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BIOACCESSIBILITY ASSESSMENT OF ^{232}TH AND ^{238}U FROM LANTHANIDE CONCENTRATE AND WATER LEACH PURIFICATION RESIDUE IN MALAYSIA

(Penilaian Bio-Kebolehcapaian bagi ^{232}Th Dan ^{238}U dalam Lantanida Pekat dan Residu Permurnian Larut Resap Air di Malaysia)

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Abstract

The aim of this case study was to estimate the bioaccessibility of ^{232}Th and ^{238}U from lanthanide concentrate (LC) and water leach purification (WLP) residue of Lynas Advanced Materials Plant by analysing the solubility of these radionuclides in synthetic gastrointestinal fluids. A DIN *in vitro* bioaccessibility method was applied to determine the targeted radionuclides from the LC and WLP residue, which were further evaluated through inductively coupled plasma mass spectrometry. ^{232}Th and ^{238}U concentrations in the gastrointestinal fluids portrayed the maximum amount of contaminants that were potentially available for intestinal absorption and transfer into the blood. The maximum concentrations of ^{232}Th in the LC and WLP residue were 0.1410 ± 0.0331 mg kg^{-1} and 0.1621 ± 0.1190 mg kg^{-1}, respectively. As for ^{238}U in the LC and WLP residue during the intestinal phase for high-risk cases, the maximum concentrations were 0.0558 ± 0.0164 mg kg^{-1} and 0.0480 ± 0.0213 mg kg^{-1}, respectively. The maximum bioaccessibility of ^{232}Th and ^{238}U was 0.14 % and 0.93 %, respectively. Based on the assessment, the committed equivalent dose and committed effective dose of ^{232}Th and ^{238}U were below the United Nations Scientific Committee on the Effects of Atomic Radiation reference values. Overall, the DIN *in vitro* bioaccessibility method is feasible to estimate the solubility of ^{232}Th and ^{238}U from LC and WLP residue, and is also useful for monitoring and risk assessment purposes for environmental, health, and contaminated samples.

Keywords: bioaccessibility, thorium, uranium, lanthanide concentrate, water leach purification

Abstrak

Tujuan kajian ini ialah mengkaji bio-kebolehcapaian ^{232}Th dan ^{238}U dari sampel lantanida pekat (LC) dan residu pemurnian larut resap air (WLP) yang terdapat di loji bahan termaju Lynas, dengan kaedah penentuan melalui kebolehlarutan radionuklid tersebut di dalam cecair sintetik gastrousus. Sampel LC dan residu WLP telah menjalani teknik bio-kebolehcapaian *in vitro* DIN, dan seterusnya sampel dianalisis menggunakan Spektrometer Jisim-Gandingan Plasma Teraruh. Kepekatan ^{232}Th dan ^{238}U dalam cecair gastrousus mewakili jumlah maksimum pencemaran radionuklid yang berpotensi diserap ke dalam badan melalui usus dan berpindah ke dalam darah. Kepekatan maksimum ^{232}Th dalam LC dan residu WLP ialah 0.1410 ± 0.0331 mg kg^{-1} dan 0.1621 ± 0.1190 mg kg^{-1}. Bagi ^{238}U dalam LC dan residu WLP semasa fasa usus bagi kes berisiko tinggi ialah 0.0558 ± 0.0164 mg kg^{-1} dan 0.0480 ± 0.0213 mg kg^{-1}. Nilai bio-kebolehcapaian maksimum bagi ^{232}Th dan ^{238}U ialah 0.14% dan 0.93%. Berdasarkan kajian, dos komited setara dan dos komited berkesan bagi ^{232}Th dan ^{238}U adalah di bawah nilai rujukan *United Nations Scientific Committee on the Effects of Atomic Radiation*. Kesimpulannya, teknik bio-kebolehcapaian *in vitro* DIN sangat berguna untuk

menganggar kelarutan ^{232}Th dan ^{238}U bagi tujuan pemantauan berterusan dan penilaian risiko terhadap alam sekitar, kesihatan manusia, dan sampel tercemar.

Kata kunci: bio-kebolehcapaian, torium, uranium, lantanida pekat, permurnian larut resap

Introduction

The world is currently facing intense demand and development of rare earth elements (REEs) for green and sustainable products in energy, armed forces, and manufacturing industries. Thus, to assist the global REEs market, the Lynas Advanced Materials Plant (LAMP) was built in the Gebeng Industrial Estate (GIE), Kuantan, Malaysia. This beneficial development brings investment profits in rare earth industry. About 0.03×10^6 t of rare earth ores production comes from Malaysia [1]. The LAMP processes lanthanide concentrate (LC) at an integrated processing site utilising physical and chemical treatment processes. Water leach purification (WLP) residue results from the leaching and purification of the water-soluble lanthanide components from the calcined and cracked concentrate. Radioactive elements, namely thorium dioxide (ThO_2) and uranium oxide (U_3O_8), are present in the rare earth concentrate that is processed by the LAMP. This plant is expected to yield approximately 65 000 t/a of rare earth concentrate with a rare earth oxide (REO) concentration of 40 %, a ThO_2 concentration of 0.17 %, and a concentration of U_3O_8 of 0.003 % [2]. According to United States Environmental Protection Agency (USEPA), the rare earth concentrate is classified as Technologically Enhanced Naturally Occurring Radioactive Material (TENORM) [3]. Even though REEs have been considered to be beneficial and profitable to Malaysia, the occupational, public safety, and health risks related to REEs should be addressed at their stages of mining, transportation, processing, and waste disposal, as well as decommissioning.

Internal irradiation can be triggered when radionuclides enter the human body by inhalation or ingestion [4, 5]. The most significant pathway for radionuclide ingestion is when radionuclides become integrated with food. Coincidental ingestion of soil material or soil dust is related to unusual soil ingestion called pica. The contaminated soil surface is transferred to hands, food and beverages, cigarettes, or other items that may cause ingestion of radioactive contaminants [6, 7]. Using *in vitro* bioaccessibility models, the digestion processes in the gastrointestinal tract can be imitated using a simplified technique. Bioaccessibility of compounds from their matrix during transit in the gastrointestinal tract can be examined as an aspect of oral internal exposure to the contaminant by applying an *in vitro* bioaccessibility model [8]. Bioaccessibility denotes the fragment of a contaminant that is propagated from soil into solution by digestive juices [9]. It constitutes the utmost number of contaminants that are available for intestinal absorption. This is the theoretical fraction convenient for adsorption through the gastrointestinal tract [10]. In this investigation, the sole medium for occupational exposure through radioactivity ingestion was when radionuclides became integrated with dust or other substances and were later exposed to food or other entities that were put into the mouth, for instance pens or fingers. Th and U cause concern for authorities as they may cause health hazards, particularly when they have been ingested. Th and U are both from chemical and radiological standpoints and their compounds are immensely toxic [11].

The *in vitro* bioaccessibility method was utilised to evaluate the LC and WLP residue radionuclide solubility potential or the ability of ^{232}Th and ^{238}U to be absorbed in the human digestive system. The study of ^{232}Th and ^{238}U solubility in synthetic gastrointestinal digestion liquid by applying a DIN *in vitro* bioaccessibility method is conducted outside the human digestive system in a system similar to the digestive systems of adults and children. Theoretically, if a fragment of discharged pollutants from soil entered the synthetic gastrointestinal fluids, then it could be implied as soluble. The absorption in the gut and transfer into the blood were represented by the maximum quantity of contaminants in the soil. This approach is also appropriate for bioaccessibility tests for allocating data in human health risk assessments. The objectives of this study were to determine the solubility level of ^{232}Th and ^{238}U in LC and WLP residue, and to analyse the effectiveness of ^{232}Th and ^{238}U solubility with synthetic gastrointestinal fluids using a DIN *in vitro* bioaccessibility method. Quantitative determination of ^{238}Th and ^{232}U in LC and WLP residue is of great interest and is vital for geological investigation. Bioaccessibility and oral bioavailability theories are significant to quantify the potential risks that are linked with oral exposure to environmental contaminants.

Materials and Methods

Sample collection and preparation

The LC and WLP residue samples used in this study were collected from the LAMP, Kuantan, Pahang. The samples were air-dried and passed through a 2 mm sieve for the later purpose of bioaccessibility assessment. The total initial concentrations of ^{232}Th and ^{238}U were analysed using a Bruker S8 Tiger X-Ray fluorescence spectrometer (XRF); the concentrations are shown in Table 1.

Table 1. Concentrations of ^{232}Th and ^{238}U before bioaccessibility method

	Concentration (mg kg^{-1})	
	^{232}Th	^{238}U
Lanthanide concentrate (LC)	18.0 – 101.0	2.0 – 6.0
Water leach purification (WLP) residue	27.0 – 155.1	2.0 – 6.9

DIN *in vitro* bioaccessibility method

The DIN *in vitro* bioaccessibility method was used to evaluate bioaccessibility. The German method E DIN 19738, which is also known as the Standardised German *In Vitro* Assay model, is a static gastrointestinal model that involves synthetic gastric fluids simulation followed by synthetic gastrointestinal fluids simulation [12]. The bioaccessibility method was started by suspending 2 g of LC or WLP residue samples in triplicate, where each sample was mixed with synthetic gastric fluids (solid to liquid ratio of 1:50) and later incubated for 2 hours at a pH of 1.4 ± 0.1. About 10 mL of the incubated gastric fluids were extracted, centrifuged at 3500 rpm for 15 minutes, and filtrated (0.45 µm filter paper) with a Rocker 400 laboratory vacuum pump. To fabricate the gastrointestinal fluids, the remaining volume of artificial gastric fluids was mixed with artificial intestinal fluids (solid to liquid ratio of 1:100). The artificial gastrointestinal fluids were further incubated for 6 hours at a pH of 7.5 ± 0.2. Then, 10 mL were extracted, centrifuged at 3500 rpm for 15 minutes, and filtrated. Both artificial fluids were incubated in a water bath that was kept at a constant temperature of 37 °C to simulate a normal human body temperature. The filtrated gastric and gastrointestinal fluids were sent for analysis with inductively coupled plasma mass spectrometry (ICP-MS) (Perkin Elmer ELAN 6000).

The elemental determination was conducted by irradiation of approximately 10 mL of each sample for 5 hours at the Malaysian Nuclear Agency, Bangi. Blanks of artificial gastric and gastrointestinal fluids without LC and WLP residue were run as controls. Table 2 portrays the preparation of artificial gastric and gastrointestinal fluids for the DIN *in vitro* bioaccessibility method. By analysing International Atomic Energy Agency (IAEA) standard reference materials (Soil-7 and 448), quality control of the analysis was conducted. The procedure was conducted to determine the concentrations of ^{232}Th and ^{238}U integrated in the gastrointestinal system at intervals of 5 hours.

Bioaccessibility of a particular radionuclide was calculated using the following equation 1:

$$\text{Bioaccessibility} = \frac{B_g}{B_s} \times 100\% \quad (1)$$

where B_q is the concentration of ^{232}Th or ^{238}U presented in artificial gastrointestinal fluids (mg kg^{-1}) and B_s is the concentration presented in samples before applying the *in vitro* bioaccessibility method (mg kg^{-1}).

The values of the committed effective dose and committed equivalent dose were calculated using the following equation 2:

$$H_A = \Sigma_j I_{Aj} h_{Aj} \quad (2)$$

where H_A is the committed effective dose or the committed equivalent dose (Sv) by ingestion, I_{Aj} is ^{232}Th or ^{238}U activity (Bq) in the samples (Bq kg^{-1}), and h_{Aj} is the ingestion dose coefficient (Sv Bq^{-1}) for the effective dose or the target organs for ^{232}Th or ^{238}U.

Table 2. Preparation for each sample (200 ml) in gastric fluid and (200 ml) in gastrointestinal fluid

	Gastric Fluid	Gastrointestinal Fluid
Bile Bovine	-	1.800 g
Calcium Chloride Dihydrate ($CaCl_2$ x $2H_2O$)	-	0.100 g
Hydrochloric acid (30% of HCl)	pH adjustment	-
Magnesium Chloride Hexahydrate ($MgCl_2$ x $6H_2O$)	-	0.040 g
Mucin	0.600 g	-
Pancreatin	-	1.800 g
Pepsin	0.200 g	-
Potassium Chloride (KCl)	0.140 g	0.060 g
Potassium Dihydrogen Phosphate (KH_2PO_4)	0.054 g	-
Sodium Bicarbonate ($NaHCO_3$ solid)	-	0.200 g
Sodium Chloride (NaCl)	0.580 g	pH adjustment
Trypsin	-	0.060 g
Urea (CH_4N_2O)	-	0.060 g
Final pH	2.0	7.5

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Results and Discussion

^{232}Th and ^{238}U concentrations

The accuracy of the procedure used for determination of total concentrations of ^{232}Th and ^{238}U in the LC and WLP residue was verified. The results are shown in Table 1. The XRF analysis showed that the concentrations of ^{232}Th in the WLP residue and LC were 155.1 mg kg^{-1} and 101.0 mg kg^{-1}, respectively, where the former was the highest concentration overall. On the other hand, the concentrations of ^{238}U in the WLP residue and LC were 6.9 mg kg^{-1} and 6.0 mg kg^{-1}, respectively. The WLP residue is the major waste material resulting from water leaching and purification processes of the LC in the rare earth industry. This process utilises magnesium oxide and water, which produces WLP residue and is considered the most toxic due to its elevated levels of U, Th, associated radioactivity, and heavy metals compared with neutralisation underflow (NUF) and flue gas desulphurisation (FGD) waste [13, 14]. The concentration of ^{232}Th varied in the LC and WLP residue, which could have been due to the geological composition and the content of ^{232}Th and ^{238}U samples from each area where the soils originated. The original ^{232}Th and ^{238}U concentrations in rocks may have varied because of alteration or metamorphic processes [15]. The concentration of ^{232}Th was highest in the WLP residue, as the WLP residue undergoes refining processes that cause ^{232}Th to easily separate from the minerals inside the soil [16].

Heavy metals and radionuclide behaviours in soil are significantly related to soil properties. Soil determinants, such as pH, ferromanganese oxides, and organic matter, may be better predictors for metal mobility [17]. According to the National Toxics Network (NTN) report, the rare earths concentrate imported from Australia is expected to have ThO_2 concentrations of 1600 mg kg^{-1} and U_3O_8 concentrations of 28 mg kg^{-1}. These concentrations correspond to a ^{232}Th activity concentration of 5.7 Bq g^{-1} and a ^{238}U activity concentration of 0.28 Bq g^{-1}. The WLP residue is expected to have a ThO_2 content of 1655 mg kg^{-1} and a U_3O_8 content of 22.5 mg kg^{-1} [15]. Based on the International Atomic Energy Agency (IAEA) report, the rare earth, Th, and U contents of the ore are shown in Table 3 [18]. These concentrations correspond to a ^{232}Th activity concentration of 5.9 Bq g^{-1} and a ^{238}U activity concentration of 0.24 Bq g^{-1}.

In this study, ^{232}Th and ^{238}U concentrations were converted to specific activity using a radioelement conversion factor, where 1 mg kg^{-1} of Th in rock is equal to 4.06 Bq kg^{-1} ^{232}Th, and 1 mg kg^{-1} of U in rock is equal to 12.35 Bq kg^{-1} ^{238}U. The specific activities of ^{232}Th for the LC and WLP residue were 0.4101 Bq g^{-1} and 0.6297 Bq g^{-1}, respectively, while the specific activities of ^{238}U in the LC and WLP residue were 0.0741 Bq g^{-1} and 0.0852 Bq g^{-1},

respectively. The specific activities of ^{232}Th and ^{238}U before the DIN *in vitro* bioaccessibility method were lower than those in the NTN report.

Table 3. Rare earth, thorium and uranium contents of Mount Weld Ore

	Concentration (%)	
	Average	**Maximum**
Total REO	17 - 18	42
ThO_2	0.075	0.18
U_3O_8	0.003	0.006

By using ICP-MS, the occupational exposure of workers to ^{232}Th and ^{238}U was evaluated by determining both concentrations in the gastrointestinal tract. Table 4 and Table 5 show the solubility of ^{232}Th and ^{238}U in the LC and WLP residue within the first 5 hour interval. The general concentrations of ^{232}Th and ^{238}U during the gastric phase were in the range of 0.0580–0.0598 mg kg^{-1} for ^{232}Th and 0.0473–0.0554 mg kg^{-1} for ^{238}U in the LC, while they were 0.4793–0.5495 mg kg^{-1} for ^{232}Th and 0.7401–0.8731 mg kg^{-1} for ^{238}U in the WLP residue. The concentrations of ^{232}Th and ^{238}U during the gastrointestinal phase were in the range of 0.1167–0.1410 mg kg^{-1} for ^{232}Th and 0.0437–0.0558 mg kg^{-1} for ^{238}U in the LC, and 0.0407–0.0480 mg kg^{-1} for ^{238}U and 0.1621–0.0779 mg kg^{-1} for ^{232}Th in the WLP residue.

Table 4. Concentration of ^{232}Th after DIN *in vitro* bioaccessibility method

Time (h)	**Concentration of ^{232}Th (mg kg^{-1})**			
	Gastric Phase		**Gastrointestinal Phase**	
	Lanthanide Concentrate (LC)	**Water Leach Purification (WLP)**	**Lanthanide Concentrate (LC)**	**Water Leach Purification (WLP)**
1	0.0598 ± 0.017	0.4793 ± 0.0755	0.1175 ± 0.008	0.1621 ± 0.119
2	0.0597 ± 0.027	0.5495 ± 0.0422	0.1167 ± 0.0198	0.0779 ± 0.0352
3	0.0597 ± 0.0257	0.5461 ± 0.0414	0.1261 ± 0.0159	0.0844 ± 0.0414
4	0.0580 ± 0.0221	0.5402 ± 0.0551	0.1260 ± 0.0347	0.0889 ± 0.046
5	0.0583 ± 0.0220	0.5222 ± 0.0414	0.1410 ± 0.0331	0.0951 ± 0.0529

Table 5. Concentration of ^{238}U after DIN *in vitro* bioaccessibility method

Time (h)	**Concentration of ^{238}U (mg kg^{-1})**			
	Gastric Phase		**Gastrointestinal Phase**	
	Lanthanide Concentrate (LC)	**Water Leach Purification (WLP)**	**Lanthanide Concentrate (LC)**	**Water Leach Purification (WLP)**
1	0.0473 ± 0.0059	0.7401 ± 0.1038	0.0437 ± 0.0086	0.0467 ± 0.0257
2	0.0523 ± 0.0048	0.8294 ± 0.0676	0.0534 ± 0.0124	0.0407 ± 0.0189
3	0.0525 ± 0.0054	0.8731 ± 0.0548	0.0535 ± 0.0132	0.0422 ± 0.0191
4	0.0554 ± 0.0045	0.8134 ± 0.0773	0.0558 ± 0.0164	0.0480 ± 0.0213
5	0.0500 ± 0.0043	0.8671 ± 0.2252	0.0517 ± 0.0098	0.0430 ± 0.0198

The maximum concentrations of ^{232}Th in the LC and WLP residue during the intestinal phase were 0.1410 ± 0.0331 mg kg^{-1} and 0.1621 ± 0.1190 mg kg^{-1}, respectively. As seen in Figure 1, the solubility of ^{232}Th in the LC during the gastric phase slightly decreased at period 6 (7-hour mark), while the solubility of ^{232}Th in the LC increased gradually during the intestinal phase. The increasing solubility of ^{232}Th in the LC during the intestinal phase was due to its content of ThO_2, which is insoluble in acid and alkali. According to Langmuir and Herman [19], ThO_2 solubility with organic ligands present is increased by 5 orders of magnitude compared with the purely inorganic solubility at a pH of 5. The range in increased solubility extended up to a pH of 8, where inorganic ligands alone only significantly affected the solubility below a pH of 7. Thus, it was proven that ^{232}Th might exist in insoluble and refractory forms in LC. After treating the LC with concentrated sulphuric acid in the plant process, ^{232}Th was removed with other impurities into the WLP residue and remained in insoluble form, which was not dissolved by strong acids or alkali. Furthermore, the differences in pH in the content of the upper gastrointestinal tract between fed and fasted states may also influence the dissolution and absorption of weakly acidic and basic of ingestion soil. The fate and mobility of Th in environmental media are governed by its chemical and biological behaviours. The quadrivalent Th compounds are very stable towards reducing agents. Because of its low solubility, Th, which is discharged as ThO_2 on water surfaces from mining, milling, and processing, is present as suspended particles or sediments in water [20]. The International Commission on Radiological Protection (ICRP) has proposed a human gastrointestinal absorption value of 0.02 % for all forms of Th [21]. Based on Johnson and Lamothe's review of literature, a human gastrointestinal absorption value of 0.1 % to 1 % was calculated [22]. Meanwhile, the United State Environmental Protection Agency (USEPA) highlighted that the average person ingests about 2 µg of U in food and water every day, but only a very minor fraction of 1 % or 2 % is absorbed into the body [23].

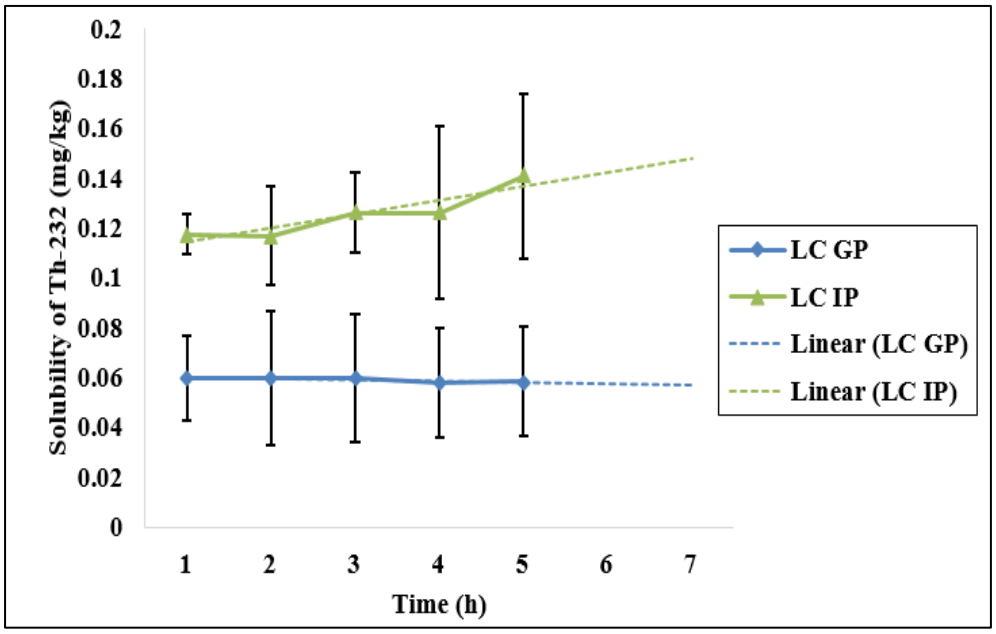

Figure 1. ^{232}Th solubility in lanthanide concentrate and water leach purification residue during gastric phase

Figure 2 shows that the solubility of ^{232}Th in the WLP residue during the gastric phase gradually increased. Contrastingly, the solubility of ^{232}Th in the WLP residue during the intestinal phase decreased. The decrease in ^{232}Th in the WLP residue could have been due to chemical precipitation at a pH of 7.5, while the solubility of ^{232}Th decreased due to adsorption in mineral soils, organic material, and other suspended solids because absorption of metals by soil is known to increase with pH [24]. Increasing pH intensifies ^{232}Th adsorption into clays, oxides, and organic matter, which is almost accomplished at a pH of 6.5 [25]. Soil properties, particularly pH and existing organic matter, influenced the absorption of radionuclides in soil [26]. Th in the tetravalent oxidation state forms insoluble crystalline or hydrous oxides that can perpetuate in low aqueous concentrations in natural waters and

waste repository environments [27]. Hydroxide and carbonate are the two dominant ligands in the groundwater system. Hydrous Th(IV) oxides are soluble at low pH values, but the solubility decreases significantly at pH values higher than 3–4. Therefore, it was practical to use amorphous hydrous Th(IV) oxide in this study, as it is the initial solid phase precipitated under oversaturation conditions and equilibrates with the aqueous phase more rapidly [28].

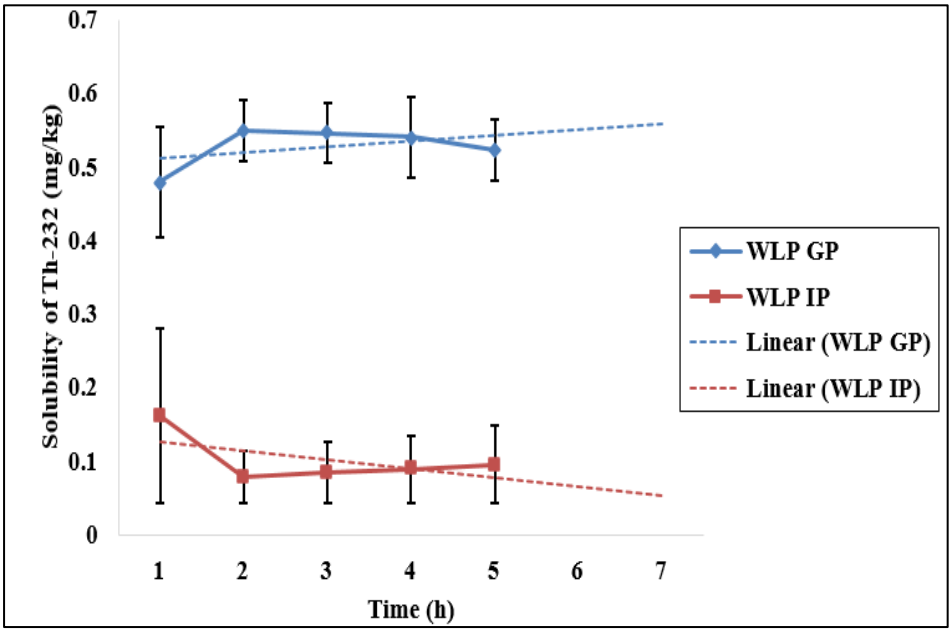

Figure 2. ^{232}Th solubility in lanthanide concentrate and water leach purification residue during gastrointestinal phase

The solubility of ^{238}U in the LC and WLP residue during the gastrointestinal phase is presented in Figure 3 and Figure 4. The results in Figure 3 show that based on the trendline pattern at 6 and 7 hours, the solubility of ^{238}U in the LC during the gastric phase and gastrointestinal phase increased with respect to time. Comparing Figure 3 with Figure 4, the following results depicted that the solubility of ^{238}U in the WLP residue increased during the gastric phase and was consistent when entering the intestinal phase. The solubility of ^{238}U in the WLP residue was higher than that in the LC during the gastric phase. The maximum solubility of ^{238}U in the LC and WLP residue was 0.8731 ± 0.0548 mg kg^{-1} during the gastric phase and 0.0558 ± 0.0164 mg kg^{-1} during the gastrointestinal phase. The overall result showed that the solubility of ^{238}U in the LC and WLP residue during the gastric phase was higher than that in the intestinal phase due to the more acidic pH in the gastric phase. As stated by Oliver et al., the solubility of trace elements can be improved by lowering the pH of stomach synthetic gastric fluid [29]. This results in ^{238}U being dissolved with acid in a chemical reaction. It can be said that ^{238}U reacts chemically under acidic conditions compared to alkaline conditions.

Lynas' report documented that over 99 % of ^{238}U in the feed LC is eliminated to WLP residue and by calcination at temperatures up to 600 °C, and ^{238}U is transformed into refractory and insoluble forms and later discarded into the WLP residue [15, 30]. The solubility of ^{238}U is very minimal when the pH surpasses 1. Contrarily, ^{238}U solubility is elevated by lowering the pH value. This affects the dissolution of ^{238}U with acid in chemical reactions [31, 32]. ^{238}U concentrations rely on the intake amount of the soil samples, volume of gastric fluid, and volume of intestinal fluid [33]. In addition, the solubility of ^{238}U shows the amount of ^{238}U that is dissolvable in gastrointestinal fluids, and it shows an association between concentration and solubility. Table 5 exhibits the maximum concentration of ^{238}U in the gastrointestinal phase for high-risk cases, which was 0.0558 ± 0.0164 mg kg^{-1}.

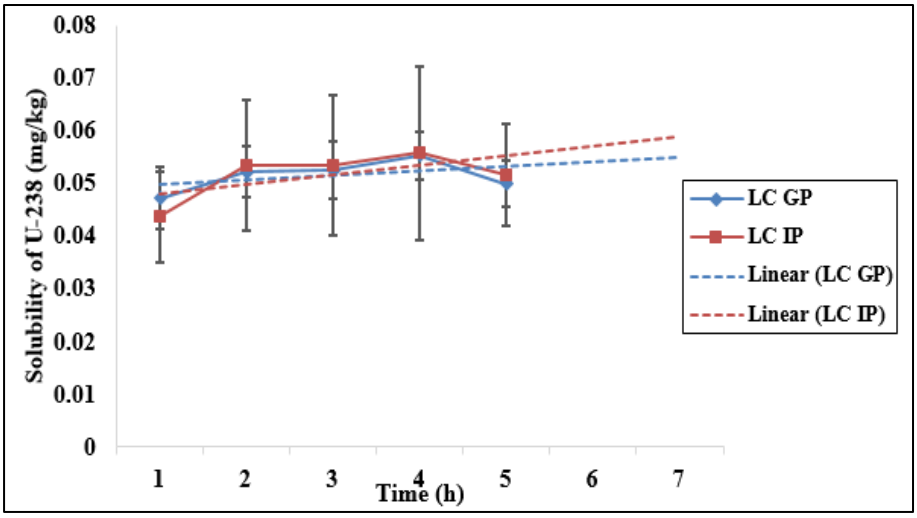

Figure 3. Solubility of ^{238}U in lanthanide concentrate and water leach purification residue during gastric phase

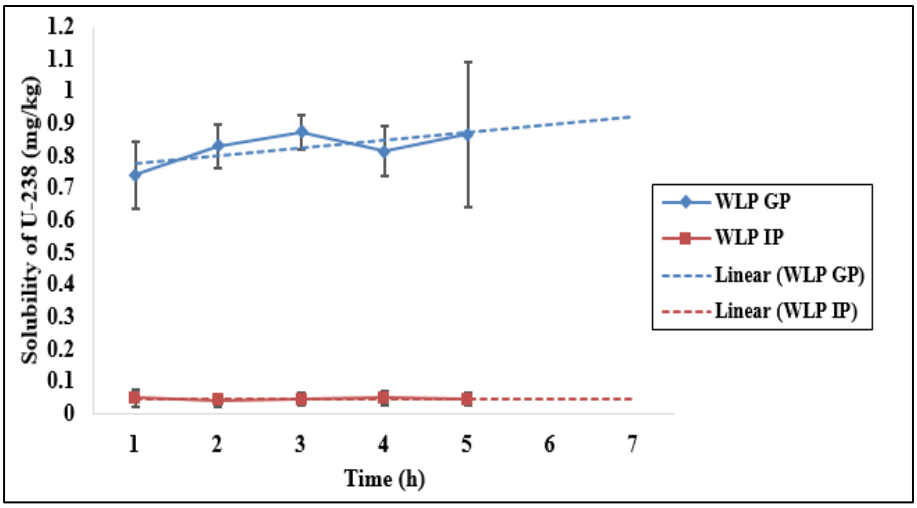

Figure 4. Solubility of ^{238}U in lanthanide concentrate and water leach purification residue during gastrointestinal phase

Specific activity of ^{232}Th and ^{238}U in the samples

Correspondingly, the maximal concentrations of ^{232}Th in the LC and WLP residue during the intestinal phase for high-risk cases were 0.1410 ± 0.0331 mg kg^{-1} and 0.1621 ± 0.1190 mg kg^{-1}, respectively. Meanwhile, the maximum concentrations of ^{238}U in the LC and WLP residue were 0.0558 ± 0.0164 mg kg^{-1} and 0.0480 ± 0.0213 mg kg^{-1}, respectively, during the intestinal phase for high-risk cases. During this study, maximum values of ^{232}Th and ^{238}U solubility were recorded to diagnose high-risk cases. Table 6 and Table 7 present the daily and annual intakes, as well as the daily and annual specific activities of ^{232}Th and ^{238}U in the LC and WLP residue during the gastrointestinal phase. In the report of the Agency for Toxic Substances and Disease Registry (ATSDR) of 1990, the daily intake of Th from food and water ingestion was 0.0023 µg kg^{-1}. Based on Table 6, it can be seen that the daily intake of ^{232}Th was lower than the ATSDR reference level [34]. The ^{238}U day-to-day intake was below the minimal risk level for intermediate-duration ingestion where the recommended oral uptakes are 0.0020 mg kg^{-1} day^{-1} [35], 0.0007 mg kg^{-1} day^{-1} [36], 0.0006 mg kg^{-1} day^{-1} [37, 38], and 0.0002 mg kg^{-1} day^{-1} [39].

Table 6. The daily concentration intakes, annual concentration intakes, daily specific activity intakes, and the annual specific activity intakes of ^{232}Th in the samples

	Maximum intake of ^{232}Th			
	Daily		**Annual**	
	(mg kg^{-1} day^{-1})	**(Bq kg^{-1} day^{-1})**	**(mg kg^{-1} year^{-1})**	**(Bq kg^{-1} year^{-1})**
Lanthanide concentrate (LC)	0.260	1.057	95.012	385.750
Water leach purification (WLP)	0.432	1.755	157.777	640.576

Table 7. The daily concentration intakes, the annual concentration intakes, the daily specific activity intakes and the annual specific activity intakes of ^{238}U in the samples

	Maximum intake of ^{238}U			
	Daily		**Annual**	
	(mg kg^{-1} day^{-1})	**(Bq kg^{-1} day^{-1})**	**(mg kg^{-1} year^{-1})**	**(Bq kg^{-1} year^{-1})**
Lanthanide concentrate (LC)	0.112	1.3783	40.734	503.065
Water leach purification (WLP)	0.096	1.186	35.040	432.749

Bioaccessibility of ^{232}Th and ^{238}U

A compound moving from its matrix (bioaccessibility) in the gastrointestinal tract is a dynamic process with constant changes in physiological conditions. By making use of *in vitro* bioaccessibility models, the digestion process in the gastrointestinal tract is imitated in a more intelligible manner by using physiological-based conditions, namely the chemical composition of digestive fluids, pH, and the usual residence times for each movement.

The gastrointestinal bioaccessibility of ^{232}Th and ^{238}U are summarised in Table 8. Based on these observations, the values of ^{232}Th radionuclide bioaccessibility in the LC and WLP residue were 0.14% and 0.10%, respectively. Concurrently, ^{238}U bioaccessibility in the WLP residue during the gastric phase was significantly higher than other values. As highlighted by Oomen et al. [9, 40], pH is probably the main factor that influences the final outcome; low pH during the stomach phase causes higher bioaccessibility values. Aside from stomach pH as a digestion parameter, residence time and bile salt concentrations also influence the bioaccessibility measurements [41]. The contaminant bioaccessibility can be determined in each compartment; however, compound absorption predominantly occurs in the small intestine, which is also known as the gastrointestinal phase. Therefore, bioaccessibility is only determined in the gastrointestinal chyme [42]. Thus, the value for the gastrointestinal phase was appraised in this study. Bioaccessibility illustrates the fraction of a chemical that desorbs from the soil matrix and is accessible for intestinal absorption.

The ^{238}U radionuclide in the LC had the highest bioaccessibility value (0.93%), whereas the ^{238}U in the WLP residue yielded lower values, which was 0.70% in the gastrointestinal phase. As specified by Morrow et al. [43], solubility in the body fluids is the best predictor of U compounds that are absorbed in the human body, rather than their water solubility [44]. The maximum bioaccessibility values for ^{232}Th and ^{238}U were 0.14% and 0.93%, respectively, which were lower than the bioaccessible fraction, i.e. $F_B < 1$. This verified that the value had lower internal exposure. The maximum amount of a contaminant available for absorption inside the human body is represented by F_B; therefore, the oral bioavailability may not be higher than the bioaccessibility. Thus, a bioaccessibility of lower than 100 % suggested that the internal exposure to the contaminant was lower compared to the external exposure, and that the internal exposure to the contaminants was overestimated [9, 40].

Table 8. Bioaccessibility of ^{232}Th and ^{238}U in lanthanide concentrate and water leach purification residue by DIN *in vitro* bioaccessibility model

	Bioaccessibility (%)	
	^{232}Th	**^{238}U**
Lanthanide concentrate (LC)	0.14	0.93
Water leach purification (WLP)	0.10	0.70

Equivalent dose and effective dose

According to International Atomic Energy Agency (IAEA) [45], the committed equivalent tissue dose per unit activity for ^{232}Th ingested by adults is 70 µSv Bq^{-1} for bone surfaces, 0.78 µSv Bq^{-1} for the kidneys, 0.74 µSv Bq^{-1} for the liver, and 2.0 µSv Bq^{-1} for red marrow. According to the ICRP [21], the committed effective dose coefficients of ^{232}Th for workers and the public are 0.22 µSv Bq^{-1} and 0.23 µSv Bq^{-1}, respectively. In contrast, the dose coefficient committed equivalent tissue dose per unit activity for ^{238}U ingested by adults is 0.71 µSv Bq^{-1} for bone surfaces, 0.25 µSv Bq^{-1} for the kidneys, 0.096 µSv Bq^{-1} for the liver, and 0.075 µSv Bq^{-1} for red marrow. Based on the ICRP 60, the committed effective doses of ^{238}U for workers and the public are 0.44 µSv Bq^{-1} and 0.45 µSv Bq^{-1}, respectively. High committed equivalent doses and committed effective doses of ^{232}Th and ^{238}U that were found in the LC and WLP residue are presented in Table 9 and Table 10, respectively. The committed equivalent doses and committed effective doses of ^{232}Th and ^{238}U in Table 9 and Table 10 were below the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) reference values.[46].

Table 9. Committed equivalent doses and committed effective doses of ^{232}Th

	^{232}Th (µSv)					
	Committed Equivalent Doses				**Committed Effective Doses**	
	Kidneys	**Liver**	**Bone Surfaces**	**Red Marrow**	**Public**	**Workers**
Lanthanide Concentrate (LC)	1.204	1.142	108.009	3.086	0.355	0.339
Water Leach Purification (WLP)	1.999	1.896	17.936	5.125	0.589	0.564

Table 10. Committed equivalent doses and committed effective doses of ^{238}U

	^{238}U (µSv)					
	Committed Equivalent Doses				**Committed Effective Doses**	
	Kidneys	**Liver**	**Bone Surfaces**	**Red Marrow**	**Public**	**Workers**
Lanthanide Concentrate (LC)	0.503	0.193	1.429	0.151	0.091	0.089
Water Leach Purification (WLP)	0.433	0.166	1.229	0.130	0.078	0.076

Conclusion

In summary, the present study illustrated that bioaccessibility of ^{232}Th and ^{238}U in the gastric phase is higher than that in the gastrointestinal phase; the values were acquired using DIN *in vitro* bioaccessibility methodology. Health risk assessments depicted the estimated daily intake, committed equivalent, and effective doses of LC and WLP residue through ingestion as significantly lower than the acceptable reference level. Therefore, there were no health

effects related to the radiotoxicity of the incorporated nuclides. Finally, future research is required in order to differentiate ^{232}Th and ^{238}U by *in vivo* bioavailability values measured using different biomarkers and non-identical animal models.

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