**Resin Treatment Using Fenton Like Process With Cu Catalysis**

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## 1. Introduction

Ion exchange resins are playing a vital role in nuclear industry since the commercialization of Nuclear power Plants. Polystyrene divinyl benzene having sulphonic acid functional group (i.e. Amberlite INR-77 called strongly acidic resin) is used for the removal of cationic contaminants, while Polystyrene divinyl benzene possessing quaternary amine as functional group (Amberlite INR-78 called strongly basic resins) are deployed for the capturing of anionic contaminants from water used in primary heat transport and moderator circuits of nuclear power plants. Once completing their useful life, they are discarded as organic radioactive waste and known as spent ion exchange resins[1, 2]. Among other resin treatment techniques, Fenton/Fenton like oxidation process is superior technique in term of the volume/weight reduction of spent ion exchange resins. In addition, the final product of residues possessing radionuclide can easily be incorporated in stable solid matrix.

The objective of this study was to perform homogeneous Fenton like treatment using Cu as catalyst for reducing the weight of spent nuclear grade mixed Hydrogen/Hydroxide form ion exchange resin, and study the effect of Cu concentration on the efficiency of weight reduction and mineralization of the spent ion exchange resin.

## 2. Experimental

### *2.1 Material and Chemicals*

All the experiments in this study were conducted under non-radioactive conditions. The IER used in this study is nuclear grade Hydrogen/Hydroxide form mixed bed Gravex GR 3-16 N Resin, product of Graver Technology USA. General physical and chemical properties of resin are shown in Table 1. All reagents including hydrogen peroxide (30% (V/V water), catalyst CuSO4·5H2O, H2SO4, and Ca (OH) 2 used in this study are equivalent to analytical grade.

### *2.2 Experimental Setup and Methods*

Experiments were performed in a 500 mL, three necked round bottom flask with a magnetic stirrer. The reactor was immersed in oil bath placed on hotplate. Temperature of reaction mixture was kept constant at $90+3^0$C for all the experiment. Catalysts pH was adjusted around 2.80 using dilute $H_2SO_4$. Fresh Gravex GR 3-16 N 10 (g) was inserted in reactor and hydrogen peroxide and catalyst CuSO4 were added using dual channel peristaltic pump with flow rate of 0.75 mL/min and 0.375 mL/min, respectively. After 2 hrs the reaction was stopped and the final pH of the solution was recorded.

Table 1. Properties of Each Resin Mixed in GR3-16N

| Properties | Cationic (GR2-0NG) | Anionic (GR1-9NG) |
|---|---|---|
| Ionic form | $H^+$ | $OH^-$ |
| Functional group | $-SO_3H$ | $-CH_2N(CH_3)_3OH$ |
| Exchange capacity | 2.4 eq/L | 1.2 eq/L |
| Average Particle size | 1.188 mm | 1.188 mm |
| Mixing Volume ratio | 1 | 2 |
| Moisture % | 36-42% | 53-59% |
| Average Moisture of GR 3-16 N Resin | 47% | |
| Metals, Dry resin basis ppm max (Na, Fe, Cu, Pb, Al, Ca, Mg, K ,Zn, SiO2 =50 ppm) | | |

### *2.3 Fenton /Fenton like Process*

Use of $Fe^{2+}$ as catalyst and $H_2O_2$ as oxidant is called Fenton reagent and reaction is known Fenton reaction. However, term Fenton like process is often used when non-ferrous metals such as Cu, Co, Ru, or Mn are used as catalyst. The Fenton process comprises the production of Hydroxyl radical ($OH^·$) by the reaction of transition metals (mainly Fe/Cu) with hydrogen peroxide $H_2O_2$ as oxidant. Production of $OH^•$ is described in Eq. (1)

$$Fe/Cu^{(n-1)} + H_2O_2 \rightarrow Fe/Cu^{(n+)} + OH^- + OH^• \quad (1)$$

Attack of $OH^•$ On ion exchange resin (IER) initiates through free radical generation mechanism which converts complex structure to simple substrate and finally into $CO_2$ and $H_2O$ as shown in Eq. (2) & (3).

$$OH^• + \text{Mixed IER} \rightarrow \text{linear Polystyrene} \quad (2)$$

$$OH^• + \text{Linear Polystyrene} \rightarrow CO_2 + SO_4^{2-}/NH_4^+ + H_2O \quad (3)$$

Both monovalent ($Cu^+$) and divalent ($Cu^{2+}$) react with hydrogen peroxide to produce $OH^•$ Moreover Cu shows better catalytic activities in broad pH range from acidic to neutral conditions.

*2.4 Extent of mineralization*

The weight of CaCO3 (mg) produced by reaction between captured gaseous CO2 and saturated Ca (OH) 2 solution was applied for assessing the amount of mineralization. Final product of CaCO3(s) was filtered using 0.45 μm Whatman nylon membrane filter paper of diameter 47 mm and dried at 700C for 24 hrs inside an oven.

*2.5 Weight Reduction of Resin*

Weight reduction (%) of Gravex GR 3-16 N Resin was calculated after vacuum filtration and 72 hrs drying at 1050C in vacuum oven. Weight reduction formula is as shown in Eq. (4)

$$\%\ Weight\ Reduction = \frac{W0 - Wi}{W0} * 100 \qquad (4)$$

Where $W_0$ is weight of fresh dry resin corrected using average moisture content; $W_i$ is weight of residue after vacuum oven drying. Weight of catalyst was ignored for weight reduction calculation.

## 3. Results and Discussion

*3.1 Effect of Catalyst concentration on weight Reduction*

Different concentrations of CuSO4.5H20 30 mM to 400 mM after adjusting their pH at 2.80 were used to study the effect of percentage weight reduction of fresh Gravex GR 3-16 N Resin upon Fenton like treatment. Up to 250 mM catalyst solution directly increases the weight reduction by Fenton like reaction. It indicates that with the increment of Cu ions concentration enhances the production of $OH^{\bullet}$ (Hydroxyl radical) which ultimately increases degradation of Mixed Resin as shown in Fig 1. However, when the concentration of catalyst solution increased above 250 mM to 400 mM, resin degradation were not increased further, but it started decreasing weight reduction after Fenton Treatment because of scavenging effect produced by Free radicals during reaction.

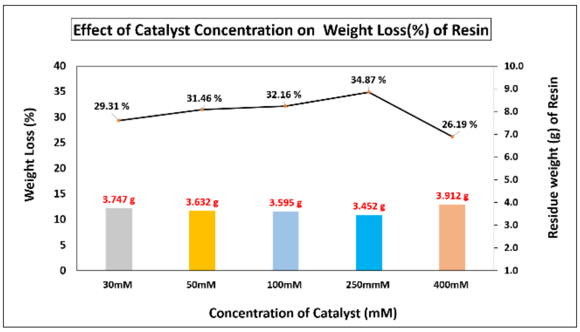


Fig. 1. Effect of Catalyst Concentration on weight reduction of resin.

*3.2 Amount of $CaCO_3$ as indicator for mineralization*

Weight (mg) of $CaCO_3$ precipitated after oxidative degradation during reactions is an indicator of mineralization of organic compound. Results indicates that % weight reduction and amount of $CaCO_3$ are directly related as shown in Table 2.

Table 2. Weight of $CaCO_3$ as Indicator of Mineralization

| Catalyst $CusO_4$ mM | Final pH | $CaCO_3$ (mg) | Weight Reduction (%) |
|---|---|---|---|
| 30 | 2.94 | 306 | 29.31 |
| 50 | 2.88 | 391 | 31.46 |
| 100 | 2.92 | 538 | 32.16 |
| 250 | 3.01 | 588 | 34.87 |
| 400 | 1.92 | 417 | 26.19 |

## 4. Conclusion

Fenton like decompossition of mixed ion exchnage resin was optimized using $Cu^{2+}$ as catalyst. The experimental results indicated that maximum 35% of weight reduction and about 588 mg of $CaCO_3$ mineralization was achieved by using 250mM $CuSO_4.5H_2O$ as catalyst and 30% (v/v water) as oxidant. Final products of such reactions are useful for the development of solidification techniques applied for the management of problematic spent resin wastes.

## REFERENCES

[1] Park, S.-C., et al., "A Study On Adsorption And Desorption Behaviors Of 14c From A Mixed Bed Resin". Nuclear Engineering and Technology, 46(6), 847-856 (2014).
[2] Wang, J. and Z. Wan, "Treatment and disposal of spent radioactive ion-exchange resins produced in the nuclear industry". Progress in Nuclear Energy, 78, 47-55 (2015).