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Management of Spent Organic Ion-Exchange Resins by Photochemical Oxidation

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ABSTRACT

Management of spent ion-exchange resin waste arising from nuclear reactor operations by traditional practice of encapsulation in cement is associated with problems such as swelling and disintegration. Complete oxidation (mineralization) is an attractive alternative option. This paper reports the development of photochemical mineralization process for organic ion-exchange resins of poly (styrene-divinyl benzene) type with sulfonic acid and quaternary ammonium functional groups. It is a two-step process consisting of dissolution (conversion of solid resin into water-soluble reaction products) and photo-Fenton mineralization of the dissolved resin.

Cation and anion resin dissolution was effected by reaction of the resin with H_2O_2 at 50-60°C in the presence of ferrous/copper sulphate catalyst. Direct dissolution of mixed resin was not efficient. However, the cation resin portion in the mixed resin could be selectively dissolved without affecting the anion portion. The solid anion resin after separation from the cation resin solution could be dissolved. About 0.5 litres of 50% H_2O_2 was required for dissolution of one kg of wet resin. The reaction time was 4-5 hours. Dissolution experiments were conducted on upto 8 litres of wet resin.

The second step, viz., photo-Fenton mineralization of the dissolved resin was effected at ambient temperature(25-35°C). Kinetic results of laboratory scale experiments in immersion type photo-reactor and pilot scale experiments in tubular flow photo-reactor were presented. These results clearly demonstrated the photo-Fenton mineralization of dissolved resin at ambient temperature with stoichiometric quantity of H_2O_2 as against 70-200% excess H_2O_2 requirement in chemical mineralization experiments under Fenton oxidation conditions at 90-95°C. Based on these studies, a treatment scheme was developed and presented in this paper.

INTRODUCTION

Ion-exchange resins of poly (styrene-divinyl benzene) type with sulfonic acid and quaternary ammonium functional groups are widely used in nuclear reactor operations. These are used, for example, in primary heat transport and moderator circuits for removal of radioactive and other ionic impurities from water. After their useful life, they are discarded as organic radioactive waste for further treatment and disposal. Annual generation and characteristics of these spent resins generated during the operation of a typical 235 MW reactor are given in Table-1(Ref.1).

Table 1. Annual Generation and Characteristics of Spent Resins from 2 x 235 MWe Pressurized Heavy Water Reactor (PHWR) in India

Purification system	Average spent resin generation rate per annum (m ³)	Radionuclides present
Moderator	5.5	Mn-54 and 56, Fe-59, Co-60
Primary Heat Transport system	2.6	I-131, Cs-134 and 137
Spent fuel storage bay	1.5	Cs-134 and 137

Management of spent resin by traditional method of immobilization in cement is associated with problems such as setting, swelling and disintegration (Ref.2). Complete oxidation (mineralization) is an attractive treatment option as it converts the unstable organic waste into a chemically inert inorganic waste which is amenable to conventional waste management practices.

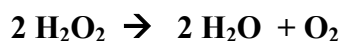
Incineration, the classical high temperature mineralization process, requires complex off-gas treatment when applied to ion exchange resins. This is on account of the release of corrosive and toxic gaseous reaction products, viz., NO_x and SO₂ and carry-over of radioactive material into the off-gas (Ref. 3)

Bio-mineralization is also made complicated by the fact that these synthetic resins are not biodegradable by naturally available microorganisms (Ref. 4)

In recent years, advanced oxidation processes are emerging as promising alternatives for mineralization of non-incinerable and non-biodegradable organic wastes, particularly toxic organic micro-pollutants in wastewaters from different chemical industries (Ref. 5). They are eco-friendly processes operating at low temperature and pressures employing clean oxidants such as ozone and hydrogen peroxide.

Among various advanced oxidation processes, those employing H₂O₂ have the potential for application to solid organic wastes such as ion-exchange resins. This is on account of the availability of H₂O₂ in high concentrations (35-50%) and its high solubility in water.

Initial studies in our laboratory as well those from others showed that it is possible to mineralize the resins by Fenton-type chemical oxidation with H₂O₂ at 90-95°C. However, the process is found to be inefficient with regard to H₂O₂ requirement which is 70-200% excess of the stoichiometric level. This is due to the wasteful self-decomposition of H₂O₂ in the following way:



Excess consumption of H₂O₂ leads to generation of large quantities of radioactive aqueous solutions which is also undesirable.

Fenton reaction requires higher temperatures for achieving reasonable reaction rates for mineralization of concentrated organic wastes. Photo-activation of Fenton reaction, however, offers the possibility of room temperature mineralization reaction. Lower temperature operation, additionally, enhances, process safety and simplicity. This reaction is widely studied for mineralization of organic micro-pollutants in waste waters (Ref. 6).

The present work is related to the development of photo-Fenton mineralization process for resins used in nuclear reactors. The developmental studies led to a two step process consisting of dissolution (conversion of water-insoluble solid resin into water-soluble degradation reaction products) and photo-Fenton mineralization reaction. Results and discussion of these studies form the content of the paper.

MATERIALS

Gel type cation resin in sulfonic acid form and anion resin in chloride/hydroxide form with poly(styrene-divinyl benzene) as the base polymer matrix was procured from Thermax (India) Ltd., Pune in bead form. Mesh size was in the range -20+50. They were of nuclear grade. Cross-linking was about 8%. The resins were used in the experiments after washing thoroughly with water followed by air-drying. Other chemicals were analytical reagent grade and used as received.

EXPERIMENTAL METHOD

Moisture content of the cation and anion resins was determined by weight loss measurement of an aliquot sample at an oven temperature of 108°C and 60°C respectively for 15 hours. Ion-exchange capacity of the resins was determined by the standard method of estimation of the consumption of alkali or acid by a given amount of the resin under batch conditions (Ref. 7).

Carbon content of the resin and stoichiometric requirement of H₂O₂ for complete oxidation of resin are necessary for monitoring the reaction kinetics and the efficiency of the reaction conditions respectively. They were determined by using an apparatus and method recommended by APHA for determining chemical oxygen demand (COD) of organic samples by open reflux method (Ref. 8). In this method, the organic matter in an aliquot sample of resin was completely oxidized at 150°C by potassium dichromate in H₂SO₄ medium in the presence of silver salt catalyst to produce CO₂ and water. Stoichiometric oxidant requirement in the reaction was estimated by determining the excess dichromate oxidant in the reaction mixture by titration with standard ferrous ammonium sulphate. CO₂ evolved during dichromate oxidation was absorbed in NaOH scrubber and the carbonate formed in the absorption reaction was estimated volumetrically (Ref. 7). From this estimate, the carbon content of the resin was calculated.

Total organic carbon (TOC) and COD were determined for monitoring the progress of the oxidation reaction. TOC was determined by acidic persulfate digestion at 100°C (8). COD was determined by colorimetric closed reflux method (Ref. 8) using E.Merk Thermoreactor model TR 200 for digestion and photometer model SQ 118.

Absorption spectra were recorded using GBC UV-visible spectrophotometer model Cintra 40.

H₂O₂ content of stock solution and experimental samples was determined by using cerimetric titration method (Ref. 7). This method is reported to be more suitable for organic-containing H₂O₂ samples.

Resin dissolution experiments were conducted in multi-neck round bottom glass flasks varying from 1000 ml to 20 litre volume. These flasks were equipped with reflux condensers, thermocouples, magnetic/mechanical agitator for mixing purposes. Known weight of resin was mixed with water and solid catalyst in the reaction flask and heated under reflux at the desired temperature with constant stirring of the reaction mixture. The temperature of the reaction mixture was controlled by placing the reaction flask in constant temperature water bath or mantle heater equipped with heat regulator. H₂O₂ was introduced into the reaction mixture at the desired rate using peristaltic pump.

Laboratory scale photochemical experiments were conducted in batch immersion type photoreactor (Ref. 9). It consisted of double-walled quartz well to accommodate the light source. The quartz well is immersed in the reaction solution contained in a glass container of suitable size and geometry. The temperature in all laboratory photochemical experiments was maintained at ambient condition by keeping the photoreactor assembly in water bath at 25°–35°C. High pressure or medium pressure mercury vapour lamp of 200 to 400 W electrical powers was used as light source. Water was continuously circulated through the annular space of the quartz well during irradiation for dissipating the heat generated by the lamp.

Pilot scale photochemical experiments were conducted in tubular flow type photo reactor developed in house. It consisted of transparent Teflon tube of four metres long and 25 mm O.D. The light source was poly chromatic emitting in the wavelength region 180-600 nm. The experiments were conducted in recirculatory mode. Fig.1 shows the photograph of the reactor system.



Fig. 1. Tubular Flow Photochemical Reactor system

RESULTS AND DISCUSSION

Table-2 gives the carbon content, moisture content and H_2O_2 stoichiometric requirement for complete oxidation of the resin.

Table 2. Characteristics of air-dried resins used in the experiments

No.	Property	Unit	Cation resin	Anion resin
1	Carbon content	% wt	38	44
2.	Stoichiometric requirement of 35% (w/v) H_2O_2 for complete oxidation	ml/g	7.9	9.6
3	Ion-exchange capacity	meq/g	3.5	2.3
4	Water content of resin	%wt	31	37

Resin dissolution experiments

The resins under investigation are negligibly soluble in water on account of the cross-linking by divinyl benzene in the polymer. Therefore, it is reasonable to expect that dissolution of the resin can be effected by degrading the cross-linking portion.

Initial work in our laboratory (Ref. 10) and studies from other laboratories (Ref. 11) on the catalytic H_2O_2 oxidation of cation resin showed that the reaction progressed in two distinct stages: complete dissolution of the resin in aqueous medium and eventual mineralization of the dissolved resin. This phenomenon was attributed to the action of OH radicals in breaking the cross-linking network (Ref. 12). It was decided to use this

chemical method of dissolution in these experiments. The dissolution reaction can be represented as follows:



Though the exact stoichiometry of this reaction is not known due to its complex nature, it appears that H₂O₂ requirement can be approximately estimated from the degree of cross-linking. This consideration led to an estimate of less than one litre of 50% H₂O₂ for dissolution of one kg of air-dried resin. This was used as a guideline for comparison of different experimental conditions.

Preliminary experiments showed that uncatalysed dissolution was not practically feasible. It was found that Fenton-type catalysts, viz., copper and ferrous sulphate were effective for dissolution reaction. Possible parallel reactions during dissolution include:

1. Dissolution of the resin
2. Oxidation of the dissolved resin
3. Self-decomposition of H₂O₂ to O₂

Reaction conditions were identified in order to minimize secondary reactions. Experiments at ambient temperature showed that cation resin dissolution was possible in 10-24 hours depending on the catalyst and H₂O₂ concentration. Results of these experiments were shown in Tables 3 and 4.

Table 3. Kinetics of cation resin dissolution*

Reaction Time	Temperature (°C)	(C/C ₀)**	Observations
Start of reaction	29	1	Solution was colourless
After 3 hours	32	0.9	Solution was colourless
After 6 hours	33	0.9	Aqueous solution was light yellow; bulk of the resin was present
After 24 hours	29	0.83	Solution is light yellow; resin was present
After 31 hours	29	0.83	Solution is dark; some resin seen
After 40 hours	29	0.65	Solution was dark; some resin seen
After 48 hours	29	0.5	Resin completely dissolved

* The reaction mixture consisted of 4 g of resin, 100 ml of 11% H₂O₂

**Ratio of hydrogen peroxide concentration at a given time to its initial concentration

Table 4. Kinetics of cation resin dissolution in 35% H₂O₂

Catalyst quantity	Temperature (°C)	Observations and comments
10 mg (333 ppm)	29	No significant change in 3 days
	50-55	No significant change in 7 hours
	80	Resin swelled and dissolved in 3 to 4 minutes accompanied by

		vigorous effervescence and rapid increase of temperature to 100°C in 2 to 3 minutes; 80% of hydrogen peroxide decomposed. The conditions, therefore, led to runaway reaction.
60 mg (2000 ppm)	29	No change observed even after 3 days
120 mg (4000 ppm)	29	In 24 hours, the resin dissolved and dark solution was obtained.
360 mg (12,000 ppm)	29-35	Complete dissolution in 10 hours

Anion resin dissolution at room temperature was not successful. H₂O₂ decomposed completely without affecting the resin. On the other extreme, experiments at near boiling conditions (90-95°C) were partially successful. Results were shown in Table-5.

Table-5 shows that varying quantities of undissolved resin resulted depending on its nature. In case of cation resin, the undissolved resin could be dissolved by further addition of H₂O₂. However, in the case of undissolved resin arising from anion and mixed resin reaction, further addition of oxidant did not effect the desired dissolution. This could be on account of the fact that functional group of anion resin dissociates more easily at higher temperature rendering the polymer backbone hydrophobic.

Table 5. Dissolution experiments at 95-100°C

Run no.	Resin type	Dry Resin wt (g)	Additives	H ₂ O ₂ (ml)	Reaction time (hr)	Temp range (°C)	Volume of unreacted resin (ml)
1	Cationic	1000	CuSO ₄ : 12.5 g Free Water : 1000 ml	1000	2.0	95-100	240
2	Anionic	1000	CuSO ₄ : 12.5 g Free Water : 1000 ml	1000	4.0	95-100	700
3	Cationic – 30% Anionic – 70%	1000	CuSO ₄ : 12.5 g Free Water : 1000 ml	1000	5.0	95-100	400
4	Cationic – 30% Anionic – 70%	1000	CuSO ₄ : 12.5 g Free Water : 1000 ml	2900	5.0	95-100	450
5	Cationic – 30% Anionic – 70%	2000	CuSO ₄ : 25 g Free water : 500 ml	5300	5.0	95 -100	860

The dissolution reaction when conducted at 50-60°C and at catalyst concentration of 0.01M led to clean and complete dissolution of cation resin. One kg of resin required 0.5 litres of 50% H₂O₂ for dissolution. Complete dissolution of anion resin required that it should be in chloride form. Hydroxide form of the resin was resistant to dissolution. This

could be on account of the catalytic action of hydroxide ion on the self-decomposition reaction of H₂O₂. It was observed that decomposition of hydroxide form of the resin with H₂O₂ led to decomposition of H₂O₂ even at room temperature. It became quite vigorous as the temperature of the reaction mixture was raised leading to almost instantaneous decomposition of H₂O₂. On the other hand, reaction with chloride form was similar to that of cation resin, being steady and under control. It was decided to use chloride form as it was found convenient to handle. Nitrate and sulphate forms of anion resin could not be dissolved under these conditions.

Dissolution experiments at 50-60°C were conducted upto 4 kg of dry resin. Temperature control and adequate mixing lead to successful dissolution. The resin dissolution reaction progressively led to increase in viscosity, swelling of the resin and its eventual dissolution. Silicone-based anti-foam reagent was added to suppress foam if formed. Catalyst concentration in millimolar range was found to be suitable for dissolution reaction. Dissolution of one litre of resin resulted in nearly two litres of solution. The reaction time was 4-5 hours. One kg of resin required about 0.5 litres of 50% hydrogen peroxide.

Photo-Fenton Mineralization of dissolved resin

Photochemical methods of mineralization are emerging as promising technologies for organic micro-pollutants in waste waters arising from chemical industries. Some of these methods are:

- UV- hydrogen peroxide photolysis
- UV- ozone photolysis
- TiO₂- photocatalysis
- Photo-Fenton reaction

UV-H₂O₂ and photo-Fenton reactions have the advantage of operating under homogeneous reaction conditions. Moreover, availability of H₂O₂ in high concentration and its high solubility in water makes these methods ideally suited to concentrated organic waste solutions. In view of these considerations, the UV-H₂O₂ method was initially investigated on cation resin solutions using medium and high-pressure Hg vapour lamps of 200/400W. Results were shown in Table-6.

Table 6. Photochemical oxidation of cation resin solution*

Reaction time(hours)	Temperature(°C)	Fraction of H ₂ O ₂ unreacted	Observations
0	24	1	Beginning of irradiation
0.5	30	1	Solution was yellow in colour; gentle effervescence
1	32	1	
1.5	32	0.9	
2	32	0.9	
3	32	0.87	
4	32	0.84	Solution was yellow in colour

*Hydrogen peroxide: 2.9M; 200W high-pressure lamp irradiation at room temperature

The monotonous decrease in H₂O₂ concentration shows that the reaction under the test conditions is very slow. This could be attributed to the nature of the absorption spectrum of the dissolved resin (Fig.2). Intense absorption band around 253.7 nm region, possibly, on account of the presence of aromatic substrates in the reaction mixture is observed.

The UV- H₂O₂ method depends on the photolysis of H₂O₂ by light of this energy to give the highly reactive OH radicals which initiate the oxidative degradation process (Ref. 13). The photolysis reaction is as follows:



Molecular absorption co-efficient at 253.7 nm is only 14.7molar⁻¹cm⁻¹. The inner-filter effect of the aromatic species and the low absorption coefficient in the active wavelength region are, perhaps, responsible for the slow progress of the reaction in this system.

These considerations led to the selection of photo-Fenton reaction for mineralization. Fenton reagent (mixture of ferrous ion and H₂O₂) is a convenient room-temperature source of OH radicals (Ref. 14), the key intermediates in photochemical and other advanced oxidation processes. The governing equation for the generation of OH radicals in Fenton reaction is as follows:



The rate constant of this reaction is 75 molar⁻¹sec⁻¹ at 20°C with low energy of activation of about 9 kcal/mol. However, OH radical generation by Fenton reaction requires that ferrous ion is used in stoichiometric quantities since ferrous ion is not a catalyst in the reaction. The photo-Fenton reaction facilitates the sustenance of this fast Fenton reaction conditions at room temperature by creating favourable conditions for the photo-reductive regeneration of ferrous ion in the medium (Ref. 6). In the light of these considerations, photo-Fenton reaction was studied in detail for dissolved resin mineralization. Initial TOC of the dissolved resin was 30-35 g/l and the catalyst concentration was 0.01M. Results of kinetic experiments on cation and anion resin solutions are given in Fig.3.

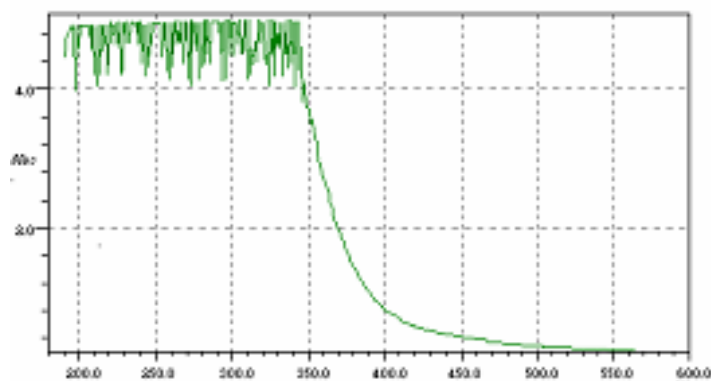


Fig. 2 Dissolved cation absorption spectrum

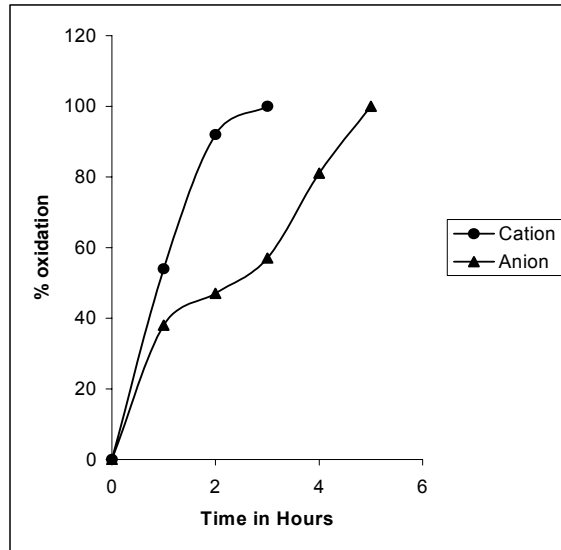


Fig. 3 Photo-Fenton mineralization of IX resins at 30°C

Fig. 4 provides the kinetic results obtained in chemical oxidation experiments under Fenton conditions at 90-95°C.

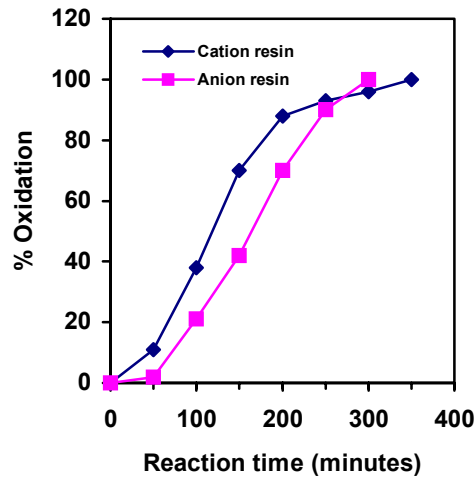


Fig. 4 Chemical oxidation of IX resins under Fenton conditions at 90-95°C

These laboratory results clearly show that the photo-Fenton mineralization of the dissolved resin is feasible at room temperature at comparable reaction rate. Mineralization occurred with stoichiometric quantity of the oxidant. In chemical mode of the reaction, on the other hand, 70-200% excess of the oxidant was used for

mineralization (10, 11). This is on account of the wasteful self-decomposition of hydrogen peroxide at 90-95°C. Copper sulphate was not effective in the photo-Fenton mineralization.

Based on these laboratory studies, photo-Fenton experiments were conducted upto 20 litres in tubular-flow type photoreactor using light source consisting of a combination of uv and visible light sources (400W) instead of the high pressure Hg vapour lamp. The mercury lamp has low radiant power efficiency (less than 50%) (9). Lot of heat is generated during lamp operation requiring adequate cooling. This reactor completely avoided the need for continuous cooling of the light source and allowed continuous and uninterrupted operation for several hours. Results of the experiments in this reactor were shown in Table-7.

Table 7. Mineralization experiments in Tubular flow photo-reactor

Cation resin solution Volume	12.5 L
50% H ₂ O ₂ added	1.0 L
Reaction temperature	25-35°C
Reaction time	3.3 hours
Initial COD	11.0 g/L
Final COD	1.1 g/L

Aqueous radioactive waste arising from mineralization is amenable to conventional nuclear waste management practices. Work carried out in our laboratory showed that a decontamination factor of >1000 could be achieved for mineralized resin solution by chemical precipitation (Ref. 15). Alternatively, the mineralized resin solution can be decontaminated using selective zeolite type inorganic exchangers which can subsequently be vitrified.

CONCLUSIONS

The experimental studies led to the development of a two-step process for complete oxidation (mineralization) of poly (styrene-divinyl benzene) type ion-exchange resins which are widely used in nuclear reactors. The process consists of dissolution (conversion of water-insoluble resin into water-soluble degradation reaction products) step and photo-Fenton mineralization step. Dissolution was achieved at 50-60°C in 4-5 hours by reaction of the resin with hydrogen peroxide in the presence of copper or ferrous sulphate catalyst. The photo-Fenton mineralization of the dissolved resin was effected at ambient temperature. This process avoided the undesirable excess requirement of hydrogen peroxide and allowed the reaction to be conducted at moderate temperature. The experiments were conducted upto 20 litres of dissolved resin solution in tubular flow photo-reactor.

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