooling water of primary circuit are classified as radioactive wastes, after the useful life. These materials become radioactive because they remove from the water the dissolved chemical elements transferred during the operation of the reactor. The usual treatment to this type of waste is the immobilization with Portland cement, which is simple and low cost. However, its low capacity of immobilization and the increase volume of waste have been the challenges [3-7].

The development of new technologies capable of destroying this waste completely by increasing its solidification is the main target due to the possibility of both volume and cost reduction. The objective of this work was to evaluate ion exchange resin degradation by Advanced Oxidative Process using Fenton's Reagent ($H_2O_2$ / $Fe^{+2}$) in different concentration and temperatures.

AOP is a process in which high reactive hydroxyl radicals are generated, causing destruction of many organic compounds. [8]. The application of this technique is described in literature [9-12] and advantages of this process in radioactive waste treatment are the moderate operating conditions and sufficient volume reduction effect [9].

## 2. MATERIALS AND METHODS

The oxidation experiments of the resins were conducted with 10 g of non-radioactive IRA-400 resin, 22 ml of distilled water, 45 ml of hydrogen peroxide 30 % and 0,15 g of ferrous sulphate as catalyst. The hydrogen peroxide was slowly dropped with a peristaltic pump and the oxidation reaction was carried out under agitation in a closed system and off-gas released was bubbled in barium hydroxide solution, as shown in Figure. 1. The temperature ranged from 25 to 100 °C and the reaction was kept for 2 hours. A hydrogen peroxide solution with highest concentration (50 %) was also tested at 25 °C.

[1] The ion exchange resin is a synthetic product in the form of small beads or spheres, constituted by cross-linked polymers of styrene and divinylbenzene, forming a structure of pores with exchange sites that can trap or release ions. There are four main types depending on the functional ion exchange groups added onto the polymer: strongly acidic (sulfonic acid groups), strongly basic (quaternary amino groups), weakly acidic (carboxylic acid groups) and weakly basic (primary, secondary and/or ternary amino groups).


**Figure 1. Experimental apparatus used in the degradation of the resin. 1. Resin + Fenton's reagent; 2. Magnetic stirrer; 3. Barium hydroxide solution; 4. Hydrogen peroxide solution; 5. Peristaltic pump.**

## 3. RESULTS AND DISCUSSION

The surface of the resins after the oxidation with Fenton's reagent is shown in figures 2 to 5. Figure 2 shows resin spheres after contact with Fenton's reagent at 25°C. The surface of the resins was slightly attacked and many resin spheres remained intact.

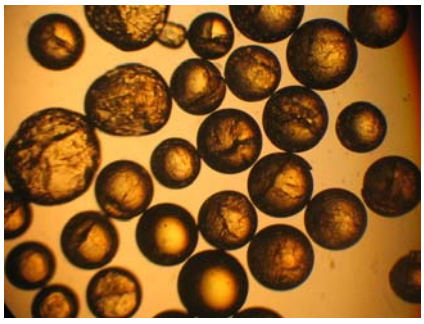

**Figure 2. Resins treated with Fenton's reagent observed at an optical microscope (40x). Assay 1: 25°C; $H_2O_2$ 30%**

When the temperature of the reactions was increased to 60$^{o}$C (Figure 3), it was observed that many resins were broken and in other resin the erosion of its surface. In addition, comparing with the first assay, an increase in the diameter of resins was observed, suggesting that there is a swelling process before the cracking.

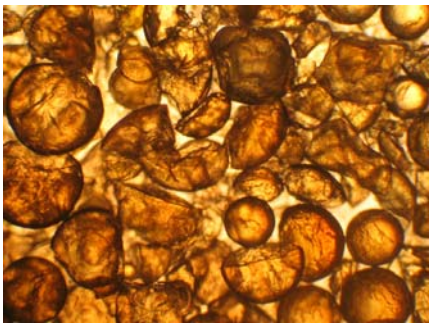

**Figure 3. Resins treated with Fenton's reagent observed at an optical microscope (40x). Assay 2: 60°C; $H_2O_2$ 30%**

The influence of the temperature at the Advanced Oxidative Process was confirmed after analyzing the resin spheres when reaction with Fenton´s reagent was performed at 100 °C as shown at Figure 4. The resins were practically degraded and the fragments were smaller comparing with the assay 2. The temperature was more effective but it is noteworthy that the use of high temperature is not interesting in processes of treatment of radioactive wastes since more investments are necessary to avoid contamination.

At the end of the reaction, 10 mL of the solution was extracted with dichlorometane and the organic phase was analyzed by gas chromatography-mass spectroscopy. The results showed organic compounds which were identified as part of the resin. This data confirmed that the resin was oxidized followed by its degradation.

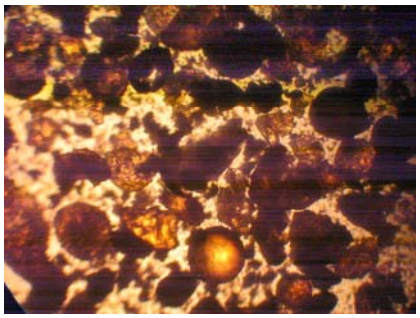

**Figura 4. Resins treated with Fenton's reagent observed at an optical microscope (40x). Assay 3: 100°C; $H_2O_2$ 30%**

The influence of the hydrogen peroxide concentration was also studied. The oxidative reaction was performed with hydrogen peroxide 50 % in place of 30 % at 25 °C. The surface of the resins was attacked but it was not sufficient to destroy them (Figure 5) This behavior could be explained by higher water and oxygen releasing from hydrogen peroxide 50 %.

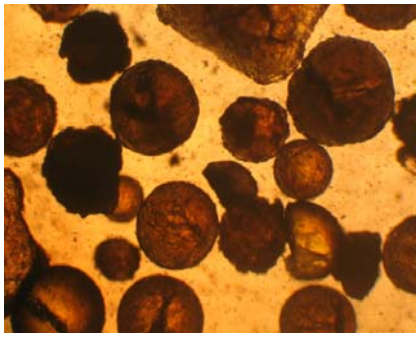

**Figura 5. Resins treated with Fenton's reagent observed at an optical microscope (40x). Assay 4: 25°C; $H_2O_2$ 50%.**

The off-gas control, with barium hydroxide solution, indicated a release of carbon dioxide gas, evidenced by the white precipitated. In all assays, it was observed high quantities of barium carbonate, except in assay 1, where the solution only became turbid.

## 4. CONCLUSIONS

The degradation of ion exchange resin with Fenton's Reagent ($H_2O_2$ / $Fe^{+2}$) seems to be efficient and it is possible to conclude:

- The Fenton's reagent is more efficient with hydrogen peroxide 30% than 50%;
- Temperature is a important parameter and influences the reaction process The higher temperatures generate the higher degradations.


## ACKNOWLEDGMENTS

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## REFERENCES


1. IAEA-INTERNATIONAL ATOMIC ENERGY AGENCY. Radioactive waste management glossary. *IAEA - TECDOC-447*. 2. ed. Vienna, (1988).

2. CNEN- COMISSÃO NACIONAL DE ENERGIA NUCLEAR. *Licenciamento de Instalações Radiativas* - CNEN-NE-6.02. Rio de Janeiro, (1985).

3. HIROMOTO, G.; DELLAMANO, J.C.; MARUMO, J.T.; ENDO, L.S.; VICENTE, R.; HIRAYAMA, T. *Introdução à gerência de rejeitos radioativos***.** São Paulo: Instituto de Pesquisas Energéticas e Nucleares, Departamento de Rejeitos Radioativos, (1999).

4. TEIXEIRA, E.M.; MARUMO, J.T.; ENDO, L.S.; GOES, M.M.; ISIKI, V.L.K.; RODRIGUES FILHO, G. Avaliação de matrizes de cimento contendo resinas de troca iônica do reator de pesquisa do IPEN. *Proceeding regional congress on radiation protection and safety*, Recife, PE, (2001).

5. HOWARD, C.G.; JOLLIFFE, C.B.; LEE, D.J. Immobilization of ion-exchange resins in cement. *Nuclear Science and Technology. Part of the shared cost programme (1985-89) on 'Management and disposal of radioactive waste' of the European Communities*, (1991).

6. IAEA-INTERNATIONAL ATOMIC ENERGY AGENCY. Improved cement solidification of low and intermediate level radioactive wastes. *Technical Report Series*. **n. 350**, IAEA, Vienna, (1993).

7. IAEA -INTERNATIONAL ATOMIC ENERGY AGENCY. Treatment of spent ion-exchange resins for storage and disposal. *Technical Report Series***. n. 254**, IAEA, Vienna, (1985).

8. LANGE, C. L.; ALVES, F. J.; AMARAL, S. C. M.; MELO JUNIOR R. W.. Tratamento de lixiviado de aterro sanitário por processo oxidativo avançado empregando reagente de Fenton. *Eng. Sanit. Ambient***.**, Rio de Janeiro, **v. 11**, n. 2, (2006).

9. JIAN, X.; WU T.; YUN G.; A study of Wet Catalytic oxidation of Radioactive Spent Ion Exchange Resin by Hydrogen Peroxide. *Nuclear Safety*, **v. 37**, n.2, (1996).

10. KOUZNETSOV, A., KNIAZEV O. Microbial treatment of ion exchange resins. . *Proceedings of the 8th Congress of Francophone Countries*, **v. 15**, n. 86, p.427-434, (2001).

11. WILKS, P. J.; HOLMAN. J.D.; HOLT S. N. Pilot scale demonstration of spent ion exchange resin treatment by wet oxidation. *Proceedings of the 1991 Joint International Waste Management Conference*. pp. 559-565, (1991).

12 TAYLOR P.A., Destruction of Ion-Exchange Resin in Waste from the HFIR, T1, and T2 Tanks Using Fenton's Reagent, *ORNL/TM-2002/197*, (2002).