Removal of Thorium from industrial waste via electrosorption technique

Eli Syafiqah Aziman¹ and Aznan Fazli Ismail¹, ²,a)

¹Nuclear Science Program, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia.
²Center of Frontier Science, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia.

a)aznan@ukm.edu.my

Abstract. Activated carbon electrode has been tested as a potential sorbent for removal of Th ions from the actual wastewater sample by electrosorption technique. The objective of this research is to investigate the performance of activated carbon electrode for remediation of real thorium sample. Adsorption of thorium ion by activated carbon electrodes was investigated with contact time up to 180 minutes by using positive potential at 0.2V (vs. Ag/AgCl), 0.4V (vs. Ag/AgCl) and 0.6V (vs. Ag/AgCl). Result shows that the condition has the highest percentage of thorium ion removal is at 0.6V (vs. Ag/AgCl) with highest specific capacity at 0.5 mg Th/g Carbon. Based on this research, the removal of thorium through electrosorption technique has the tendency to remove thorium ion and parameter such as contact time of electrosorption and voltage applied should be studied in more depth, where the removal of thorium is expected to increase.

1. Introduction
Wastewater is a by-product in the form of liquid produced by human activities be it by domestic, industrial, commercial or agricultural activities. Wastewater may contain physical, chemical or biological pollutants which exceed the limit that has been set by the authorities. If this wastewater is not handled properly, they may cause environmental contamination. There has been reports made regarding contamination of water supply with high concentrations of thorium in Malaysia. Bukit Merah, Malaysia 1992, was an incident where water supply were contaminated with a high concentration of thorium which leads to congenital disabilities and leukemia among nearby residents [1, 2].

Electrosorption is one of the promising techniques that enables the removal of thorium from wastewater aside from other conventional technique such as adsorption, ion-exchange and membrane filtration [3]. This process uses an electric current as a force that helps drive the metal ion to be adsorbed at the negative carbon electrode. Electrosorption is a non-faradaic process, the nature of electrostatic force where lead to electrical double layer capacitance (EDLC) causes the movement of ion to be adsorb to the surface of carbon electrode [4,5]. Electrosorptive capacity on activated carbon strongly depends on the physical properties such as surface area, pore size distribution, surface functional groups, surface polarity and surface wettability [6,7]. The objective of this paper is to investigate the performance of fabricated activated carbon electrode for remediation of thorium real sample through electrosorption technique.
2. Material and method
A carbon slurry was prepared by mixing activated carbon powder (DARCO 100; Sigma Aldrich, St Louis, MO, USA) with polyvinylidene fluoride (PVDF, M.W. \( \frac{1}{4} 534,000 \), Sigma Aldrich) in an N,N-dimethylacetamide (DMAc, 99%; Alfa Aesar, Ward Hill, MA, USA) solution at 21°C. A stainless steel gauze (40 mesh woven with 0.25 mm diameter wire, Type 304; Alfa Aesar) was coated with the carbon slurry and dried in an oven at 80°C for 6 hours to form an activated carbon electrode. Solution contain thorium in this research were obtained from real sample of leach solution of radioactive waste. Concentration of thorium in the leached solution was 1 mg/L with the presence of other REE earth elements such as U, Ce, Nd, La, Sm and others at various concentration.

Batch-mode adsorption experiment was carried out using a three-electrode electrochemical cell. Three electrodes used in this experiment were functioning fabricated activated carbon electrode with platinum wire (A-002233; Bio-Logic) and Ag/AgCl (RE-1S; Bio-Logic, Grenoble, France) as counter electrode and reference electrode respectively. The electro-chemical cell was connected to a potentiostat (VersaSTAT 3; Princeton Applied Research). The activated carbon electrode was kept under positive bias potential at 0.2V, 0.4V and 0.6V (vs Ag/AgCl). Thorium removal efficiency (\( \text{Th}_{\text{removal}} \)) and the total thorium adsorbed, \( \text{Th}_q \) (mg/g) at time, \( t \) was determined as shown in Eq. 1 and Eq. 2 respectively [8].

\[
\text{Th}_{\text{removal}} = \frac{c_0 - c_t}{c_0} \times 100\% \\
\text{Th}_q = \frac{(c_0 - c_t)}{W} \times V
\]

where,
- \( c_0 \) = initial thorium concentration in aqueous waste (mg/L)
- \( c_t \) = Thorium concentration after electrosorption at time, \( t \) (mg/L)
- \( V \) = volume of aqueous waste
- \( W \) = mass of activated carbon electrode (g) at time, \( t \)

3. Result and discussion

3.1. Characterisation of activated carbon electrode
The surface area and porosity of the activated carbon electrode was derived from the adsorption branch of the isotherm as shown in Fig. 1, based on the Brunauer Emmett Teller (BET) method using physisorption analyser (ASAP 2020 from Micromeritic). The BET surface area for activated carbon electrode is shown in Table 1. The surface morphology by Scanning Electron Microscope (SEM) analysis of the carbon electrode is shown in Fig. 2 shows that the stainless steel gauze was excellently covered by activated carbon electrode. However, the surface area of activated carbon electrode is reduced. This is due to the use of PVDF polymer as an agent to bind the activated carbon particles effectively.
Figure 1. Nitrogen adsorption–desorption isotherms of activated carbon electrode.

Figure 2. Surface morphology of activated carbon at 100µm.

Table 1. Pore structure of activated carbon powder and the fabricated activated carbon electrode.

| Characteristic       | AC powder | Activated carbon electrode |
|----------------------|-----------|-----------------------------|
| Surface area         | 1.024 m²/g | 158.07 m²/g                 |
| Total pore volume    | 0.8 cm³/g  | 0.22 cm³/g                  |
| Pore size            | 3.1 nm     | 5.79 nm                     |
3.2. Batch-mode electrosorption experiments

Effect of potential voltage on electrosorption of thorium from aqueous waste is shown in Fig. 3. The optimum voltage applied in this research was 0.6V vs Ag/AgCl. The highest specific capacity obtained was 0.5 mg/g with removal percentage at 22% like shown in Fig. 4.

Aside from activated carbon electrode acting as an adsorbent, organic waste adsorbent such as banana peel nano sorbent (BPN) were also used to remove thorium ion from wastewater generated by mining activity [8]. Even though removal of thorium ion by BPN adsorption technique is higher compare activated carbon electrode in this research however BPN requires a longer time of contact specifically 24 hours. The initial concentration used in activated carbon electrode is lower, specifically at 1 mg/L while the initial concentration of thorium used in BPN adsorbent is at 18.8 mg/L. BPN recorded 80% removal of thorium was due to the higher probability of thorium ion collision with BPN adsorbent compared activated carbon electrode. Aside from that, the initial concentration was different, the impurities in the sample is also a crucial factor. Actual sample in this research contains other elements besides thorium ion, therefore ion competition to be adsorb by activated carbon may be higher compared to thorium ion when comparing to the BPN experiment. Thus, activated carbon electrode has its own advantages depending on the parameter chosen in this research. Table 2 shows comparison of experimental parameter between activated carbon with previous research.

![Figure 3. Effect of potential voltage of Thorium.](image-url)
Figure 4. Removal percentage of thorium ion from sulphate aqueous waste.

Table 2. Comparison experimental parameter by previous research.

| Adsorbent                        | Initial concentration (mg/L) | Specific capacity (mg Th/g adsorbent) | Time of contact (minutes) | Impurities in sample | References |
|----------------------------------|------------------------------|--------------------------------------|---------------------------|----------------------|------------|
| Magnetic ion-imprinted chitosan resin | 20.0                         | 39.0                                 | Not Stated                | -                    | [9]        |
| BPN                              | 18.8                         | 10.1                                 | 1440                      | Th,U                 | [8]        |
| Activated carbon electrode       | 1.0                          | 0.5                                  | 180                       | Th,U,REE             | This study |

4. Conclusion
Activated carbon electrode has a high tendency in the removal of thorium from actual waste water samples through electrosorption technique. The best condition recorded in this research is where the voltage used was 0.6V (vs. Ag/AgCl) and the highest specific capacity was 0.5 mg Th/ g carbon. It is should be noted that the specific capacity value was not at the maximum yet. Various parameter should be studied still. Also, theoretically, an increase in the contact time of electrosorption and voltage applied should increase the removal of thorium.
5. References

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