ABSTRACT

Coagulation-flocculation, membrane separation and ion-exchange are traditional methods for treatment of radioactive wastewater generated primarily from the front end processes of the fuel cycle. Electrocoagulation presents a robust and novel alternative to conventional coagulation process. The present study involves the establishment of electrocoagulation as a treatment process for thorium bearing non-process effluents in batch mode. This involved an electrolytic reactor with iron electrodes. The non-process effluent was subjected to coagulation and floatation by Fe(II) ions dissolved from the anode with the resultant flocs floating on the surface after being captured by hydrogen gas bubbles generated at the cathode. The effect of various operational parameters like initial pH, residence time, current density and initial thorium concentration on the removal efficiency was investigated. Maximum decontamination factor obtained was of the order of $10^4$.

Keywords: Electrocoagulation, Electrofloatation, Sacrificial electrode, Thorium, Wastewater treatment

INTRODUCTION

Indigenously designed Advanced Heavy Water Reactor (AHWR–LEU) utilises thorium and LEU in the form of (Th-LEU)O$_2$ MOX as fuel$^{[1]}$. In this view, the issues related to the treatment and management of thorium bearing effluent arising from the front end of the cycle i.e. fuel fabrication, reject recycle, non-process effluent etc. are required to be addressed. Since Hyderabad is a land locked area, treatment and containment of the effluent are critical before it can be disposed to public domain as per the directives of the regulatory authority. The biological half-life of thorium is greater than uranium and also the daughter products of thorium decay like $^{228}$Ac and $^{208}$Tl are more radioactive as compared to uranium decay products. Hence, more stringent measures are to be followed in case of thorium bearing effluent treatment and disposal.

Electrocoagulation is emerging as the most sought after treatment technique in treatment of waste water primarily arising from tannery and textile industries. It is already being widely used in removal of heavy metals like arsenic, cadmium etc. Inspite of its vast deployment in other areas, electrocoagulation has not been used in the treatment of low level radioactive waste. The most common methods being used presently for treatment of low level radioactive waste are chemical treatment, membrane separation and ion-exchange.

Sinha et al. demonstrated that co-precipitation process involving calcium phosphate and cerium oxalate may be used for the separation and removal of thorium from the effluents$^{[2]}$. Removal of thorium from nitrate medium by Ammonium Molybdophosphate (AMP) was studied by Ali et al$^{[3]}$. AMP is an inorganic ion-exchanger having high affinity for thorium and was used in its separation from uranium. The efficiency of chemical treatment is sensitive to the counter ions present in the effluent whereas membrane separation is not suitable for effluents having high dissolved salt content. On the other hand, ion-exchange generates secondary effluents whose disposal is a concern. These disadvantages of the conventional methods compel the use of

Thorium exists in various forms depending upon the pH of the aqueous solution. Below pH 3 the hydrolysis of Th$^{4+}$ is negligible. Beyond pH 3.5, thorium exists in monomeric hydroxides like Th(OH)$_2$$^{2+}$,
Th(OH)$_3$ etc. or polymeric complexes like Th$_2$(OH)$_2$$^{6+}$, Th$_4$(OH)$_8$$^{8+}$, Th$_6$(OH)$_{15}$$^{9+}$ etc. [4]. At pH around 8, thorium exists predominantly in suspended form as Th(OH)$_4$$^0$.

![Figure 1 Speciation of Thorium in Water as a function of pH](image)

**FUNDAMENTALS OF ELECTROCOAGULATION**

**Principle**

Electrocoagulation is an electrochemical technique, in which a variety of unwanted dissolved particles and suspended matter can be effectively removed from an aqueous solution by electrolysis. In the process of electrocoagulation, electrodissolution of the sacrificial anode to the wastewater leads to the formation of hydrolysis products (hydroxo-metal) species that are effective in the destabilization of the radionuclides and/or formation of particles with reduced solubility that entrap the radionuclides. The production of the hydrogen bubbles in the cathode promotes a soft turbulence in the system and bond with the radionuclides decreasing their relative specific weight thereby enhancing flocculation process [6]. Vik et al. [7] demonstrated that for the same cation dosing, the sludge formation in case of electrocoagulation was much less than conventional chemical coagulation, possibly due to the presence of counter anions in the latter case. In the simplest form, an electrocoagulation reactor is mainly made up of an electrolytic cell with one cathode and anode. The electrodes may be made of same or different materials. The interactions occurring in an electrocoagulation reactor is shown in Figure 1.

There are many advantages of electrocoagulation. A few of them are:

1. It is simple to design, easy to operate and has less maintenance due to no moving parts.
2. The sludge formed in the process of electrocoagulation easily settles and it is easy to dewater.
3. Flocs formed by electrocoagulation can be separated by faster by filtration.
4. The resultant effluent has less total dissolved solids.
5. Smallest of the colloidal particles are also easily removed.

**Mechanism**

Electrocoagulation is a complex process occurring in many steps. When the current passes thorough the electrochemical reactor, it must overcome the various resistances like, equilibrium potential difference, over potential of cathode and anode and the potential drop in the solution. The anode potential involves activation over potential, concentration over potential and the potential due to the passivation of electrode.

The electrodissolution of anodes result in the formation of the respective metal ions. These ions form a range of coagulant species and metal hydroxides by hydrolysis. The hydrolysis product may form many
monomeric metal hydroxide and/or polymeric hydroxyl complexes depending on the pH of the aqueous solution \[8\]. Due to the electrophoretic action, negative ions that are produced at the cathode move toward the anode. The combination of the metal cations with these negative particles results in the phenomenon of coagulation. Due to the continuous passage of current into the solution, the electrolysis of water takes place. Oxygen is generated at the anode whereas hydrogen is liberated at the cathode. The liberation of gases provides the necessary turbulence in the system. The flocculated particles get attracted to the gas bubble and float on the surface. The various processes occurring in an electrolytic cell is shown in Figure 2. The electrochemical reactions occurring at the electrodes can be shown as,

For iron anode,

At Anode: \[4\Fe (s) \rightarrow 4\Fe^{2+} + 8e^-\]

\[4\Fe^{2+} (aq) + 10\H_2\O + \O_2 \rightarrow 4\Fe(OH)_3 + 8\H^+\]

At Cathode: \[8\H^+ + 8e^- \rightarrow 4\H_2\]

Overall:

\[4\Fe (s) + 10\H_2\O (l) + \O_2 (g) \rightarrow \Fe(OH)_3 (s) + 4\H_2 (g)\]

An alternate mechanism is also proposed for iron anodes, which is given as,

At Anode: \[\Fe (s) \rightarrow \Fe^{2+} (aq) + 2e^-\]

\[\Fe^{2+} (aq) + 2\OH^- \rightarrow \Fe(OH)_2 (s)\]

At Cathode: \[2\H_2\O (l) + 2e^- \rightarrow \H_2 (g) + 2\OH^- (aq)\]

Overall:

\[\Fe (s) + 2\H_2\O \rightarrow \Fe(OH)_2 (s) + \H_2 (g)\]

As a result of the oxidation in the electrolysis system using iron electrode, monomeric [\Fe(OH)_3] and polymeric hydroxyl complexes of iron such as \Fe(H_2O)_6^{3+}, \Fe(H_2O)_5^{2+}, \Fe(H_2O)_4(\OH)_2^{+}, \Fe(H_2O)_3(\OH)_2^{2+}, \Fe(H_2O)_2(\OH)_2^{3+}\] are produced depending on the pH of the medium. Electrocoagulation can be thought of as an accelerated corrosion process and the performance of the concerned metal electrode with variation in pH can be predicted by its Pourbiax diagram. The Pourbiax diagram for Fe is shown in Figure 3.

---

**Figure 2 Processes in an EC Reactor**

**Figure 3 Pourbiax diagram for Fe**
In any electrochemical reactions like electrocoagulation, electroplating, electorefining etc. the current density is the most important parameter for controlling the rate of the reaction. The current density determines the production rate of the coagulant species, bubble production, size and distribution of the bubbles, thereby affecting the growth of the flocs. The current density \((J)\) can be calculated as:

\[
\text{Current Density (J)} = \frac{\text{Current in A}}{\text{Surface Area of the electrode in m}^2}
\]

The entire process of electrocoagulation is dependent on the Faraday’s Laws of Electrocoagulation. From the Faraday’s Laws of Electrolysis, it can be seen that, for constant current electrolysis, the moles of metal dissolved can be estimated as

\[
n = \frac{(I \times t)}{(F \times z)}
\]

where, \(n\) is the moles of metal ions generated, \(I\) is the current, \(t\) is the duration of experiment, \(F\) is Faraday’s Constant \((96485 \text{ Cmol}^{-1})\) and \(z\) is the number of electrons transferred per ion.

**EXPERIMENTAL STUDY**

**Apparatus**

A laboratory batch scale electrocoagulation was carried out using iron electrodes (dimensions \(155 \times 61.5 \times 1.16 \text{ mm}\)). The arrangement of the electrolytic cell arrangement is shown in Figure 4. The electrodes were dipped 95 mm into the aqueous solution of thorium nitrate \((800 \text{ mL})\) in a glass beaker. The gap between the two neighbouring electrodes was maintained at 35 mm. Direct current \((0-30 \text{ V}, 0-1.5 \text{ A})\) from a DC power source (Make: Aplab) was passed through the solution through the electrodes. The cell voltage and the current were displayed and was readily maintained using the digital power supply. The pH of the solution was determined by a commercial pH meter fitted with glass electrode.

**Experimental Procedure**

The influence of experimental parameters on the removal of thorium was done with synthesized effluent in batch mode. Thorium nitrate solution of the required concentration was achieved by dilution of the stock solution having concentration of 400 gpl Th and free acidity of 2.6 N by demineralized water. Ammonium hydroxide and nitric acid was added for the pH adjustment. The electrode set was washed with dilute acid and demineralized water to remove any passive layers before each experimental run. Electrocoagulation experiment was carried out for varying time intervals to study the effect of residence time on the removal efficiency. Current was changed over the range 0.5 to 1.5 A but was kept constant for each run. Compressed air was introduced into the electrolytic cell to produce soft turbulence which would enhance floc growth. After each run, the solution was allowed to settle and the supernatant was filtered using Whatman 42 filter paper. The filtered solution was then analysed for thorium concentration and pH. The loss in weight of the electrode was measured to estimate the metal concentration in the solution. The analysis of thorium was done by ICP-AES.
RESULT AND DISCUSSION

Effect of Initial pH

A graph indicating the effect of initial pH on the removal of thorium is shown in Figure 7. It can be deduced from the graph that removal of thorium increased with the increase in initial pH of the solution. This could be attributed to the rapid formation of Fe(OH)_3 coagulant and presence of thorium as neutral hydroxide form.

![Figure 7 Effect of Initial pH on Th removal](image)

Effect of Residence Time

The results of the effect of residence time on the removal of thorium were plotted in a graph (Figure 8). It is observed from the graph that the decontamination factor obtained for the removal of thorium from the effluent increased with the increase in residence time. This is due to the increased generation of coagulant species Fe^{3+} which is a function of time of application of constant current.

![Figure 8 Effect of Residence Time on Th removal](image)

Effect of Current Density

A plot showing the effect of current density on the removal of thorium is shown in Figure 9. It can be concluded from the plot that the decontamination factor increases with the increase in current density. This can be attributed to the fact that Fe^{3+} ions dissolution into the solution increases with increase in current, in accordance to Faraday’s Law.

![Figure 9 Effect of Current Density on Th removal](image)

Effect of Initial Thorium Concentration

The graph showing the effect of initial thorium concentration is shown in Figure 10. It is seen from the plot that the decontamination for thorium increases with increase in the initial concentration of thorium. In low concentration levels, the active sites of the coagulant are not completely occupied by thorium. As the concentration increases, more thorium is available for sorption onto the unoccupied active sites. This results in high decontamination factor with increase in initial concentration of thorium. However, beyond a threshold concentration, decontamination factor tends to become constant due to unavailability of free sites for sorption.

![Figure 10 Effect of Initial Thorium Concentration](image)
CONCLUSION

From the results obtained from through experimentation, it can be concluded that thorium could be effectively removed from effluent using electrocoagulation. The removal of thorium was increased with increase in the initial pH, residence time, current density and initial thorium concentration in the solution. Maximum decontamination factor obtained for thorium was of the order of $10^4$.

ACKNOWLEDGEMENT

The authors would like to thank Shri. Y. Balaji Rao, SM (Control Lab and Library) and his team for their continued support and cooperation during the entire course of this work.

NOMENCLATURE

<table>
<thead>
<tr>
<th>DC</th>
<th>Direct Current</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td>Electrocoagulation</td>
</tr>
<tr>
<td>LEU</td>
<td>Low Enriched Uranium</td>
</tr>
<tr>
<td>MOX</td>
<td>Mixed Oxide</td>
</tr>
</tbody>
</table>

REFERENCES

5. “Understanding variation in Partition Coefficient, $K_d$ values”, Volume II, United States EPA, EPA 402-R-99-004B.