



Original Article

Investigation of thorium separation from rare-earth extraction residue via electrosorption with carbon based electrode toward reducing waste volume

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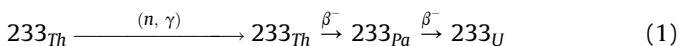
ABSTRACT

Rare-earth (RE) industries generate a massive amount of radioactive residue containing high thorium concentrations. Due to the fact that thorium is considered a non-economic element, large volume of these RE processed residues are commonly disposed of without treatment. It is essential to study an appropriate treatment that could reduce the volume of waste for final disposition. To this end, this research investigates the applicability of carbon-based adsorbent in separating thorium from aqueous phase sulphate is obtained from the cracking and leaching process of solid rare-earth by-product residue. Adsorption of thorium from the aqueous phase sulphate by carbon-based electrodes was investigated through electrosorption experiments conducted at a duration of 180 minutes with a positive potential variable range of +0.2V to +0.6V (vs. Ag/AgCl). Through this research, the specific capacity obtained was equivalent to 1.0 to 5.14 mg-Th/g-Carbon. Furthermore, electrosorption of thorium ions from aqueous phase sulphate is found to be most favorable at a higher positive potential of +0.6V (vs. Ag/AgCl). This study's findings elucidate the removal of thorium from the rare-earth residue by carbon-based electrodes and simultaneously its potential to reduce disposal waste of untreated residue.

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1. Introduction

Naturally occurring thorium occurs exclusively as ^{232}Th and is four times more abundant than uranium in nature [1]. ^{232}Th is categorized as a fertile isotope which does not undergo fission reactions by itself but can be converted to fissile ^{233}U following neutron absorption and via two beta decays [1] as represented in the following Equation (1).



The modern nuclear industry relies on the economic availability and extraction of uranium resources. The total confirmed amount of uranium reserves has been estimated to be about 7 million tonnes while the speculated amount hovers about 10 million

tonnes [2]. These resources are adequate for the near future, but could become limiting within 80–250 years, depending on global expansion of nuclear energy and increased demands on uranium reserves. Due to the limited availability of uranium, there has been an increasing amount of research done on thorium usage as fuel in breeder reactor technology. Thorium has been suggested as a future nuclear fuel in Generation IV nuclear reactor in the Generation IV International Forum (GIF) due to several reasons [3,4]. Thus, the utilization of thorium fuels will complement uranium, ensuring the long-term sustainability of nuclear power.

The world's total thorium sources are reported to be about 1,400,000 [5] to 5,307,800 tonnes [6]. According to Jorden et al. [7], an estimated total amount of 317,657 tonnes of thorium could be recovered from by-product production or joint production of thorium. The recovery of thorium is essential for thorium's historical and future viability as a fuel source. In Malaysia, the thorium source originates mainly from mineral monazite, with an estimated thorium content of about approximately 4,500 tonnes [5]. Therefore, Malaysia could utilize domestic thorium reserves to develop a

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thorium-based nuclear fuel cycle for energy generation.

Rare earth extraction is partially among the human activities that produces a vast amount of by-products waste containing thorium. Malaysia is among the countries that has a rare-earth processing plant, where according to the latest report, is claimed that the production of by-product residue from the plant has accumulated 64000–75000 tonnes of residue annually. The by-product residue contains thorium with a concentration of approximately 1500 ppm, equivalent to 94 tonnes that can be potentially recovered or extracted from the residue annually [7].

However, thorium is currently considered as a nuisance or non-economic element in rare-earth deposits due to its radioactive nature and small market demand. Thus, it is commonly treated as waste at rare-earth mines. The rare-earth industry faces a common problem of accommodating large volumes of radioactive waste during storage. In Malaysia rare-earth processing activities produces more than 450000 tonnes of radioactive waste containing high thorium concentration which is significant burden to the country. According to Kim et al. [8], recovery or removal of radionuclide from such radioactive waste by an appropriate treatment could reduce the volume of waste to be disposed of, resulting in a reduction in the disposal cost and enhanced.

In principle, the separation of thorium from its ores or solid waste streams consists of several processes, including leaching, solid-liquid separation, ion exchange, solvent extraction, and precipitation [9–11]. Apart from that, other conventional techniques could also be applied to separate thorium ion from aqueous phases, such as membrane filtration [12], ion exchange [13], and adsorption means [14]. Cracking and leaching of solid streams are crucial processes at the initial stage of thorium separation, whereby these processes determine the solubility of thorium either in acid or alkali to form an aqueous solution. The solution concentration can be further modified by using various conventional methods [15].

A consolidation of electrochemical treatment and adsorption process has led to a promising rapid technique, so-called electrosorption. This technique uses electrical potential as the driving force that renders metal ions to adsorb at a negative carbon electrode. Without electrical potential, the carbon electrode itself mimics the physical adsorption [16]. In the aqueous phase, the metal ions are effectively trapped by an opposite charge on the electrode surface due to the nature of electrostatic forces. In other words, the metal ions are adsorbed and fixed on the electrode surface by the electrical double layer phenomena. Compared to other techniques, electrosorption treatment uses fewer chemicals and produces less sludge. Moreover, the presents of an electrical potential during electrosorption accelerates the separation process compared to the conventional adsorption techniques [17]. Hitherto, this method has been widely employed in separating metal ions such as arsenic [18], copper [19], chromium [20], and uranium [21,22] from aqueous phases. The separation of thorium in the aqueous phase via adsorption technique is widely used alongside various adsorbents [23,24]. However up to our knowledge, there has yet to be a comprehensive study covering the implementation of an electrical potential in an adsorption technique specifically in the removal of thorium ion from aqueous phase.

A vast amount of studies have previously been invested in developing new cross-linked polymer adsorbents with a specific characteristic towards the targeted material. However, selecting a cost-effective adsorbent material also plays a significant role, aside from the adsorbent's applicability [25]. Recently activated carbon has been widely used in removing metal ions. Primarily due to it having a large internal surface area and pore volume, tunable pore size, high mechanical strength, and easy fabrication [26,27]. Besides that, the carbon-based electrode is generally known to be a low-cost adsorbent [28], giving them an additional advantage over

polymeric materials. Aside from that, several works regarding adsorbent has reported its viability and capability in removing thorium from the aqueous phase, which could potentially helps treating radioactive waste. Kim et al. [29], in their works, it is proved that solid radioactive waste generated from the dismantling of nuclear facility could be reduced for final disposal by separating uranium through the leaching process followed by adsorption. However, there is yet work to be done regarding how adsorbent is to be disposed of for long time-storage or final disposition that could reduce large amounts of thorium in radioactive waste.

To this end, the main aims is investigating the use of carbon-based adsorbent for the separation of thorium from rare-earth by-product residue in sulphuric acid leach liquor through the electrosorption technique. This paper might not provide details on isotherm and kinetic of carbon-based adsorbent in removing thorium ion from leachate of radioactive waste but it gives an idea of converting large volume of radioactive wastes to small waste packages. This experiment's findings will extrapolated to develop a conceptual design of a rare-earth residue disposal radioactive waste storage drum for accommodating the final disposal of activated carbon.

2. Materials and methods

2.1. Fabrication of activated carbon electrode

Carbon-based electrode utilised in this research was fabricated using powdered activated carbon (DARCO 100, Sigma Aldrich). In brief, a carbon slurry was prepared by mixing the activated carbon powder with polyvinylidene-fluoride (PVDF, M.W. $\frac{1}{4}$ 534,000, Sigma Aldrich) in N, N- dimethylacetamide (DMAC, 99%, Alfa Aesar) solution. The PVDF polymer content was 25 wt% of the activated carbon electrode. In forming a carbon electrode with imperative homogeneity, the carbon slurry was consistently stirred. The carbon slurry was then coated onto a stainless steel gauze (40 mesh woven with 0.25 mm diameter wire, Type 304, Alfa Aesar) and dried in an oven at 80°C for 6 hours, resulting in the formation of the carbon electrode as the end product. The prepared carbon electrode's effective surface area was 70 mm × 5 mm, as shown in Fig. S-1 (refer to supplementary material).

2.2. Characterisation of the fabricated activated carbon electrode

The nitrogen adsorption-desorption isotherm of the fabricated electrode was obtained via surface and pore size analyser (ASAP 2020, Micromeritics Instrument Corp). The specific surface area was determined by employing the Brunauer-Emmette-Teller (BET) method in accordance with the nitrogen adsorption data of relative pressure range $P/P_0 = 0.99$. Whereas, the pore size distributions were ascertained by applying the Barrett–Joyner–Halenda (BJH) method with context to the nitrogen adsorption isotherms at 77 K.

The activated carbon electrode's molecular conformation was determined via Fourier-transform infrared spectroscopy (FTIR; model spectrum 400 FT-IR/NIR, Perkin Elmer) characterisation while scanning electron microscopy (SEM-EDX; PHILIPS XL 30) was utilised in determining the physical surface structure of the fabricated activated carbon electrode. The post-electrosorption process and the alteration of activated carbon electrodes in terms of surface morphology were determined using field emission scanning electron microscopy-energy dispersive X-ray (FESEM-EDX; ZEISS Merlin).

2.3. Preparation of thorium leach liquor solution

The cracking and leaching of rare-earth by-product residue were carried out with sulphuric acid (18 mol/L H₂SO₄ (98%), V800412, supplied by Sigma Aldrich) with a sample to acid ratio of 1:5 and key parameters sets as per reported in our previous work [16]. This wet digestion process was conducted by heating and continuously stirring the complex for 2 hours at 150 °C via an open heating system using a conventional hot-plate along with a magnetic stirrer. This open heating system is regarded as an established and widely used technique due to its capability in reaching maximum dissolution of thorium during the digestion process [16]. Distilled water was then added to dissolve the metal sulphate. After 1 hour, the leaching process materialises at room temperature, and the solution was subsequently filtered in producing a purified leach liquor solution. The total volume of distilled water used to make final volume of leach liquor was recorded, where the sulphate concentration contribute from sulphuric acid (H₂SO₄) was then calculated based on dilution. The concentration of thorium and other elements in the leached solution was determined via inductively coupled plasma mass spectrometry (ICP-MS, model ELAN 9000; PerkinElmer SCIEX). The amount of thorium and others element in the prepared leach liquor were about 2% of H₂SO₄. Then, the leach liquor was be diluted to the desired concentration and tested in the electrosorption process. The initial pH of the leach liquor was fixed at 3 using a pH meter (model EUTECH ph700; Thermo Scientific) where deviations were corrected using 0.1 mol/L H₂SO₄ and 0.1 mol/L NaOH.

Modeling via Visual MINTEQ requires defined parameters such as concentration, ionic conductivity, and temperature to analyze the free metal ion and bound-metal distribution as a pH function. The ionic strength, *I_s*, was estimated from the measurements of conductivities of the leach solution that contains a thorium concentration of 0.5 mg/L along with others REE element and was calculated by using Equation (2). The ionic conductivity of leach solution was measured by using portable water testing conductivity equipment SD 320 Con from Lovibond.

$$I_s = 7.5 \times 10^{-5} \times SpC \left(\mu S cm^{-1} \right) \quad (2)$$

Where SpC is the specific conductance in micro Siemens per centimeter. The values obtained from this estimation were used as input for the model.

The estimated concentrations of thorium and other elements were then used as the input parameters for the Visual MINTEQ version 3.1 code. This simulation software was developed by an international supervisory body, the United States Environmental Protection Agency (USPEA) and maintained by KTH Royal Institute of Technology. The distribution of thorium ion species and other ions species in the leach solution of various pH, ranging from 1.0 to 10.0, was then calculated. Salt effect or ionic strength is one of the condition factor that influences the thorium ion adsorption properties. Previous study shows that different background salts concentrations 0.1–1.0 mol/L of NaCl, KCl, MgCl₂ and NaNO₃ influences the ionic strength however does not significantly affect the thorium adsorption capacity [30–33].

This is due to the fact that thorium was adsorbed through the electrostatic effect by various adsorbent (eg: poly sulfonamide/nano-silica composite multi-walled carbon nanotubes, PVA/TiO₂/ZnO nanofiber, β-CD(AN-co-AA) hydrogel) where the effect of ionic strength is negligible whereas the pH of the solution has a serious effect on adsorption [30–33]. Besides that, solubility of metal ions and metal speciation were extremely dependent on the pH of solution [31,33]. Thus the ionic strength effect was not investigated

further, whereas pH of the leach solution was strictly monitored in this study since previous work reported that pH has a more significant influence on ion adsorption [30–33].

2.4. Electrochemical measurement

The cyclic voltammetric (CV) performance of the fabricated carbon electrode was evaluated using an electrochemical workstation (VersaSTAT 3, Ametek) equipped with a three-electrode system. The three-electrode cell consisted of Ag/AgCl (3 M NaCl), Pt, and the fabricated carbon electrode as the reference, counter, and working electrode, respectively. Cyclic voltammograms of the carbon electrode were obtained in a potential window of –0.3 to 0.7 V at different scan rates (5–50 mV/s), with 1 mg/L sulphate leach liquor as the electrolyte. CV was performed at a scan rate of 50 mV/s at ambient temperature using electrolytes of different concentrations, ranging from 2 mg/L to 8 mg/L as a leach solution.

2.5. Electrosorption experiments

The electrosorption test was conducted in a batch-mode experiment manner with the use of a potentiostat (VersaSTAT 3, Ametek). The electrochemical set-up for this study consists of three electrodes, specifically the Ag/AgCl electrode in 3 M NaCl (RE-1S, Bio-Logic, Grenoble, France), platinum wire electrode (A-002233, Bio-Logic) and the fabricated activated carbon electrode with an activated carbon mass of 0.1–0.15 g, which irrespectively functions as the reference, counter and working electrode.

Aqueous phase sulphate containing thorium used in this study was obtained from the leached solution, the end product of the cracking and leaching process of rare-earth by-product residue, previously elaborated in section 2.3. Due to the limited amount of the leached solution, the maximum concentration of thorium used in this study was fixed at 10 mg/L. It is noted that other metal ions or impurities with various concentrations were also present in the leached solution. Thorium in aqueous waste with varying concentrations (0.02, 0.1, 0.5 and 1.0 mg/L) was evaluated in this study, with the leach solution of 120 mL constant volume used throughout the experiment. The electrosorption experiments were carried out in a batch mode experiment manner at positive bias potentials of +0.2V, +0.4V and +0.6V (vs. Ag/AgCl). The electrosorption experiment was conducted at a duration of 180 minutes. Fig. S-2 shows the schematic diagram of the electrochemical cell arrangement used in this study.

The amount of adsorbed thorium was determined via ICP-MS based on the difference between the initial and final concentrations of thorium in the leach liquor solution. The detection limit for thorium by ICP-MS in the He-mode was approximately 0.01 ppt. ICP-MS directly measured samples with low initial thorium concentrations (0.02, 0.1, 0.5 and 1.0 mg/L). Conversely, samples with high initial thorium concentrations (5 and 10 mg/L) were priorly diluted using deionised water by a factor of 10–50, depending on the initial concentration. The quantification of the thorium content in the samples was based on a 6-point calibration curve constructed from thorium standard sample (ICP-MS-61N-5, AccuStandard, USA), concentration ranging from 0.01 to 10 mg/L, measurements were in triplicate. The adsorption amount, *q_t* (mg/g) at time, *t* was calculated according to Equation (3);

$$q_t = \frac{(C_0 - C_t) \cdot V}{m} \quad (3)$$

where *V* (mL) is the volume of the feed solution; *m* (g) is the mass of the electrode; *C₀*, and *C_t* (mg/L) represent the initial concentration and concentration at time *t*, respectively.

3. Results and discussion

3.1. Characterisation of the fabricated carbon electrode

Fig. 1(a) demonstrates the nitrogen adsorption-desorption isotherms of the carbon electrode. The pore size distribution of the carbon electrode was derived from the isotherm's adsorption branch in accordance with the BJH method. The nitrogen adsorption-desorption isotherms exhibit a type IV shape with a narrower hysteresis loop at high relative pressures, insinuating the mixed microporous and mesoporous structure of the carbon electrode [34]. According to IUPAC, pore size can be classified into three groups, namely, micropores (diameter <2 nm), mesopores (diameter = 2–50 nm), and macropores (diameter > 50 nm). As shown in Fig. 1(b), pore size analysis suggests that the carbon electrode is essentially mesoporous, as a majority of the pore diameters is valued in the range of 2–50 nm.

From the nitrogen isotherms, the samples' structural parameters, including the BET surface area and pore volume, were calculated; the BET specific surface area was equivalent to 158.07 m²/g, while the total pore volume and average pore size were 0.22 cm³/g and 5.79 nm, respectively. SEM analysis of the carbon electrode surface morphology is as shown in Fig. S-3. Through the image, it is clearly seen that the PVDF polymer binder was adequately bonded with the activated carbon particles, coherently with the active coating of the carbon on the stainless steel gauze.

The molecular conformation of the activated carbon electrode surfaces was determined by FTIR spectroscopy. Fig. 2 presents the FTIR spectra of the activated carbon electrode. Vibration bands at wavelength 1050 cm⁻¹, 1230 cm⁻¹ and 1735 cm⁻¹ are attributed to the complex's C–O bond, whereas peaks detected at 1783 cm⁻¹, 1746 cm⁻¹, 1798 cm⁻¹, 1769 cm⁻¹ and 1834 cm⁻¹ corresponds to the C=O bond. In addition to the large surface area of the activated carbon powder, the presence of C–O and C=O functional groups could enhance the adsorption performance of the complex [35]. The amine functional group stemming from the DMAC solvent could be observed at peak 1017 cm⁻¹, whereas the peak at 1182 cm⁻¹ corresponds to the alkyl halide group (C–F) present in the PVDF polymer. Furthermore, the peak formation at 1165 cm⁻¹ is due to the –CF₂ symmetric stretching [36] of the activated carbon electrode. In general, the FTIR spectra indicates that the DMAC amide functional group does not chemically react with the

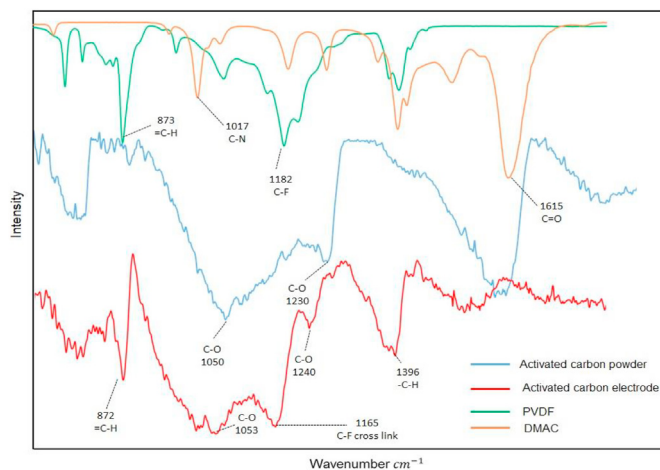


Fig. 2. FTIR spectra of the activated carbon electrode.

activated carbon, while the presence of the C–F functional group on activated carbon electrode is significantly due to the physical cross-linking.

3.2. Concentration content of thorium and other elements

As previously mentioned, apart from the thorium ion, other metal ions are also present in the sulphate leach solution. Table 1 shows the concentration of elements in the leach solution. It could be deduced that cerium is the most prominent element in the leach solution, with concentrations higher than thorium by a factor of 15. Determined ion concentration is then furthered extrapolated as the input parameter for Visual MINTEQ code. The leach solution's distribution of thorium ion species was calculated at various pH, ranging from 1.0 to 10.0. The estimated thorium distribution is as illustrated in the speciation diagram in Fig. 3. Simulation speciation analysis was carried out using parameter concentration of thorium ion in leach solution at 0.5 mg/L (present of others REE elements with ratio concentration to thorium like shown in Table 1) while the sulphuric acid concentration, ionic conductivity, and temperature were 0.3 mol/L, 15.89–15.95 mS/cm and 25 °C respectively.

As shown in Fig. 3, the thorium ionic complex $Th(SO_4)_3^{2-}$ began to form at a pH value of 1.0 and rapidly becomes the dominant ionic species at pH valued above 3.0, while instantaneously declining at a pH value of 5.0. Moreover, it is observed that at a pH value of 3.0, approximately 15% of the thorium ions exist as $Th(SO_4)_2$. It is noted that the thorium leach solution during the electrosorption experiment has a pH value adjacently equivalent to 3.0; thus, it can be deduced that only two thorium species, specifically $Th(SO_4)_3^{2-}$ and $Th(SO_4)_2$, are directly implicated in the electrosorption process. According to Allen & McDowell [37], the speciation of thorium in a sulphate system, with the acidity of H₂SO₄ fixed at 6.4×10^{-5} M (pH 3.89), resulted in the formation of highly concentrated

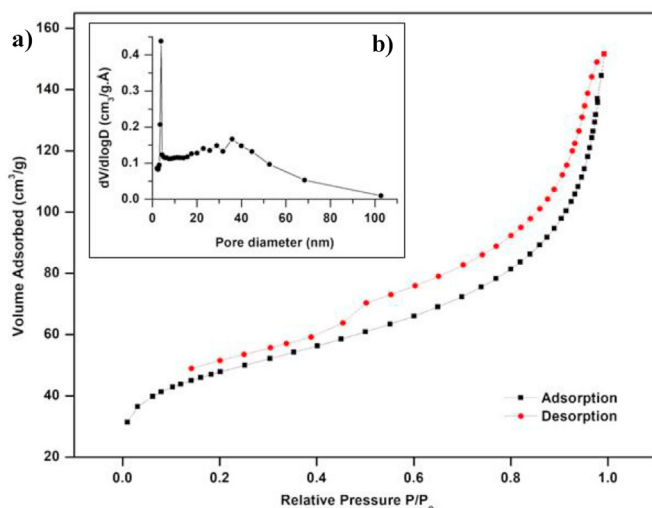


Fig. 1. a) Nitrogen adsorption-desorption isotherms; b) pore size distribution of the carbon electrode.

Table 1

The concentration of impurities in the sulphate leach solution determined by ICP-MS.

Element	Concentration (mg/L)	Ratio metal ion to thorium (M _{metal} : Th)
Ce	290	14.5:1
La	86	4.3:1
Nd	52	2.6:1
Pr	12	0.6:1
Th	20	–

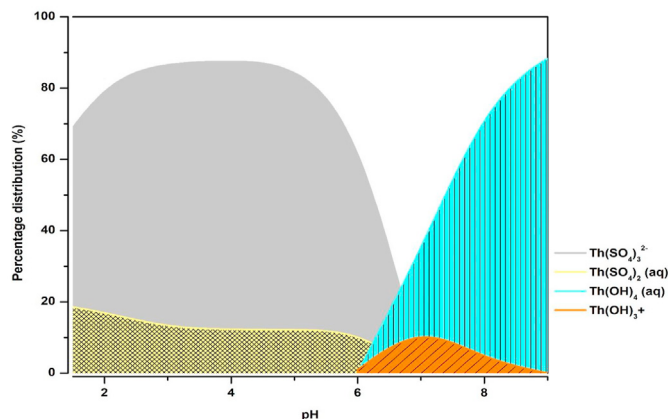


Fig. 3. Speciation analysis of 0.5 mg/L thorium in the leach solution.

$Th(SO_4)_3^{2-}$ ionic species, consistent with the speciation analysis at pH 3 to 4 findings of this present study. In conjunction with this, it was observed that the leach solution also contains rare-earth element (REE) species, specifically $REE(SO_4)_2^-$ and $[REESO_4]^+$ (as shown in Table 2), as expected during the electrosorption experiment at pH value of 3.0.

3.3. Electrochemical analysis

In order to ensure that the thorium ion in the aqueous phase sulphate, obtained from the leaching process, was not oxidised or reduced during the electrosorption process, the applied potential of electrosorption was rigorously controlled. The cyclic voltammetry of aqueous phase sulphate was measured by the electrochemical workstation with sweep rates between 5 and 50 mV/s, and the results are as shown in Fig. 4 (a). The observed steady increment and decrement of current with electric potential, in the range of -0.3 V to 0.7 V, indicated that no oxidation or reduction has occurred in the aqueous phase sulphate. Therefore, the electrosorption was carried out in this potential range to prevent the thorium ion in the aqueous phase sulphate from being reduced or oxidised. The thorium ions are eventually removed from the aqueous phase sulphate owing to the electrical double layer

Table 2
Rare-earth element (REE) speciation analysis of leach solution containing 0.5 mg/L thorium at pH 3.

Component	% of total concentration	Species name
SO_4^{2-}	96.24	SO_4^{2-}
	3.71	HSO_4^-
Ce^{+3}	0.03	$Ce(SO_4)_2^-$
	1.21	Ce^{3+}
	66.79	$Ce(SO_4)_2^-$
La^{+3}	32.00	$CeSO_4^+$
	0.87	La^{3+}
	76.12	$La(SO_4)_2^-$
Th^{+4}	23.01	$LaSO_4^+$
	85.21	$Th(SO_4)_3^{2-}$
	14.41	$Th(SO_4)_2(aq)$
Nd^{+3}	0.38	$ThSO_4^{2+}$
	1.20	Nd^{3+}
	65.79	$Nd(SO_4)_2^-$
Pr^{+3}	33.01	$NdSO_4^+$
	1.61	Pr^{3+}
	55.92	$Pr(SO_4)_2^-$
	42.48	$PrSO_4^+$

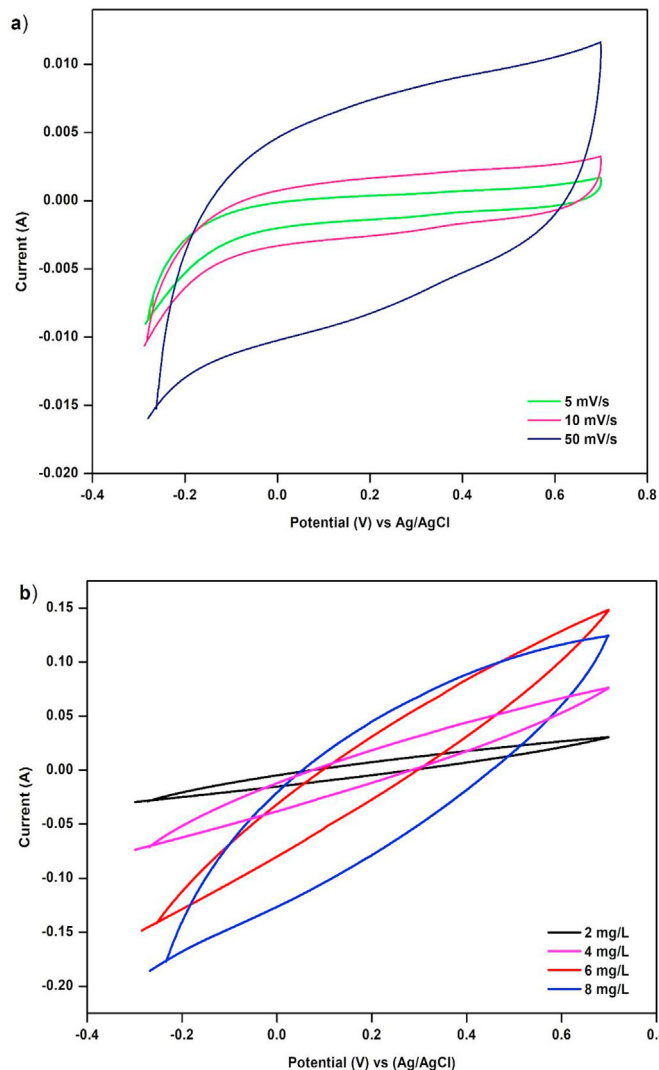


Fig. 4. Cyclic voltammogram of the activated carbon electrode (a) in 1 mg/L aqueous sulphate waste with a scan rate of 5, 10 and 50 mV/s, and (b) in different concentrations of aqueous sulphate waste (2–8 mg/L).

phenomena [34].

In determining the activated carbon electrode's electrosorption capacity, CV analysis was performed on aqueous solutions with different thorium concentrations (2–8 mg/L) in aqueous sulphate waste solution shown in Fig. 4 (b). It can be observed that the CV curves exhibited similar shape, regardless of the thorium ion concentration in the aqueous waste solution. Whereby the induced current had a directly proportional relationship with the waste solution concentration. Highly due to the reason that more ions can be electrostatically adsorbed and that the electrical double-layer surface overlap effect is weaker at higher concentrations [38].

3.4. Electrosorption test

3.4.1. Effect of applied voltage

Fig. 5 shows the effect of voltage applied specifically at 0.2V, 0.4V and 0.6V vs. Ag/AgCl on different concentrations of thorium (0.02 mg/L, 0.1 mg/L, 0.5 mg/L & 1.0 mg/L) in the leach solution.

The result shows that, as the applied voltage increases, the specific capacity increases concomitantly. Such phenomenon can be explained as follows: direct contact between the carbon

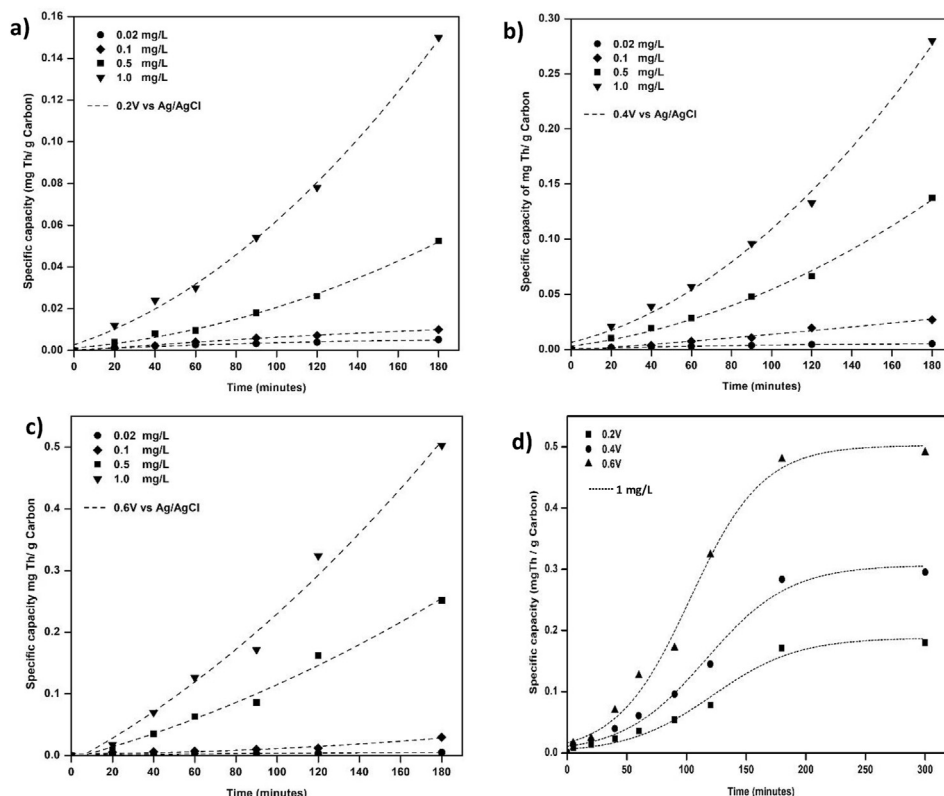


Fig. 5. Effect of different concentrations of thorium in the leach solution at applied voltage of a) 0.2V vs. Ag/AgCl, b) 0.4V vs. Ag/AgCl; c) 0.6V vs. Ag/AgCl; d) 0.6V vs Ag/AgCl on 1 mg/L at 300 minutes.

electrode and the aqueous sulphate solution causes the build-up of the electrical double layer (EDL) effect. Increasing the applied voltage leads to thicker EDL and stronger Coulombic interactions between the carbon electrodes and charged ions [39]. The correlation between the applied voltage and the specific capacity exhibits a similar trend upon changing thorium's initial concentration. However, the specific capacity becomes more significant with increasing initial concentration of thorium in the leach solution. Such phenomenon was observed highly due to the reason that the carbon electrode has not entirely reached the maximum electrosorption capacity. From the adsorption curve shown in Fig. 5 (d), the adsorption equilibrium of the activated carbon electrode started to reach the saturation state of the electrosorption process at 180 minutes.

3.4.2. Effect of competing ions

The performance of the activated carbon electrode in thorium removal with the presence of competing ions are shown in Fig. 6. In mediums with competing ions, carbon electrode shows a greater tendency to adsorb ions of higher concentration. This pattern was also observed in a study conducted by Handley-Sidhu et al. [40], where an excess amount of a particular metal ion tends to block the adsorption sites of other metal ions that are less dominant in the solution.

In a sulphate system, ionic species of REE and thorium ion consist of different ionic radii. The ionic radius is one of the criteria that influences the selectivity of adsorbent toward metals [41]. According to Hillel 1998 [42], the smaller the ionic radius, the more closely and strongly is the ion adsorbed. As previously mentioned, ionic species $Th(SO_4)_3^{2-}$ and $REE(SO_4)_2^-$ were designated as the thorium and dominant REE ion species directly involved in the

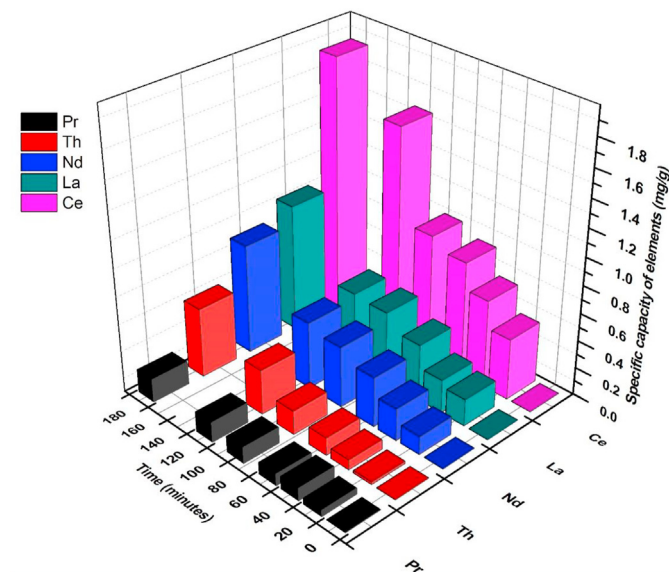


Fig. 6. Effect of competing ions on Th removal (1 mg/L concentration) from the leach solution at 0.6V vs. Ag/AgCl.

electrosorption process. Generally, the ionic radii shortens with increasing positive charge and lengthens with increasing negative charge [43]. Previous studies reported that the lanthanide group, REE, generally has smaller ionic radii compared to the actinides group, with a difference of +/- 0.10 Å [44]. Thus, the complex ion $Th(SO_4)_3^{2-}$ is postulated in having a slightly larger ionic size in

comparison with $REE(SO_4)_2$. Thus the mobility of thorium ion is slightly slower in comparison to the $REE(SO_4)_2$ ion. Therefore, the carbon electrode is presumed to favour the adsorption of Ce, La, and Nd ions, given that these REE are more dominant and agile in the leach solution in comparison to the thorium ion. Even though the Th ion would face high competitiveness with other dominant ions, the carbon electrode is still relevantly applicable for the Th ion's adsorption.

3.4.3. Effect of thorium ion initial concentration

The effect of thorium ion initial concentration on the electrode adsorption specific capacity was further investigated, as shown in Fig. 7. Due to the limited amount of the prepared leach stock solution, the maximum concentration of thorium ion evaluated in this study was fixed at 10 mg/L. The maximum capacity of thorium adsorbed onto the carbon electrode was equivalent to 1.0 mg-Th/g-Carbon in the presence of other impurities ion. The efficiency of thorium ion of removal from leach liquor shown in Fig. 7(a) was decreasing simultaneously at higher concentration due to the limited number of active sites of the adsorbent, which saturates at a particular concentration. Besides, the adsorption capacity will increase with the increase in initial concentration, but the concentration will inversely impact the adsorption efficiency because of the limited adsorption sites available for the uptake of metal ions [45].

This result is rather intriguing as it was previously demonstrated, based on the isotherm data, that other competitive ions were present aside than Th. It is hypothetically expected that the

maximum adsorption capacity could be increased if the analysis was carried out with a leach solution of higher thorium ion concentration. Despite the number of works previously reported in relation to the removal of thorium using various adsorbent, this present study's findings further extends in the elaboration on the presence of other competitive lanthanides rather than solely on Th. Table S-1 illustrates the adsorbent performance of thorium adsorption obtained in this work compared to previously reported studies. Moreover, this work also highlights the use of activated carbon electrode in the electrosorption technique as a novel approach for removing thorium ion. This technique can remove thorium within a shorter period to several adsorbents previously studied (shown in Table S-1).

Furthermore, limitation in controlling the parameters that govern the leach liquor's production was further compensated by performing electrosorption of thorium from the sulphate medium, specifically thorium hydroxide ($ThOH_4$) dissolute in sulphuric acid. Electrosorption was conducted in the absence of other impurities in determining the maximum value of thorium uptake by the carbon electrode. Fig. 7(b) shows the highest specific capacity of carbon electrode obtained at various potential values. The highest capacity was equivalent to 5.14 mg-Th/g-Carbon. However, it should be noted that other parameters (eg: initial concentration and potential) should be further studied to improve the carbon electrode's maximum optimal capacity. Even though the electrode's highest capacity value in this study was achieved in the absence of impurities, it is hypothesised that this could be further enhanced by increasing the applied potential, even in the presence of impurities.

Throughout the study of removing thorium from leach solution, the main problem that poses a significant effect on the removal capacity of thorium by carbon electrode is the high concentration of competing ions. Elimination of competing ions could help in increasing thorium removal capacity. However, RE elements left behind in the residue are not economical to be separated in the rare-earth industry due to low concentrations.

Based on the international regulatory IAEA body's guidelines regarding radioactive waste management, reduction of volume for radioactive residue being disposed of is essential to be obeyed by any activities related [16]. Therefore, investigating carbon electrodes' capability to remove thorium in this paper gives new information where it is possible to separate thorium from leachate of radioactive waste even in high competing conditions with a rapid process. Besides that, the study introduces an idea where radioactive residue being disposed from the rare-earth industry could be reduced, which allowing industries to meet guidelines set by regulating bodies. This study suggests that without get rid of competing ions, the capacity of thorium removal could be increased by improving the selectivity of carbon electrode itself. Therefore, in future works, the study should consider improving the carbon electrode selectivity by embedding suitable and the economical ligand or chelating material to be incorporated into the adsorbent material.

3.4.4. Characterisation of carbon electrode post electrosorption process

Fig. 8 presents the physical surface structure and FESEM/EDX photomicrograph of the activated carbon electrode post electrosorption process. It is evidently seen that white deposits are present on the surface of the carbon electrode post electrosorption process, as shown in Fig. 8 (a). Surface morphology analysis via FESEM demonstrates that the white deposits consist of grains with an angular shape (Fig. 8 (b)). Whereas EDX mapping in Fig. 8 (c) shows that the thorium and REE element are adsorbed randomly on the carbon electrode's surface.

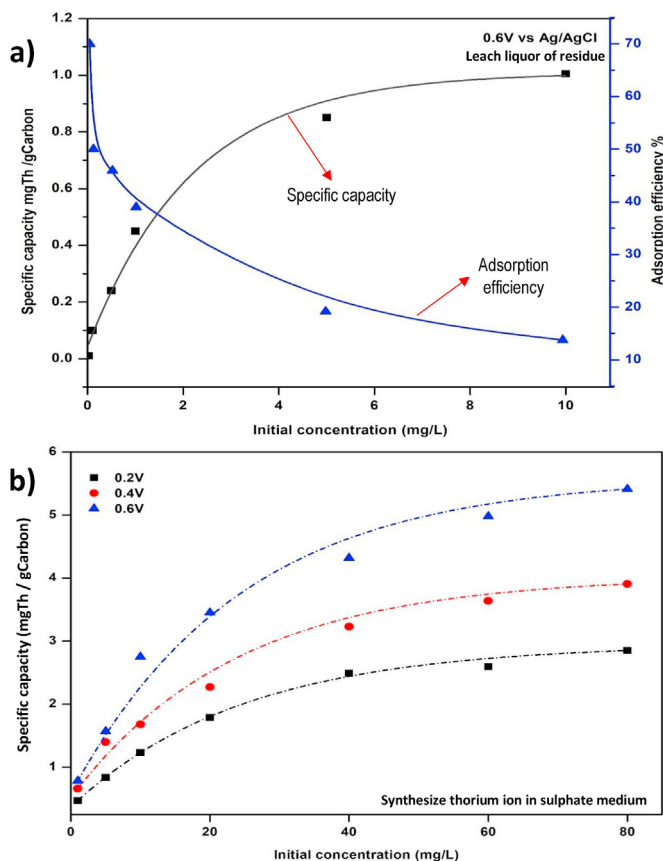


Fig. 7. Effect of different thorium ion initial concentrations on the electrode specific capacity and adsorption efficiency a) 0.6V vs Ag/AgCl at 180 minutes of leach liquor of radioactive residue; b) 0.2V–0.6V vs. Ag/AgCl, at 180 minutes of synthesize thorium ion in sulphate medium.

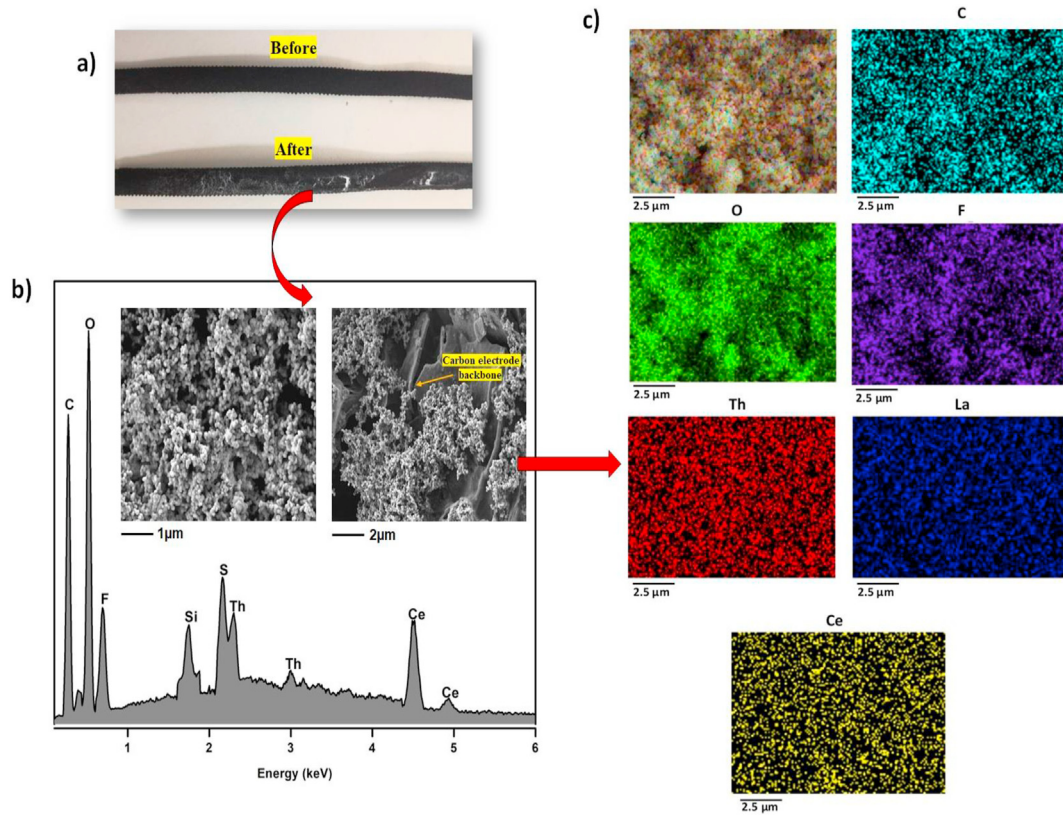


Fig. 8. (a) Physical surface structure of the carbon electrode before and after electrosorption process; (b) surface morphology of the activated carbon electrode observed via FESEM and (c) EDX mapping of the carbon electrode.

3.5. The significant effect of thorium separation from rare-earth processed residue

Separation of thorium from rare-earth processed residue will provide sustainable thorium resources, approximately 94–106 tons per year concomitantly with the continuous operation of rare-earth processing plants [7,46]. These sustainable thorium resources will provide benefits for industrial sectors, specifically the nuclear industry. Separation of thorium from rare-earth processed residue is expected to reduce the volume of generated waste. In Malaysia, the annual increment of radioactive residue from the rare-earth processing plant has resulted in public negative perceptions and concerns in relation to its environmental and radiological impact even though the related industry has complied with the Malaysia's regulation as required by the Atomic Energy Licensing Board (AELB). Thus, it is vital to extrapolate this experimental study's findings in reducing the volume of rare-earth processed residue.

According to IAEA, NORM residue will be treated as a radioactive waste if it is not feasible to be recycled or used as a by-product [47]. These radioactive waste will eventually undergo a conditioning process prior to its disposal. Conditioning is generally carried out by immobilizing the material, by depositing it into containers, commonly 200 L of steel drums [47,48]. The dimension and area of 200L drum was calculated in Equation (4):

$$A_{SD} = 2\pi rh + 2\pi r^2 \quad (4)$$

where A_{SD} represents the area of steel drum (cm^2) which r is radius and h is the height of steel drum, which are 27.2 cm and 82.9 cm, respectively.

In conjunction with this, a conceptual design of a rare-earth

residue disposal radioactive waste storage drum was developed to accommodate the activated carbon electrode (adsorbent material) used in separating thorium via electrosorption.

Lynas generates an average of 64000–75000 tons of waste annually during operation and requires 320,000–375,000 of 200 L disposal drums to store the end product waste in long term disposal facilities. The estimated number of the drums storing Lynas's radioactive residue were calculated using Equations (5) and (6) as follows:

$$V_R (\text{gal}) = T_R (\text{tons}) \times CF \quad (5)$$

where V_R represents volume of waste (in gallon) while T_R and CF represents the mass of radioactive residue (in ton) and conversion factor tons of wet sludge to gallon respectively.

$$D_{WT} = \frac{V_R (\text{gal})}{V_{SD} (\text{gal})} \quad (6)$$

where D_{WT} denotes of steel drum required to disposed waste without treatment while V_R and V_{SD} denotes volume of waste (in gallon) and volume of steel drum (in gallon) respectively.

The conventional 200 L disposal drum's design parameters were used for further assessment in storing the fabricated carbon electrode. The proposed carbon electrode's size details consisting of 1 kg activated carbon/PVDF was calculated by using Equation (7):

$$A_{1\text{kg-CE}} (\text{cm}^2) = A_{e-CE} (\text{cm}^2) \times EF \quad (7)$$

where $A_{1\text{kg-CE}}$ represents the area of 1 kg carbon electrode (in cm^2) while A_{e-CE} and EF denotes the area of experimental carbon

electrode (in cm²) and enlargement factor respectively.

As previously discussed, the carbon electrode fabricated in this study has the capability to remove 5g of thorium for every 1 kg of carbon electrode used, which highest capacity achieve in this study. In order to remove 94–106 tons of thorium from 64000 to 75000 tons of generated rare-earth residue, in relation to Lynas facilities, it requires approximately 18,800–21,200 tons of carbon electrode which was calculated using Equation (8);

$$m_c = \frac{m_{Th}}{CE_u} \quad (8)$$

where m_c denotes mass of carbon adsorbent required to remove thorium (in ton) while m_{Th} and CE_u represents mass of thorium inside the radioactive waste (in kg) and specific capacity of carbon adsorbent (kg Th/tons carbon adsorbent) respectively.

A 200 L disposal drum could accommodate 58–81 sticks of carbon electrode with area of every stick carbon electrode was between 233.3 cm² to 350.0 cm² which was calculated using Equation (9);

$$T_{CE} = \frac{A_{SD}}{A_{1kg-CE}} \quad (9)$$

where T_{CE} represents the number of sticks carbon electrode could accommodate in steel drum while A_{SD} and A_{1kg-CE} denotes the area of steel drum (in cm²) and area of 1 kg carbon electrode (in cm²) respectively.

Thus the total amount of disposal drum required in storing the electrodes post the electrosorption process is approximately 232,099–365,517 drums which was calculated using Equation (10);

$$D_{AT} = \frac{m_c}{T_{CE}} \quad (10)$$

where D_{AT} represents the number of steel drum required to disposed carbon electrode after electrosorption treatment while m_c and T_{CE} denotes the mass of carbon adsorbent required to remove thorium (in kg) and number of sticks carbon electrode could accommodate in steel drum respectively.

Reduction percentage of waste after electrosorption treatment was calculated based on Equation (11). It is clearly elucidated that the volume of waste would be reduced up to 40% through the additional employment of electrosorption treatment prior to storage. Parameters used in determining the reduction of rare earth residues for landfill disposal through electrosorption techniques are summarized in Table S-2.

$$\text{waste reduction (\%)} = \frac{D_{WT} - D_{AT}}{D_{WT}} \times 100 \quad (11)$$

where % denotes reduce percentage volume steel drum being disposed while D_{WT} and D_{AT} represents the number of steel drum required to disposed waste without treatment and number of steel drum required to disposed carbon electrode after electrosorption treatment respectively.

It should be noted that the specific capacity of thorium removal by the fabricated carbon electrode had an efficiency percentage of 90% in a single process based on our previous works [16]. Consequently, the amount of thorium, 94–106 tonnes, used in this estimation might vary, but it is considered that the multiple cracking and leaching process of rare-earth residue could increase the removal efficiency of thorium into the leach solution. In Malaysia, industrial waste disposal was supervised by two departments: The Department of Environment (DOE) and the Atomic Energy Licensing Board (AELB). AELB supervises any activities that related

the use and produced of radioactive material. Thus, 10% of thorium remains in the residue after the cracking and leaching process containing activity concentration below 1 Bq/g is considered non-radioactive waste and no longer subject to AELB enforcement, which later can be disposed of it as a conventional industrial waste based on regulator body under DOE. Besides that, the remaining leach solution containing RE elements and thorium post electrosorption process could be purified to obtain a valuable REE or further precipitated with the purpose of it being disposed of as a conventional industrial waste follow Malaysia's regulatory body under DOE.

In our study, we perceived that the fabricated carbon electrode has the potential to reduce the volume of REE processed residue. Additionally, the electrode's selectivity towards the thorium ion could be further developed in future studies for an improved outcome. This study aimed to evaluate the potential of a low-cost adsorbent, specifically activated carbon [17,49], in separating thorium ion from radioactive residue in a short period via electrosorption technique, simultaneously facilitating the conversion of waste in huge volumes to a small waste package for final disposal. Even though the adsorbent's high selectivity properties are of primary intention, the adsorbent's relative cost-effectiveness is crucial and should be considered in benefiting the specific industry.

4. Conclusion

The fabricated activated carbon electrode employed for thorium adsorption in the electrosorption process indicated good performance and promising results. The thorium uptake by the carbon electrode is 1.0–5.14 mg-Th/g-Carbon at an electrosorption process of 180 minutes, which is considered a rapid technique compared to some previous adsorbent. It is deduced that increasing tested potential would further increase the carbon electrode's thorium uptake.

In lieu of pretreatment for RE removal, this study indicates that a high concentration of thorium compared to competing ions could improve the efficiency of thorium removal. However, in future works, the study looks to turn the focus in improving the carbon electrode's selectivity to increase removal capacity. Moreover, this study demonstrated that the electrosorption technique has the potential to separate thorium ion at a shorter period during the sorption process. Hence, separated thorium from rare-earth residue may provide a sustainable thorium resource in the future. Additionally, the removal of thorium from the rare-earth residue by carbon electrode is expected to facilitate in reducing the volume of intended disposal waste up to 40%. In conclusion, the separation of thorium and the potential reduction volume of rare-earth residue could give positive sentiments and perceptions towards Malaysia's rare earth industry and ultimately further develop the sector in the nearest future.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.net.2021.03.032>.

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