Article

Reaction of Ion Exchange Resins with Fenton's Reagent

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Abstract: One of the most common treatment methods for spent ion exchange resins is their immobilization in cement, which reduces the release of radionuclides into the environment. Although this method is efficient, it considerably increases the final volume of the waste due to its low incorporation capacity. This work aims to evaluate the degradation of ion exchange resins by the Fenton process (H_2O_2/Fe^{2+}). The resin evaluated was a mixture of cationic and anionic resins, both non-radioactive. The reactions were conducted by varying the catalyst concentration (25, 50, 100, and 150 mmol L^{-1}) and the volume of hydrogen peroxide. Three different temperatures were evaluated by varying the flow of reactants, which were 50, 60, and 70 $^\circ$C. Cement specimens were prepared from the treated solutions and two parameters were assessed—namely, final setting time and axial compressive strength. The results showed that the experimental conditions were suitable to dissolve the resins, and the Fe^{3+} produced as precipitate during the experiments increased the resistance of the final product. The immobilized product complied with the limits established by regulation.

Keywords: waste management; ion exchange resin; infrared spectrometry; Fenton; solid waste

1. Introduction

Ion exchange resins (IER) are among the most common radioactive wastes generated from nuclear reactors. They are used to purify the cooling water from the primary circuit and, after its useful time, the resin is considered radioactive waste and must be handled in accordance with the country regulations. As a radioactive waste, safe storage is required, with a material capable of reducing the possibility of radionuclides released into the environment. Generally, Portland cement is used as a simple and low-cost method and has good mechanical properties [1]. However, the incorporation capacity of this material in the cement is low, due to the characteristic of contraction and expansion of the resins, increasing the final volume of the wastes. Therefore, there are many treatment methods under development at research institutes, capable of degrading the resin and increasing its incorporation in the cement matrix. These techniques aim to reduce waste volume and cost compared to a common direct immobilization approach. In this context, Advanced Oxidation Processes (AOPs) are considered a good option, since they are performed at room temperature and pressure [2,3]. AOPs are capable of degrading many organic compounds by means of highly reactive hydroxyl radicals [4]. There are many techniques considered as AOP, such as the Fenton's reaction (H_2O_2/Fe^{2+}), one of the most used due its low cost and ease of operation [5]. According to [6], the immobilization of IER treated by Fenton's reagent may reduce costs regarding final disposal and transport by 50% when compared to direct immobilization.

The reactions involved in Fenton processes are [7,8]:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + HO\bullet \quad k_1 = 76 \text{ L mol}^{-1} \text{ s}^{-1} \tag{1}$$

$$Fe^{2+} + HO\bullet \rightarrow Fe^{3+} + OH^- \quad k_2 = 3.2 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1} \tag{2}$$

$$Fe^{3+} + H_2O_2 \rightarrow FeOOH^{2+} + H^+ \quad k_3 = 0.001 - 0.01 \text{ L mol}^{-1} \text{ s}^{-1} \tag{3}$$

$$FeOOH^{2+} \rightarrow Fe^{2+} + HO_2\bullet \tag{4}$$

$$Fe^{2+} + HO_2\bullet \rightarrow Fe^{3+} + HO_2\bullet \quad k_5 = 1.3 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1} \tag{5}$$

$$Fe^{3+} + HO_2\bullet \rightarrow Fe^{2+} + O_2 + H^+ \quad k_6 = 1.2 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1} \tag{6}$$

$$H_2O_2 + HO\bullet \rightarrow HO_2\bullet + H_2O \quad k_6 = 2.7 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1} \tag{7}$$
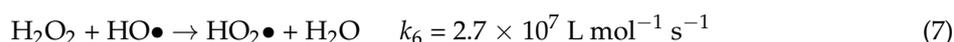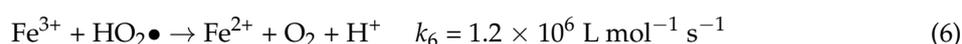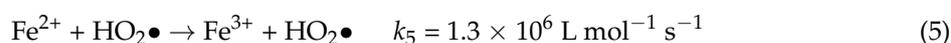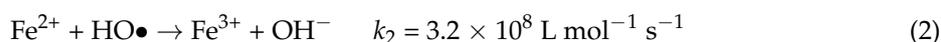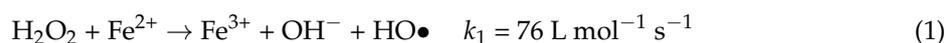
In [9], they proposed the dissolution of IER by the hydroxyl radical:

$$HO\bullet + IER \rightarrow \text{Linear polystyrene (soluble)} + CO_2 + (SO_4^{2-})/(R_4N^+ + H_2O) \tag{8}$$

$$\text{Linear polystyrene} + HO\bullet \rightarrow \text{simple aromatic acids} + CO_2 + H_2O \tag{9}$$

$$R\bullet + Fe^{3+} \rightarrow R^+ + Fe^{2+} \tag{10}$$
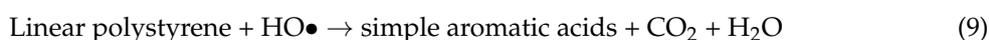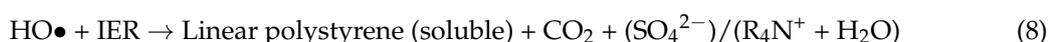
The same authors also proposed the following Equations (Equations (11)–(14)), which are usually expected in the dissolution of resins:

$$C_8H_8SO_3 + 20H_2O_2 \rightarrow 8CO_2 + 23H_2O + H_2SO_4 \tag{11}$$

$$C_{10}H_{10} + 25H_2O_2 \rightarrow 10CO_2 + 30H_2O \tag{12}$$

$$C_8H_8 + 20H_2O_2 \rightarrow 8CO_2 + 24H_2O \tag{13}$$

$$C_{12}H_{19}NO + 31H_2O_2 \rightarrow 12CO_2 + 38H_2O + NH_4OH \tag{14}$$
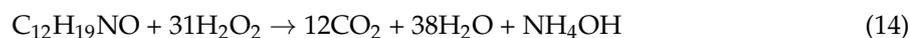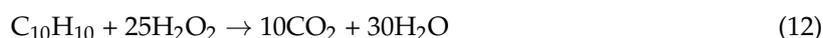
Equations (11)–(14) indicate IER dissolution reactions with their characteristic functional groups, and Equations (12) and (13) demonstrate, individually, the reactions for the crosslinking agent and styrene unit. These equations are not necessarily the same for our work, since the resins employed in this study are distinct from those used by [9]. However, they are shown here as examples of IER degradation by AOP process.

Although some articles [10,11] demonstrate that the optimum pH in the Fenton process is 4, a study [2] revealed that a wide range of pH (3–7) was sufficient to reduce the total organic carbon (TOC) content. This information is important, because smaller amounts of reactants would be required, decreasing costs for an AOP application aimed at degrading ion exchange resins.

This paper re-examines the degradation of ion exchange resins by Fenton's reagent. AOP was used in the pretreatment step, aiming at the modification of resin properties and improving cement immobilization efficiency.

A recent review of the literature on this topic found that various approaches have been proposed to address this issue [1,4,12–14]. These articles have studied or reviewed the degradation of ion exchange resins by thermal Fenton oxidation. However, a key problem with much of the literature on IER degradation is that, despite its good results in achieving high rates of degradation and mineralization, there is a lack of information on the handling of this material after Fenton's reaction regarding the solidification process. Furthermore, they controlled the pH and used an external heater to maintain the desired temperature, which may be inadequate or unnecessary in an industrial process. To the best of our knowledge, a complete study on the analytical aspect of IER degradation under Fenton oxidation and cementation of the treated material has not been previously investigated taking into account its transformation into soluble and less heavy compounds in the circumstances described herein.

2. Materials and Methods

It is worth mentioning that preliminary experiments were performed to determine the reactant concentrations and the masses of IER used in this work. The experiments were conducted with 10 g of non-radioactive resin in glass reactor under stirring. The resin evaluated was a mixture of cationic resin (Amberlite®IR 120P-Exchange capacity $\geq$1.8 meq mL^{-1}) and anionic resin (Amberlite®IRA 410-Exchange capacity $\geq$1.25 meq mL^{-1}), both provided by Sigma-Aldrich. Oxidation reactions with the Fenton's reagent were conducted by varying the amounts of the ferrous sulfate heptahydrate (Merck) catalyst and reactant H_2O_2 25% (Sigma Aldrich, Saint Louis, MO, USA) (*w/w*). As is known, masses of ion exchange resins are usually linked to an equivalent concentration of functional exchange sites. However, we find it more interesting to relate these masses to molar concentrations, since we are not concerned with the ion exchange process itself, but in its degradation through an AOP.

Two aliquots of the catalyst solution were added to, first, 200 mL to saturate the resin exchange sites for 15 min, and second, 120 mL were added during the reaction. The concentrations of the catalyst solutions were 25, 50, 100, and 150 mmol L^{-1}, prepared with FeSO$_4$·7H$_2$O and distilled water. All solutions were acidified with 2 mL of 1 mol L^{-1} H_2SO_4 (P.A) solution to avoid air oxidation. After the saturation period saturation of the exchange sites with the catalyst solution, a solution of H_2O_2 was added in a flow rate of ~2.3 mL min^{-1}, to control the reaction. The volume of the H_2O_2 solution ranged from 335 to 460 mL. As the oxidation process is an exothermic reaction, the temperature was controlled by the flow rates of the reactants. The temperature reactions were controlled with a thermocouple coupled to a digital multimeter equipment of the brand ICEL (model MD-5660C) to maintain the temperature in the range of 50–60 °C, avoiding the thermal decomposition of the hydrogen peroxide, which is above 60 °C. All reactions were conducted in triplicate for 180 min. The initial pH was set at 7 at the beginning of the experiments, measured periodically over time. Table 1 shows the main experimental conditions.

Table 1. Experimental conditions in 10 g resins oxidation process.

FeSO$_4$·7H$_2$O Concentration (mmol L^{-1})	H$_2$O$_2$ Volume (mL)
25	460
50	335
100	350
150	340

2.1. Total Organic Carbon Concentration (TOC)

TOC analysis was performed in a Shimadzu TOC-VCS device. This equipment employs thermal oxidation in the presence of acid and measures TOC indirectly by the difference between the total carbon (TC) content of the sample and the inorganic carbon (IC) content. TOC was measured periodically (15, 30, 45, 60, 120, and 180 min) to evaluate the IER mineralization during the experiments. Since ion exchange resins are insoluble in water, the first measurement was at 15 min.

2.2. Dissolved Oxygen (DO)

DO was measured by an AKSO OD-SX751. DO concentrations were quantified with the use of an electrode, which through a permeable membrane allows diffusion of oxygen. The cathode in the equipment reduces the oxygen present in the sample and forms the oxidation product at the anode. The measured electric current is proportional to the amount of oxygen in the analyzed sample. DO content was measured periodically (15, 30, 45, 60, 120, and 180 min). According to the supplier, the maximum measurement uncertainty is $\pm$0.10 mg L^{-1}.

2.3. Fourier Transform Infrared Spectrometry (FTIR)

Infrared spectra were obtained by a Bomem spectrometer MB-series to observe the structures of the resins before and after treatment. It is worth noting that no liquid analysis was carried out; since our major concern was focused on evaluating ion exchange resins in pretreatment and non-dissolved IER after Fenton oxidation. The results were analyzed using the software Knowitall® Informatics System 9.5, and compared with frequency tables of characteristic groups and also with the results presented in the literature [15]. The spectral resolution was 4 cm^{-1} and the observed frequency was from 400 to 4000 cm^{-1}.

2.4. Residual Resin Mass

The solids remaining after Fenton's oxidation were quantified by sieving (0.045 mm mesh), drying for 12 h in Fanem oven (315SE-model) at 70 °C, and subsequent weighing with Mettler-Toledo analytical balance (AG204-model). Precipitated ferric ion was previously removed by sieving in order to avoid a wrong mass measurement of the remaining ion exchange resins. The precipitate ferric ion presented a higher granulometry, besides having an orange color easily identified when compared to the degraded resin, of dark coloration.

2.5. Cementation

After the oxidation reactions, the final suspensions were solidified in cement to evaluate improvements in loading capacity. An increase in capacity was expected in relation to that observed in direct immobilization, which is around 8–10% of resin (*w/w*). The suspension/cement ratios evaluated were 0.28, 0.30, and 0.35 (mass/mass) with suspensions with and without pH adjustment. pH was 2, 7, or 10. The specimens were prepared in disposable plastic molds, 5 cm diameter and 10 cm height. The cement paste was premixed, transferred to the plastic molds, and held sealed for 28 days at 22 °C.

The parameters evaluated were the free liquid after 24 h, setting time (solidification time), and mechanical strength. A Vicat needle was employed to determine the setting time, or softening point [16] at the time when it was not possible to penetrate the sample. The assays were performed in triplicate.

3. Results and Discussion

3.1. Effects of Temperature and Catalyst Concentration

The temperatures and volumes of the 25% H_2O_2 obtained and employed using the catalyst concentration in solution of 25, 50, 100, and 150 mmol L^{-1} are shown in Table 2.

Table 2. Residual resin masses after the oxidation process under different temperatures and volumes of hydrogen peroxide.

FeSO$_4$·7H$_2$O Concentration (mmol L^{-1})	Dry Resin Mass (g)	Temperature (°C) $^\alpha$	H$_2$O$_2$ 25% Volume (mL) $^\alpha$	Residual Resin Mass (g) $^\alpha$	Average Degradation (%)
25	5.6	41 ± 1	480 ± 20	1.56 ± 0.03	76.14
50	5.6	60 ± 6	323 ± 6	0.01 ± <LOD $^\beta$	99.82
100	5.6	53 ± 1	345 ± 26	0.11 ± 0.07	98.03
150	5.6	54 ± 1	337 ± 13	0.65 ± 0.07	88.39

α: X ± S (Average ± Standard Deviation); β: Limit of detection.

Table 2 shows that all conditions were adequate to degrade more than 70% of the initial resin masses. Given that our findings are based on temperature control by the flow rates of the reactants into the reactor, the results for such analysis should consequently be treated with the utmost caution. The contrasting values of temperature as regards the catalyst concentrations of 50, 100, and 150 mmol L^{-1} reflects the difficulty in maintaining the temperature without an external heater. For instance, the contrast at observed temperatures, e.g., 60 ± 6 °C (50 mmol L^{-1} of FeSO$_4$·7H$_2$O), and

53 ± 1 °C (100 mmol L^{-1} of $FeSO_4 \cdot 7H_2O$) does not mean that an inferior concentration of catalyst generated more energy than a superior one, but indicates a difficulty regarding the control of the flow rates of the reactants.

The lowest concentration of $FeSO_4 \cdot 7H_2O$ (25 mmol L^{-1}) was not sufficient to increase the reaction rate and generate enough heat to reach and maintain the temperature around 60 °C, which affected the reaction. On the other hand, the residual mass of the reactions conducted with the highest concentration indicates that an excess of catalyst may interfere negatively. The solutions of 50 and 100 mmol L^{-1} were the most effective, degrading about 100% of the resins. A similar result was obtained by the authors of [3], who used 180 mL of 50% H_2O_2 to completely degrade 20 g of a mixed resin. Total Organic Carbon (TOC) was studied to evaluate the efficiency of the reaction. Figure 1 shows the behavior of TOC as a function of time.
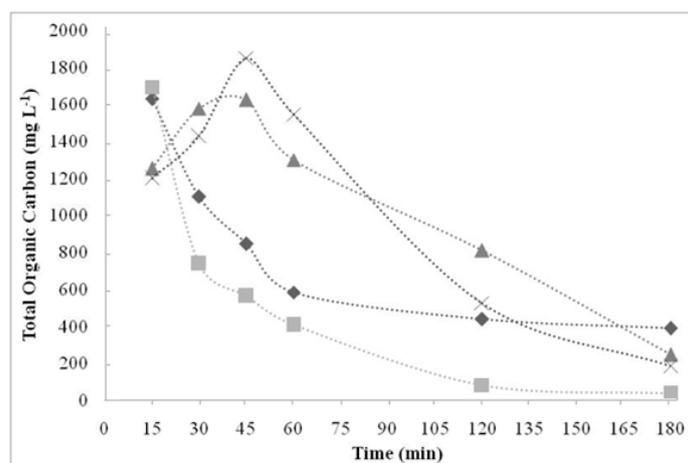
Figure 1. Total Organic Carbon as a function of time. Condition ($[FeSO_4 \cdot 7H_2O]_0$, mmol L^{-1}): ($\blacklozenge$) 25; ($\blacksquare$) 50; ($\blacktriangle$) 100; ($\times$) 150.

Smaller amounts of catalyst showed a progressive decrease in TOC since the beginning. On the other hand, in larger quantities, an increase in TOC content was observed within 1 h of reaction, followed by a decrease to the end. TOC was influenced by the catalyst concentration, interfering at the beginning of the degradation process.

This behavior can be explained by the excess of Fe^{2+} ions that can act as "scavenger" of free radicals HO•, as shown in Equation (2), reducing the availability of these radicals in the reaction process, and delaying the degradation. Besides, the ion exchange resin is initially solubilized, increasing the TOC and finally decreasing as long as the soluble organics are oxidized in carbon dioxide [3].

The constant rate of the radicals with Fe^{2+} is 3.2×10^8 L mol^{-1} s^{-1}, much higher than the Fenton reaction with 76 L mol^{-1} s^{-1} [14], as previously shown in Equations (1) and (2).

TOC removal efficiency was evaluated as the control parameter of the reaction. Their values were compared with the degradation of IER in %. Degradation of IER (%) and TOC removal are shown in Table 3.

Table 3. Degradation of IER and Total Organic Carbon (TOC) in percentages.

Catalyst Concentration (mmol L^{-1})	Degradation of IER (%)	TOC Removal (%)
25	62–75	58–78
50	92–100	94–99
100	97–99	83–98
150	87–93	86–94

As anticipated, TOC is an efficient parameter for determining resin degradation rates. The degradation reactions were not efficient with 25 and 150 mmol L^{-1} $FeSO_4 \cdot 7H_2O$ solutions, since the

stoichiometric ratios were not appropriate. These inappropriate ratios were excess of H_2O_2 or catalyst concentration. It is common knowledge that excess H_2O_2, as concerns rate constants and the target compound, can negatively interfere with process efficiency, whereas inappropriate concentrations of H_2O_2 may act as a $HO\bullet$ scavenger [17].

pH measured over time decreased from 7 to 3 during the oxidation process and no significant difference was observed for the different conditions employed in the experiments.

Figure 2 indicates that the reaction with 25 mmol L^{-1} $FeSO_4 \cdot 7H_2O$ showed, after 15 min, a high DO concentration compared to the concentrations of 50 and 100 mmol L^{-1} of $FeSO_4 \cdot 7H_2O$, reaching its maximum value in 45 min.
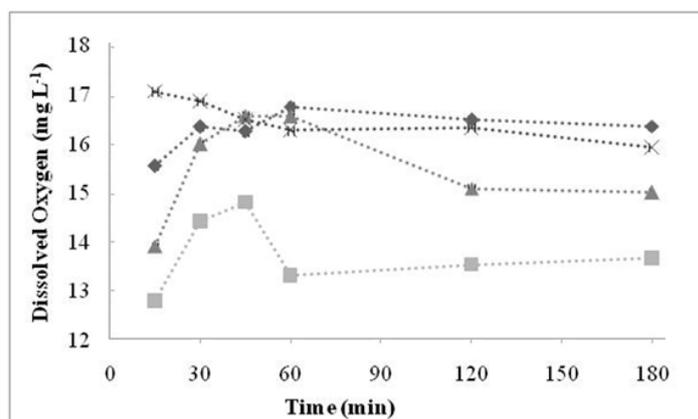
Figure 2. Dissolved oxygen concentration as a function of time, from oxidation reactions with different catalyst concentrations; Condition ([$FeSO_4 \cdot 7H_2O$], mmol L^{-1}): (◆) 25; (■) 50; (▲) 100; (×) 150.

The increase in the DO concentration may indicate an excess of H_2O_2 compared to the ferrous sulfate concentration, showing that there is a strong kinetic element conducting the oxygen/time profile of the reaction system studied [18].

As observed in Equation (7), the excess of the oxidant can compete for the hydroxyl radicals, generating the radical $HO_2\bullet$. These radicals act to oxidize Fe^{2+} to Fe^{3+} and reduce Fe^{3+} to Fe^{2+} as shown in Equations (5) and (6), resulting in increased dissolved oxygen formation compared to other catalyst concentrations. The concentration of 150 mmol L^{-1} $FeSO_4 \cdot 7H_2O$ also resulted in a high concentration of DO, as shown in Figure 2. The increase of Fe^{2+} leads to higher formations of Fe^{3+} and hydroperoxyl radical as shown in Equation (5). The hydroperoxyl radical is responsible for the increase in O_2 concentration, as shown in Equation (6).

The untreated cationic and anionic resins and the mixture of both post Fenton reactions were analyzed by Fourier Transform Infrared Spectrometry (FTIR). Figures 3–5 illustrate the spectra.
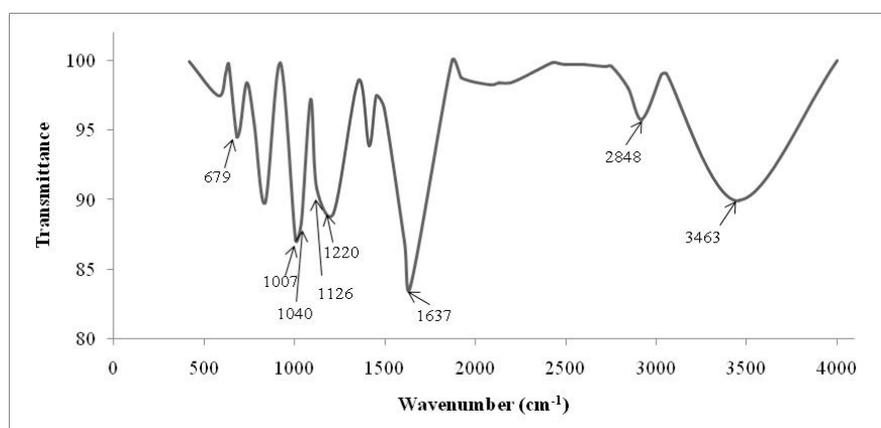
Figure 3. Infrared spectrum from strongly acid cationic resin.
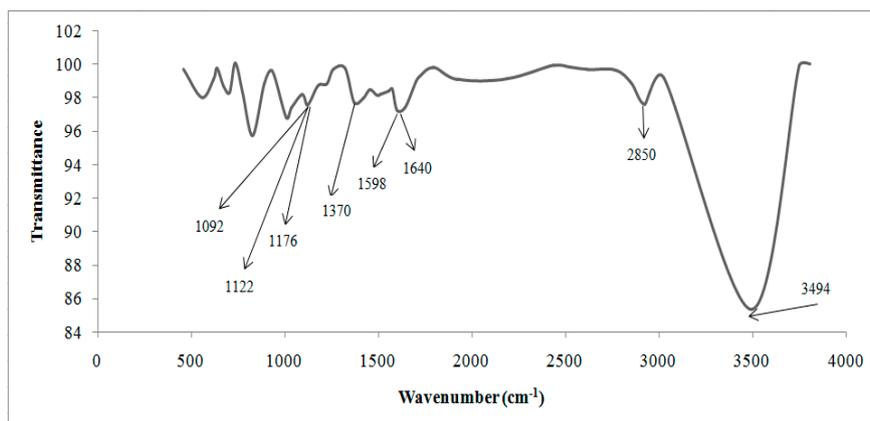
Figure 4. Infrared spectrum from strongly basic resin.
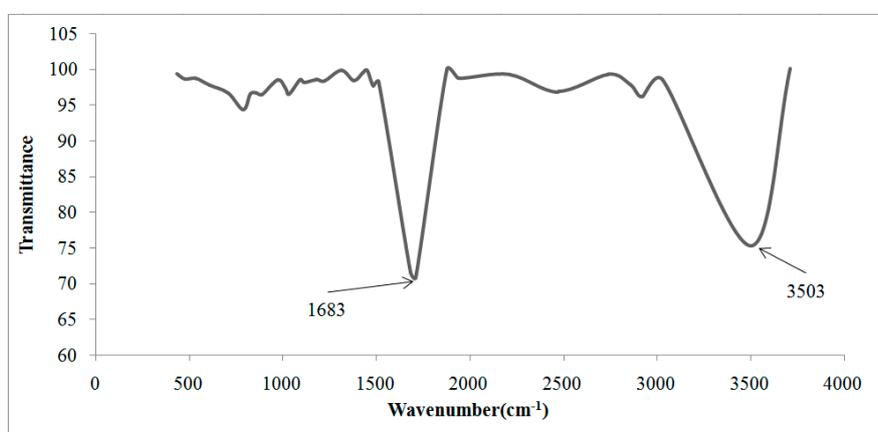
Figure 5. Infrared spectrum from the mixture of resins after Fenton's treatment.

It has been suggested [6] that the degradation of anionic and mixed resins is much harder to achieve than cationic resins and the reasons were presented by the authors.

Spectrum analysis was performed and identification of groups and chemical bonds are shown in Table 4.

Table 4. Summarized infrared spectrum analysis of the cationic and anionic resins without treatment and the residual resins after Fenton's oxidation.

Cationic without Treatment	Anionic without Treatment	Residual Resins (Cationic and Anionic Resins)	Attribution
3463 S	3494 S	3503 S	O–H water
2848 m	2850 m	-	Stretch C–H from alkanes
-	-	1683 S	Carboxylate ions
1637 S	1640 w	-	Stretch of the benzene rings from water hydration
-	1598 w	-	Bond N–H
-	1370 m	-	N–CH$_3$ of quaternaries amine
1220 S, 1126 S, 1040 S and 679 S	-	-	Sulfonic acid
-	1176 m	-	C–N from aliphatic quaternary amines
1126 Sh 1040 S, 1007 S	-	-	SO$_3$ symmetric stretch
-	1122 S 1092 S	-	Aliphatic amines (usually they are shown in double peaks)

"S" = strong, "m" = medium, "w" = weak, and "h" = high.

The main components of the cationic and anionic resins were identified, as the organic compounds of sulfur, found as sulfonic acid at 1220 cm^{-1}, 1126 cm^{-1}, 1040 cm^{-1}, and 679 cm^{-1}, with strong intensity. The amines (from the anionic resins) were identified on the quaternary amine N–CH$_3$ bond at 1370 cm^{-1}, 1176 cm^{-1} and the C–N bond, also on quaternary amines, from the N–H bond at 1598 cm^{-1} with strong intensity. This method was chosen because it is one of the most practical ways of showing that the residual resins may contain a large amount of carboxyl functionality. However, carboxyl groups are known to be very reactive with hydroxyl radicals produced by the Fenton reaction. The analysis of the residual resin (after Fenton's reaction) showed the characteristic peak of the O–H bond at 3503 cm^{-1}, besides the strong presence of carboxylate ion at 1683 cm^{-1}, because the oxalic and the formic acids could have been formed during the reaction. According to the literature [4], the production of these acids is a qualitative parameter to verify the degradation of aliphatic and aromatic rings, respectively. This result can be directly compared to that obtained in the TOC content analysis. FTIR indicated that most of the groups identified in the spectra of the individual resins disappeared after Fenton treatment. These groups in solution may have degraded until transformed into CO$_2$ and water, while the remaining solid had organic acids. The presence of these organic acids resulted in the presence of carbon contents in the TOC analyzes at the end of the experiments. Remaining non-degraded resins would be easily mineralized since these organic acids are little resistant to the attack of hydroxyl radicals. Further data collection would be needed to determine the organic compounds, since IR-spectroscopy alone is not a definitive means to identify such compounds.

3.2. Immobilization with Portland Cement

Cement specimens were prepared with different suspension/cement (s/c) ratios in order to establish the appropriate ratio. The s/c ratios were 0.28, 0.30 and 0.35 s/c. The 0.30 and 0.35 ratios were considered inadequate, since a volume of segregated water of more than 0.5% of the total was observed after 24 h. These values were above the limit established by Brazilian regulations [16]. As a result, the s/c ratio of 0.28 was selected for studies of the specimens at different pH. Good workability during the molds and no segregation were observed for all mixtures before the final setting time. Table 5 shows the setting time and the axial compressive strength for different pH.

Table 5. Setting time and axial compressive strength in hours.

pH	Setting Time (hours)	Axial Compressive Strength (MPa) *
Acid	8	16 ± 1
Neutral	5	8 ± 2
Basic	6	8 ± 1

Specimens reference: 23 ± 3 MPa; * $\overline{x} \pm S$ (Mean $\pm$ Standard deviation).

All specimens reached the setting time of up to 8 h and this is sufficient for an industrial scale mixing [19]. A review of the literature on this matter [20,21] indicated that different types of cement were applied to immobilize the spent resins. In [20], the authors employed slag cement, and the compressive strength of the solidified final wastes was greater than 7.35 MPa. On the other hand, [21] applied sulfoaluminate cement, and the results showed a great compressive strength, 20 ± 2 MPa.

In this study, the acidic solutions presented the highest axial compressive strength (Table 5). Furthermore, these specimens would be the only ones accepted by the Brazilian regulations [22], since the minimum value is established at 10 MPa. This result can be explained by the high concentration of sulfate available in the acid suspensions and precipitated in the neutral and basic forms.

According to [23], the sulfate reacts with the calcium aluminate to form ettringite (Ca$_6$Al$_2$(SO$_4$)$_3$(OH)$_{12}$·26H$_2$O). The ettringite fills the pores of the cemented material, increasing its volume and resistance. In addition, the reaction occurs during the hydration of the cement and the ettringite undergoes decomposition generating monosulphaluminate. The monosulphaluminate is generated after the entire sulfate use [21]. Consequently, the high concentration of sulfate ions in

the acid solution may have prevented this conversion, resulting in a product with higher resistance. The sulfate is added in all commercial cement as gypsium ($CaSO_4$) and aims to delay the setting time and allow the workability. The absence of gypsium causes the cement to harden almost instantly in contact with water [19]. Therefore, increasing the sulfate concentration in acid suspensions also resulted in an increase in the setting time.

Part of the remaining suspensions of resin degradation was evaporated and concentrated to 40% solids content. The axial compression strength was measured after 3 days of cure, resulting in 9 ± 1 (MPa), similar to the minimum permitted in the regulation, 10 MPa [22]. It is known that cement hydration is a process that occurs as a function of time and interferes in mechanical resistance. Therefore, it is possible that these values, after 28 days, are superior to those permitted in regulation. Finally, further work is required to evaluate sulfate resistant cement in the immobilization process. Moreover, a kinetic study is necessary, which can be used for process optimization and scale-up.

4. Conclusions

The degradation of ion exchange resins by the Fenton's reagent was evaluated. Residual resin mass, different catalyst concentrations, dissolved oxygen, total organic carbon content, temperature, functional groups analysis, and the immobilization load of the final suspension were the evaluated parameters and the conclusions are:

- The catalyst concentration interferes in oxidation reaction. Concentrations of 50 and 100 mmol L^{-1} were more effective than those of 25 and 150 mmol L^{-1}. However, the 50 mmol L^{-1} was the most efficient, since less catalyst is required compared to that of 100 mmol L^{-1} to treat 10 g of resin.
- It was possible to degrade resins efficiently without external heating. The temperature of 60 °C was the most adequate.
- As predicted, TOC was efficient as a reaction parameter to determine resin degradation rates.
- The suspension/cement ratio of 0.28 was suitable to produce an immobilized product, which comply with the limits established by Brazilian regulation.
- The evaluated degradation processes and the evaporation allowed the incorporation of a mass three-fold higher when compared with direct immobilization.

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