Synthesis of a humic acid-silica gel as a low cost adsorbent for uranium and thorium removal from wastewater

（汚染水からウランとトリウムを除去する経済的な吸着剤としてのフミン酸–シリカゲル複合体の合成）

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…in the name of Allah, the most gracious and the most merciful…

…for June Magdalène and Cézáre

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(汚染水からウランとトリウムを除去する経済的な吸着剤としてのフミン酸-シリカゲル複合体の合成)

Environmental pollution by heavy metals and radioactive elements e.g. thorium (Th) and uranium (U) is a major problem in many countries especially developing countries due to its impact to the ecosystem and human health. Apart from the environmental concern, both Th and U possess important role in future energy, hence several separation and pre-concentration techniques have been developed. Among these, solid phase extraction holds several advantages due to its capability and versatility to deal with very low concentration of pollutant.

Several adsorbents have been synthesized for solid phase extraction of Th and U. However, many of these are considered expensive due to complicated procedure and special and even toxic chemicals used in their preparation, which hinder their wide applicability and future scale up. This problem inspired the need to synthesize a new adsorbent in this research by using cheap and widely available material and easy procedure, which possess advantageous features such as selectivity and reusability. To reach that goal, humic acid and silica gel would be proposed as inexpensive precursor materials for adsorbent synthesis. Further in this study, there are three objectives, first is to clarify the availability of humic acid as functional group of an adsorbent for Th and U removal. Second is to develop low-cost humic acid-silica gel adsorbent, which exploits

their respective advantages. Third is to highlight the advantages of synthesized adsorbent in terms of its performance in Th and U removal.

This dissertation consists of 5 chapters. Chapter 1, General Introduction, explains the background, the purpose and objective of the study. In Chapter 2, the content is focused on the clarification of Th and U adsorption by humic acid attached covalently to the surface of silica gel by conventional method silylation. Adsorption parameters such as pH, adsorbent dose, kinetics, sorbate initial concentration, salinity effect, reusability, and lanthanide effect were studied and the results would be set as comparison for results in next chapters. Chapter 3 describes further simplification in humic acid-silica gel adsorbent synthesis, which employed single pot sol-gel method. The characterization results confirm the success in adsorbent synthesis and the performance test in Th and U removal showed comparable results to those described in previous chapter.

Chapter 4 proposed easier and inexpensive method in attaching humic acid to the surface of silica gel by replacing organosilicon with cross-linked chitosan to solve problems encountered by sol-gel method i.e. applicability at narrow pH range and high saline matrix. The success in adsorbent synthesis using chitosan was confirmed by characterization results. The adsorption tests showed the adsorbent is available for wide range pH and high saline condition.

In final chapter, General Conclusions, it is concluded that humic acid and silica gel are suitable low cost functional group and support material respectively. Based on the study results, the combination of humic acid and silica gel to produce adsorbent could be developed by several schemes in order to increase its economical merit i.e. sol-gel and chitosan coating. The success in each process was confirmed by the characterization results. The study also concluded that the performance of humic acid-silica gel adsorbents synthesized in this research have advantages

compared to adsorbents previously reported in terms of capacity, equilibrium time, reusability, salinity, and separation ability.

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CHAPTER 1

GENERAL INTRODUCTION

1.1 Background

Environmental pollution by heavy metals and radioactive elements, e.g. thorium (Th) and uranium (U) is considered as major concerns in many countries, especially developing countries due to their impacts to the ecosystem and human health. The effects of both elements have been documented including deterioration of kidney, brain, liver, heart and other system in human body [1, 2] and exposure to Th could increase the risk of bone and lung cancer since this radioactive element is accumulated in these organs [3].

Several activities could release both elements to the environment including mining activities, processing and utilization [4, 5]. Mining activities, which target these elements or produce these elements as by-products due to their close association in nature, i.e. rare earth elements in monazite, xenotime and bastnasite and tin in cassiterite minerals. These minerals are generally found as placer deposits associated in beach environment, which are common in Indonesia, Malaysia and Australia. Yusof et al. [5] reported the U content in water sample from abandoned tin mining pools in Malaysia was 27.7 – 110.5 μg L^{-1} while Th was 41.8 – 297.2 μg L^{-1}.

Apart from the environmental concern, both Th and U possess important roles in future energy [6]. Therefore, several separation and pre-concentration of Th and U have been developed including liquid-liquid separation, chemical separation, electrochemical treatment, intracellular sequestration, e.g. phytoextraction and solid phase extraction. Among these methods,

solid phase extraction holds several advantages since this method is cost effective, versatile, very little chemical and waste produce in its application [7]. Besides, the outstanding feature of this method compared to the others is its ability to deal with very low concentration of pollutant which is suitable to recover Th and U in radioactive waste [8].

Several adsorbent have been synthesized for solid phase extraction of Th and U including composite of polyacrilonitrile on zeolite [9], amine modified silica gel for U [10], 5-mercapto-1-methyltetrazole derivative modified clays for Th [11], tri-octylphosphine oxide coated silica gel for Th [12], glycidyl methacrylate for U [13], tin oxide nanoparticle for U [14], manganese oxide coated zeolite for U [15]. However, most of adsorbent synthesized so far are deemed expensive because of complicated procedure and toxic chemicals used in their preparation, which further hinder the application of this method especially in developing countries where the environmental problems frequently occur. This problem inspired this research to develop alternative low-cost adsorbent material based on humic acid and silica gel.

1.2 Humic acid and silica gel as precursors of low cost-adsorbent

The term adsorption in general could be defined as a process to bind a certain material at solid surface from liquid or gaseous phases [16]. There are two major classes of adsorption namely physical and chemical adsorption. In physical adsorption, the attraction between target material and solid surface is generated by intermolecular forces (van der Waals forces) and due to its relatively weak nature, the adsorption reaction is reversible. In the case of chemical adsorption, the interaction between target and solid surface is caused by a chemical bonding and due to strong attraction, the reaction is generally irreversible.

As previously mentioned, due to many advantages of adsorption to deal with pollutants, researchers have proposed numerous adsorbents, which are unfortunately still emphasized on the novelty whether in the raw material used or method in the synthesis, dismissing their wide applicability and possible future scale up. In recent years, the trend to develop low-cost adsorbent becomes apparent. In spite of many review papers addressing the subject of low cost adsorbent including [17-20], until now low-cost adsorbent is still vaguely defined. Bailey et al. [20] assumed the low cost adsorbent is made of material which is abundant in nature and mostly as by-product or waste of another industry and requires little processing.

According to this assumption many low-cost materials have been proposed as adsorbent including fly ash [21], lignite [22], egg shell [23], coconut coir dust [24], and even human hair [25]. However, many researchers in low-cost adsorbent are still focusing on the simplicity in producing the adsorbent with little or no processing and did not address important points such as selectivity and reusability of the adsorbent. Reusability could be included in the term of low-cost since the reusable adsorbent for several cycles could reduce the remediation cost and reduce further waste. Besides, in the regeneration process, in case the target elements are not only toxic but also possess economical value like Th or U, they could be recovered for further use. The selectivity is considered important since this parameter encourages the application of solid phase extraction not limited to environmental restoration but also other area such as separation and purification. To address these points, the preparation factor should be considered. According to Siswoyo [26], an adsorbent possess high adsorption capacity with low preparation cost could be considered as low-cost adsorbent. In this research, the term low-cost adsorbent is defined as adsorbent synthesized by simpler schemes, which require less chemicals, precursors, preparation time and cost, including side effect cost i.e. disposal, after compared with other adsorbent synthesized from the

same raw materials, without significant difference in terms of adsorption performance e.g. capacity, selectivity and reusability. The raw materials proposed in this research are humic acid and silica gel.

Humic acid is a major organic component in soil, peat and coal, and could be found also in aquatic environment such as river, lake and seawater [27]. Humic substance is produced by the degradation of organic material and further the humic substance could be categorized into 3 components: humic acid, fulvic acid and humin according to their solubility in water. Humin is insoluble component, in contrast to fulvic acid, which is soluble in both acid and basic solution, while humic acid is only soluble in basic solution. Humic acid and fulvic acid are extracted from soil by strong basic solution such as sodium or potassium hydroxides and humic acid is further separated from fulvic acid through coagulation by decreasing the solution pH to 1 using hydrochloric acid.

Humic acid has the ability to bind metal ions to form complex due to the presence of certain functional groups such as carboxyl, phenol and mixed ligand [28]. This ability coupled with its omnipresent distribution, make humic acid be considered as low-cost precursor material in adsorbent synthesis. To the best of author's knowledge, the publication reported the humic acid as precursor in adsorbent synthesis is still very limited which is mainly caused by the difficulty in the separation of humic acid from the aqueous phase. This major problem was solved by attaching humic acid to an insoluble micro-particle as supporting material [7, 29, 30] or other techniques including thermal treatment up to 330° C [31] and insolubilization [32], in order to make separation by sedimentation or centrifugation is deemed possible. Among supporting material, silica gel as proposed by Prado et al. [33] and Koopal et al. [34] possesses advantages in terms of physical strength, easily controlled structural parameters (surface area, pore size, particle shape) and stability [35]. Besides, silica gel have been intensively used in

chromatographic studies [34] and its omnipresence in nature which is frequently associated with humic acid [36].

1.3 Objectives and advantages of this study

The main purpose of this study is to develop low-cost humic acid-silica gel based adsorbent, which exploit their respective advantages. Unstable humic acid with high binding capacity while silica gel with low binding capacity would be served as functional groups and supporting materials, respectively. Further in this study, there are three objectives, first is to clarify the adsorption process of Th and U with humic acid attached covalently to the silica gel through silylation process. The humic acid-silica gel adsorbent synthesized by silylation would be served as comparison to appraise cost-affectivity of other adsorbents produced in this research, since the silylation is regarded as one of the most common method used in adsorbent synthesis. Further, the possibility to recover Th and U and their separation from lanthanides are also studied. The second objective is to synthesize a composite of humic acid-silica gel by cheap and simple sol-gel process as a low cost adsorbent for Th and U removal. This method is proposed as substitution of expensive and complicated silylation method. The third objective is to develop the method in attaching humic acid to the surface of silica gel by using cross-linked chitosan in order to address limitation encountered in previously synthesized adsorbent.

The methods proposed to produce adsorbents in this study could be regarded as fundamental information to develop other low-cost adsorbents, not only for humic acid but also for other functional groups. The results demonstrate that proposed low-cost method could be used to produce adsorbent with high capacity comparable to that of adsorbent synthesized with conventional method. All materials used in this study are inexpensive materials and widely

available especially in developing countries. This is considered important since in these countries the environmental problems are still regarded as crucial issues due to limited resources and technology. Therefore, the results of this study are expected to solve the problem of water pollution and wastewater treatment.

1.4 Organization of the dissertation

The dissertation entitled "Synthesis of a humic acid-silica gel as a low cost adsorbent for uranium and thorium removal from wastewater" consists of five chapters. In the study, three kinds of absorbents were developed using humic acid and silica gel as precursors which development progressed in order of versatility of their preparations. The next progress was responses to the problems encountered in previous stage.

Chapter 1, General Introduction, explains the background, the purpose and objectives of the study including the description of humic acid based adsorbent development. In Chapter 2, the content is focused on the clarification of Th and U adsorption by humic acid attached covalently to the surface of silica gel by conventional method silylation. Adsorption parameters such as pH, adsorbent dose, kinetics, sorbate initial concentration, salinity effect, reusability and lanthanide effect including Th and U recovery by acid leaching process were studied and the results would be set as comparison for results in next chapters. Chapter 3 describes simplification in humic acid-silica gel adsorbent synthesis, which employed single pot sol-gel method. The characterization results confirm the success in adsorbent synthesis and the performance test in Th and U removal showed comparable results to those described in previous chapters.

Chapter 4 addresses the synthesis problem in previous chapter. This chapter proposed easier and inexpensive method in attaching humic acid to the surface of silica gel by replacing

organosilane used in conventional method by cross-linked chitosan to solve problems encountered by sol-gel method. The success in adsorbent synthesis using chitosan was confirmed by FT-IR, SEM and SEM-EDS characterization. The adsorbent performance in Th and U removal was also tested, which showed the results were comparable to the performance of adsorbent synthesized by conventional method in previous chapter. Chapter 5 is General Conclusions, which summarizes the results of each study objective and conclusions in general.

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CHAPTER 2

SOLID PHASE EXTRACTION OF THORIUM AND URANIUM AND THEIR SEPARATION FROM LANTHANIDES USING HUMIC ACID MODIFIED SILICA GEL AS LOW COST ADSORBENT

Abstract

Solid phase extraction and separation of thorium (Th), uranium (U) and lanthanides were achieved using humic acid modified silica gel (Si-HA). The adsorption capacity, the effects of contact time, pH, and adsorbent dose were examined at room temperature. The maximum sorbent capacity (pH = 3) for Th and U was 28.0 and 43.9 mg g^{-1}, respectively. The isotherm parameters denoted the adsorption was favorable, and optimum condition was attained within 90 min. The kinetic data conformed well to pseudo-second order and intra particle diffusion model. The separation of these elements was possible through sequential leaching with EDTA, citric acid and nitric acid to recover lanthanides, U and Th, respectively. The salinity did not significantly affect the Si-HA ability to extract Th and U. The sorbent stability and reusability were also assessed through four-adsorption-desorption cycles. The simplicity of the proposed separation method along with the stability of the sorbent and high regeneration efficiency in acidic conditions demonstrated the merit of the Si-HA as low cost sorbent.

Keywords: solid phase extraction, separation, thorium, uranium, lanthanides, humic acid

2.1 Introduction

Thorium (Th) and uranium (U) have an important role in economic and environmental domains. Mining activities, ore processing and nuclear-energy programs produce wastes which pollute soil and groundwater. To reduce the risk, the removal of these elements is mandatory prior to release into the environment. These radioactive elements are closely associated with lanthanides in nature e. g. monazite and bastnaesite minerals [1]. Since lanthanides are also economically essential elements in modern technology [2], separation technique to remove Th, U and lanthanides is important not only in terms of environmental restoration but also in hydrometallurgy and nuclear fuel treatment [3].

Several methods had been developed for the extraction and recovery of Th, U and lanthanides, such as precipitation, liquid-liquid separation, electrochemical and phytoextraction. Generally, liquid-liquid separation [4-6] is applied to separate Th and U from lanthanides. However, these techniques also had limitations, which are solved by solid-liquid separation technique: cost effective, convenient, fewer chemicals used and less waste produced. Also the separation by solid sorbents is considered amenable for low metal and pollutant concentration e. g. radioactive waste [7, 8].

Various sorbents have been investigated to pre-concentrate Th and U from aqueous solutions [9-15], but the reports described their recovery and separation from lanthanides are still limited. Besides, many sorbent materials investigated were not cost effective due to expensive and not widely available chemicals. Complicated preparation procedure also hinders its application to larger scale. On the other hand, humic acid offers the solution to the problems since it is inexpensive and widely available and has high ability to bind metal elements [16].

Unfortunately, the applicability of humic acid is hindered by the difficulties in its separation from the liquid phase. This problem has been overcome by attaching humic acid molecules to larger inorganic or organic particles as a support, including zirconium pillared clay [7] and silica gel [17]. Silica gel is one of the most popular supports because of its advantages in terms of stability, physical strength and easily controlled structural parameters [18]. One of the most common schemes for attaching a functional group, including humic acid, to the silica gel surface is silylation [16] (Fig 2.1).

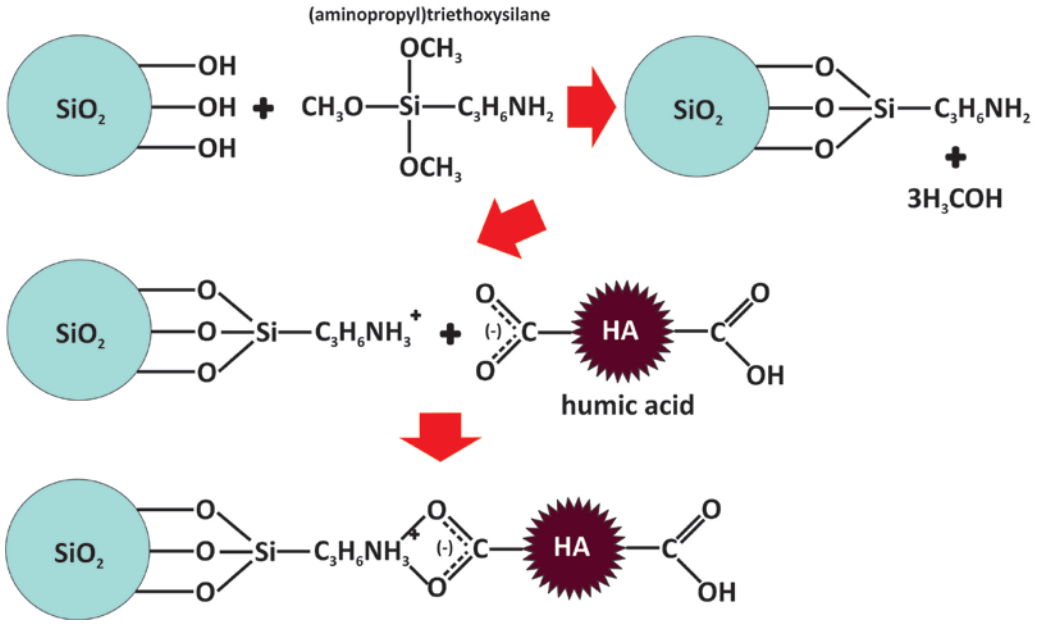

Fig 2.1 Silylation process to attach functional group (in this case humic acid) on silica gel surface (Si-HA), (modified from Prado et al. [16]).

Silica gel modified with humic acid (Si-HA) so far had been used to study the binding interaction between humic acid and metals including transition metals [17, 19] and transuranic cations [20-22]. However, the applicability of humic acid supported by silica gel to recover Th

and U including the separation between them and separation of these elements from lanthanides remains unknown.

In this chapter, it is examined the feasibility of Si-HA for pre-concentration and separation of Th, U and lanthanides through the following experiments: 1) solid phase extraction of Th, U and lanthanides by Si-HA from aqueous solution as a function of acidity, sorbent dose, metal concentrations and their adsorption kinetics; 2) recovery and separation of Th and U from lanthanides retained by Si-HA; 3) applicability of Si-HA in Th, U and lanthanides extraction in high saline condition; 4) reusability studies to assess the stability and economic merit of the Si-HA sorbent.

2.2 Materials and methods

2.2.1 Instrumentation and chemical reagents

The pH was measured by pH meter F-52 Horiba. Elemental analysis for mixture solution was performed by using inductively coupled plasma-atomic emission spectrometry (ICP-AES) SPS-7700; Seiko Instrument Co. Single solution was analyzed using spectrophotometric method based on color complex of Th, U and lanthanides with Arsenazo III (Alfa Aesar, USA). Solutions of Th and U were prepared by appropriate dilution of thorium nitrate and uranyl nitrate hexahydrate salts (Wako Chemical Japan), while lanthanide (La, Nd, Dy and Yb) solutions were prepared by dilution of ICP standard solutions (1000 mg L^{-1}) provided by Cica-Merck, Japan. All dilutions were performed using purified water (Milli-Q system, Millipore). Commercial humic acid provided by Acros Organic USA was purified by published procedure [23]. A 10 gram humic acid sodium salt was dissolved in 1 L of sodium hydroxide 0.1 M, stirred for 12 hours and centrifuged at 2500 rpm for 30 minutes to separate the undissolved matter. To precipitate the

humic acid fraction, hydrochloric acid was added to supernatant solution to bring pH to 2. The mixture again was stirred for 24 hours and centrifuged at 2500 rpm for 30 minutes to precipitate humic fraction. The precipitate was then washed with hydrochloric 0.01 M to remove the soluble fraction and inorganic salts. The humic acid fraction was finally dried at 50°C.

2.2.2 Sorbent preparation

The silica gel modified by humic acid (Si-HA) used in this study was prepared by modified procedure from Prado et al. [17] as follows. Twenty grams activated silica gel (particle size of 40–63 µm) was suspended in 100 ml of dry toluene. Twenty milliliters of 3-aminopropyltrimethoxysilane was added to this suspension, and refluxed at 140 ℃ for 72 hours to produce a Si-NH_2 suspension. The suspension was separated by centrifugation, washed with water and dried at 50 ℃. One gram Si-NH_2 was suspended in 30 ml of 0.1 M sodium hydroxide containing 300 mg of the purified humic acid (pH 7.5) and stirred for 20 hours at room temperature to produce Si-HA suspension. The suspension was separated, washed with 0.2 M sodium chloride solution pH 10 and 1 mM hydrochloric acid and finally dried at 120℃ for 24 hours. Koopal et al. [23] reported that the amount of humic acid immobilized on silica gel surface was 42 mg g^{-1} SiO_2 and amount of humic acid released after washing with basic solution (pH 11) for stability test was 2.4%.

2.2.3 Optimum condition by batch adsorption experiments

Batch experiments of metal ion adsorption onto Si-HA were carried out to elucidate the optimum condition in the adsorption process by varying the pH, sorbent dose, metal ion concentration, adsorption kinetics, effect of salinity and ionic strength and also to test the

regeneration or reusability of the Si-HA sorbent. In the batch method, 50 mg of sorbent was equilibrated with 25 ml of metal solution by stirring at 500 rpm at room temperature. Preliminary experiments showed that equilibrium was attained within 3 hours. The supernatant solution was separated by centrifugation, and the metal ion concentrations were determined.

The effect of the acidity of the aqueous phase on the recovery of metal ions was carried out at pH 0.5 to 7 (adjusted by hydrochloric acid and sodium hydroxide) by equilibrating Si-HA sorbent with metal solution with initial metal concentration (C_i) of each ion of 2 mg L^{-1}. The effect of the sorbent dose on the metal adsorption was examined in the range 0.5 – 7.0 g L^{-1} (sorbent weight/solution volume) at pH 3 (Th and U) or 6.5 (lanthanides). The isotherm adsorption experiments were performed by varying the initial concentration (2–250 mg L^{-1}) of each element at the optimum pH. The mixture was then centrifuged, and the equilibrium metal concentration in the aqueous phase (C_E) was determined. The amount of metal adsorbed per unit mass of sorbent, namely the adsorption capacity (q, mg/g), was calculated by the equation $q = (C_i - C_E)Vm^{-1}$. Where V is the volume of aqueous phase (ml), and m is the sorbent added (mg).

In the adsorption kinetic studies, the metal uptake by sorbents was determined in the time intervals of 15, 30, 60, 90, 120, 180 and 240 min at constant temperature (25℃). To study the effect of salinity and ionic strength, Si-HA sorbent was equilibrated with metal solution which contain various concentration of sodium chloride (0.05 – 2 mol L^{-1}) or calcium chloride (1.25 – 50 mmol L^{-1}) respectively. In the reusability studies, Th or U adsorbed by Si-HA was recovered using 10 ml of 1 M or 2 M nitric acid. Before reused in the next sorption process, the sorbent was washed thoroughly using doubly distilled water and dried at 50℃.

2.2.4 Separation studies by batch experiments

The feasibility of recovery and separation of Th, U and lanthanides was studied in batch experiments by adsorption and desorption process. In adsorption process, the Si-HA sorbent (50 mg) was stirred with 25 ml of Th, U and lanthanides mixture solution (each initial concentration 2 mg/L) over a pH range from 0.5 to 6.0 to elucidate the pH effect to distribution coefficient of each metal ion. While in the desorption experiments, 2 ml of leaching solution at varied concentrations were introduced to 25 mg Si-HA sorbents containing the mixture of Th, U and lanthanides (each metal content 1 mg g^{-1}). The leaching solutions tested were hydrochloric acid (0.1–4 M), EDTA (0.1–10 mM) and citric acid (1–10 mM).

The viability of separation of two metal ions is predicted by their separation factor (α) by equation ($\alpha = D_1/D_2$), where D_1 and D_2 refer to the first and second metal ion distribution coefficient. The distribution coefficient (D) was calculated based on equation $D = C_S/C_L$, where C_L (mg L^{-1}) and C_S (mg/g) were the metal concentration in supernatant solution and metal concentration in the sorbent, respectively.

2.3 Results and Discussion

2.3.1 Variation on humic acid

It is widely accepted that humic acid is organic material without certain chemical composition since it is derived from different organic material. To address the effect of its variation on the properties of Si-HA adsorbent, three samples of humic acid from different sources were used to synthesize the adsorbent i.e. Across humic acid (AC), Wako humic acid (WK) and Mesuji humic acid (MSJ). AC and WK are commercial humic acid obtained from Across Chemical and Wako chemical respectively, while MSJ was extracted from carbonaceous

mudstone stratum on the top of Tertier Coal layer, Lampung, Indonesia. Humic acid extraction and purification was carried out according to Koopal et al. [23]. Each humic acid sample was attached on the surface of silica gel according to the procedure described in Section 2.2.2. to produce Si-HA-AC, Si-HA-WK and Si-HA-MSJ.

Three adsorbents were then analyzed its functional group i.e. carboxylic and phenolic. Besides, the sorption capacity of the adsorbent in Th and U removal also determined by equilibrating each adsorbent in 250 mg L^{-1} Th or U solution at pH 3, solid–liquid ratio 2 mg/ml for 3 hours, which results are shown in Table 2.1. The table indicates that variation of humic acid to the properties of adsorbent is not significant. Therefore, in this research, only one humic acid sample used in further experiment (Across humic acid).

Table 2.1 The characteristics of SI-HA adsorbent synthesized by using different humic acid.

Adsorbent	Carboxylic (meq/g)	Phenolic (meq/g)	U (mmol/g)	Th (mmol/g)
Si-HA-AC	0.28	4.31	0.10	0.14
Si-HA-WK	0.44	3.42	0.07	0.13
Si-HA-MSJ	0.28	3.95	0.11	0.18

2.3.2 Effect of acidity on adsorption

The effect of initial pH on the adsorption of Th and U ions is shown in Fig 2.2a. Thorium requires a pH higher than 1.5 for optimum adsorption. U ions were quantitatively retained at higher pH (> 3). In the case of lanthanides (La, Nd, Dy and Yb) optimum adsorption occurred at slightly acidic to neutral pH (Fig. 2.2b). Lanthanides affinity for humic acid correlate positively with atomic number, especially in aqueous solutions with very low concentration of lanthanides

due to the lanthanide contraction effect [24]. The adsorbent possesses higher sorption capacity for Th compared with that for U at very low pH indicating that humic acid as a functional group has a higher affinity toward Th, due to greater ionic radii and charge factors [25].

The adsorption mechanism is shown in Fig 2.3. At lower pH, low adsorption was due to the electrostatic repulsion between the protonated ligand (represented by carboxylic and phenolic) site and ions with the same charge. As the pH increase the ligand site became dissociated into negative charged functional group which attracted the positive target ions in aqueous phase.

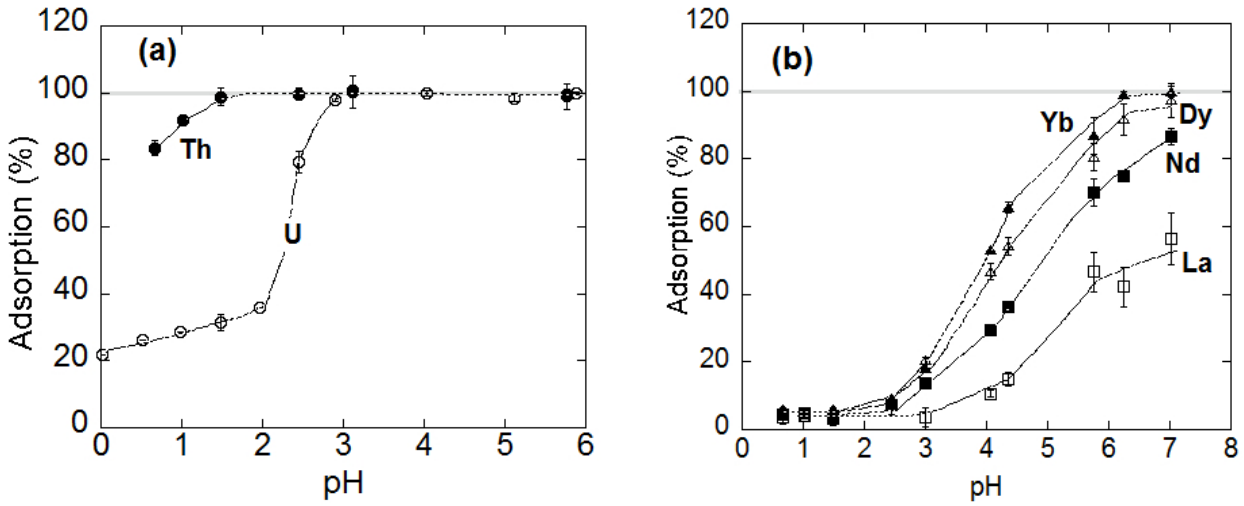

Fig 2.2 Influence of initial pH on metal adsorption onto Si-HA sorbent with at 2 g L^{-1} sorbent dose and 2 mg L^{-1} initial concentration of each ion: (a) U and Th; (b) La, Nd, Dy and Yb.

2.3.3 Effect of adsorbent dose on adsorption

The influence of Si-HA sorbent dosage on Th and U adsorption was shown in Fig 2.4a. Th was quantitatively adsorbed at 1.8 g L^{-1}, while U had slightly higher ratio at 2 g L^{-1}. A batch experiment was also carried out for the four lanthanides by varying the sorbent/solution ratio

from 1 to 5.5 at pH 6.5 (Fig 2.4b). Figure 2.4b indicates that the minimum sorbent dosage for uptake of each species of trivalent lanthanide tends to correlate negatively with the atomic number for the smallest dosage. These data seem to support the stronger affinity of heavier rare earth element species for humic acid.

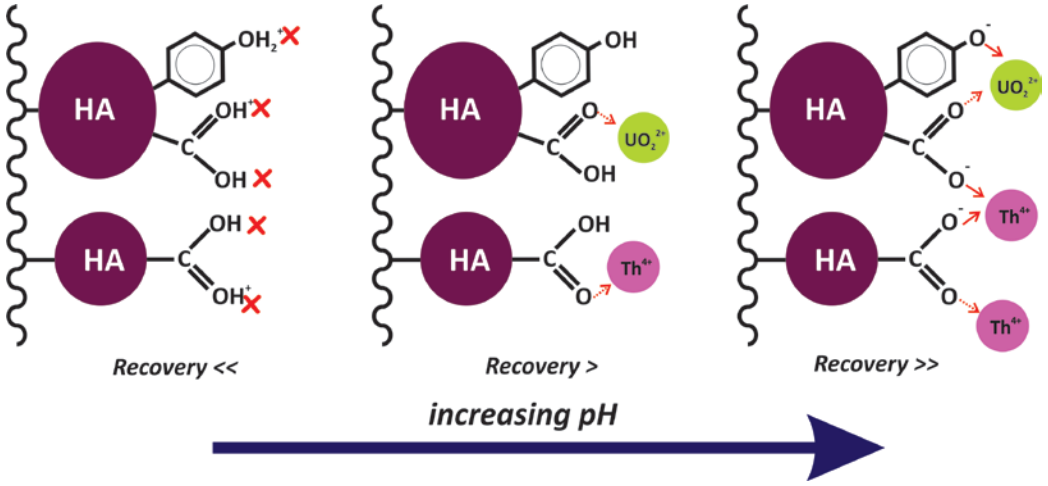

Fig 2.3 Adsorption mechanism of ion target (represented by Th and U) by Si-HA adsorbent. Ligand site of humic acid (HA) shown are carboxylic and phenolic functional group.

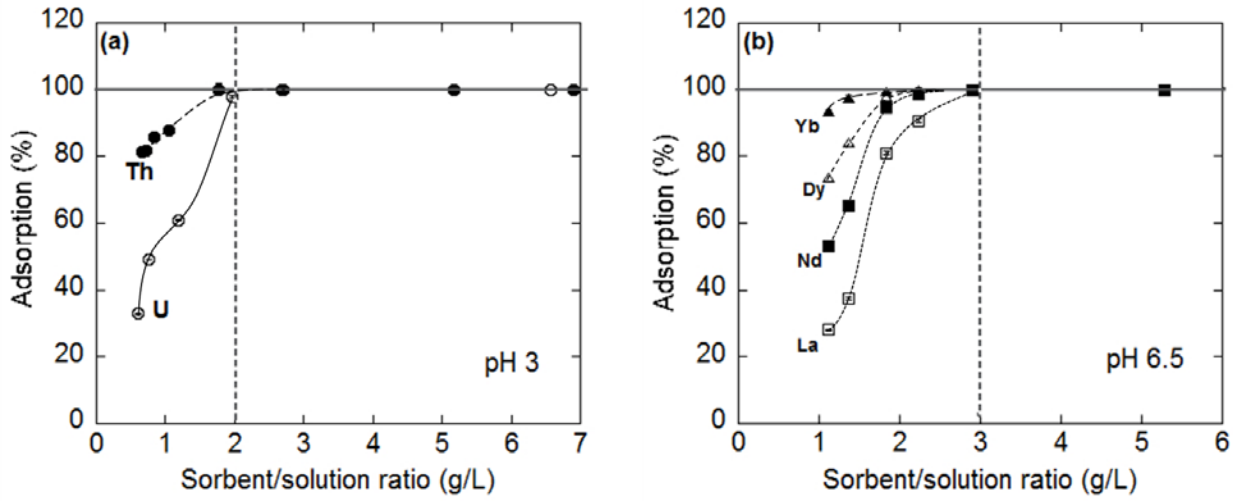

Fig 2.4 Effect of adsorbent dose on the adsorption by Si-HA sorbent with 2 mg L^{-1} initial concentration of each ion: (a) U and Th; (b) La, Nd, Dy and Yb. The dotted line represents the lowest ratio at the optimum dose for adsorption of each metal ion group.

2.3.4 Adsorbent capacity and isotherm

Adsorption was described by isotherm functions of the quantity of the adsorbate on the adsorbent, e.g., Langmuir and Freundlich models. Figure 2.5a described the adsorption by Si-HA sorbent by linearized Langmuir model (specific adsorption; $C_E/\ q_E$ against equilibrium concentration; C_E), where q_E was the adsorption capacity at equilibrium (mg g^{-1}). The adsorption maximum capacity (q_{max}) and binding constant value (K) were determined by the equation (1):

$$q_E = \frac{QKC_E}{(1 + KC_E)} \tag{1}$$

The Freundlich adsorption isotherm model (Fig 2.5b) was applied to determine the Freundlich constant, which relates to the capacity (K_F) and intensity of adsorption ($1/n$) by the equation (2):

$$q_E = K_F C_E^{1/n} \tag{2}$$

$$RMSE = \sqrt{\frac{1}{m}\sum_{i=1}^{n}\left(q_{E\ exp} - q_{E\ cal}\right)^2} \tag{3}$$

The Langmuir and Freundlich parameters, and root mean square error (*RMSE*, equation 3) of this study are listed in Table 2.2. $q_{E\ exp}$ and $q_{E\ cal}$ are equilibrium sorption capacity based on experimental data and modeling respectively, while m is the number of observation. The data were fit to both models. However, based on RMSE value, the Freundlich model fits better to the experimental data, due to heterogeneous functional group present on the adsorbent surface.

The maximum adsorption capacities (q_{max}) of the six metal ions onto Si-HA were far higher than the values for unmodified silica gel (untreated Si in Table 2.2), indicating that Si-HA has good adsorption capacity and effectively removes lanthanide ions, as well as Th and U from waste solutions. The critical feature of the Langmuir adsorption isotherm is the dimensionless constant named the equilibrium parameter (R_L), which is described by the following equation (4):

$$\mathrm{R_L} = \frac{1}{(1 + \mathrm{KC_o})} \tag{4}$$

Where K is the binding constant (L mg^{-1}), and C_o is the initial concentration (mg L^{-1}). A favorable and reversible condition is reached if $0 < R_L < 1$ [26]. The R_L values in this study were found to be 0.01–0.96, indicating that the adsorption of these metal ions onto Si-HA was favorable and reversible.

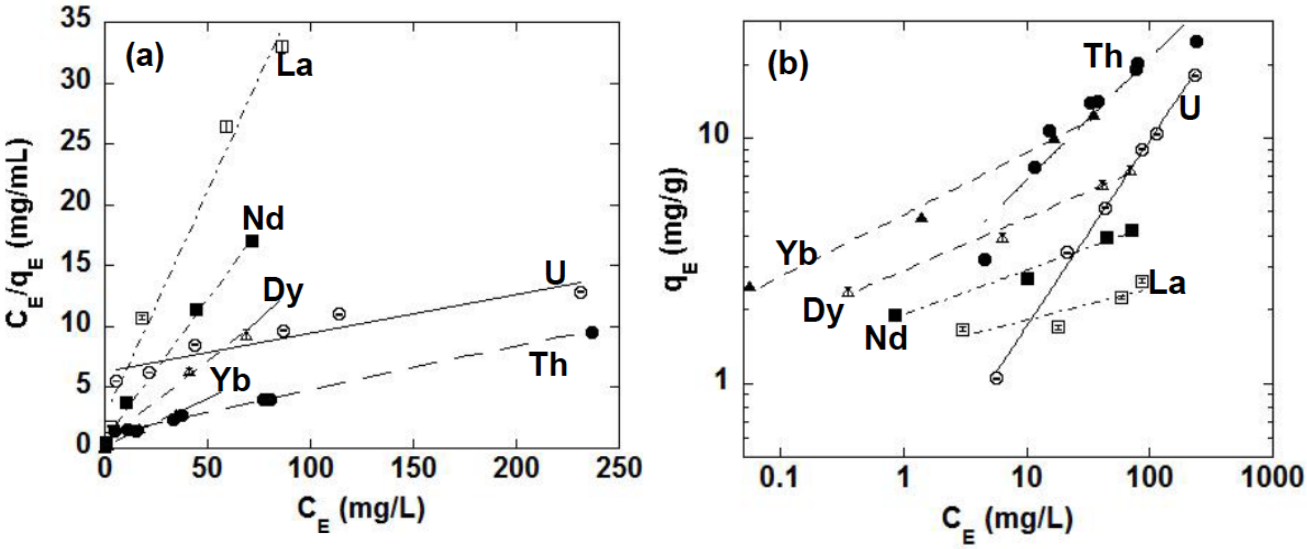

Fig 2.5 Experimental isotherms for adsorption of lanthanides at pH 6 and U and Th at pH 3 onto Si-HA: (a) Langmuir model; (b) Freundlich model.

The *n* value of the Freundlich parameter indicates the degree of nonlinearity between solution concentration and adsorption. Generally, *n* values from 1-10 represent physical adsorption but not chemical adsorption. The *n* value was found to be 1.4, 2.8 and 1.8 - 4.6 for U, Th and lanthanide ions, respectively, indicating favorable physical adsorption of these metal ions onto Si-HA in this study [27]. Table 2.2 shows that the maximum adsorption capacity (q_{max}) of lanthanides tend to correlate positively with the atomic number of lanthanides. This result confirmed the increasing affinities of lanthanides for humic acid based on atomic number [24].

Table 2.2 Estimated isotherm parameters for adsorption of ions to Si-HA sorbent at 25°C.

		Langmuir				**Freundlich**		
Metal			**untreated Si**					
ion	**pH**	q_{max} **(mg g^{-1})**	**(mg g^{-1})**	***K*** **(L mg^{-1})**	***RMSE***	***n***	K_F	***RMSE***
U	3	43.9	2.0	0.003	0.46	1.4	0.33	0.22
Th	3	28.0	10.3	0.042	1.81	2.8	3.72	1.72
La	6	2.3	0.2	0.250	0.57	3.1	0.63	0.56
Nd	6	3.8	0.4	0.914	0.59	1.8	5.17	0.44
Dy	6	7.3	0.3	0.259	1.01	2.7	4.32	0.54
Yb	6	12.4	1.3	0.447	1.23	4.6	3.59	0.58

Table 2.3 shows the list of the maximum adsorption capacity values (q_{max}) of several sorbents to retain Th and/or U from the literatures. Generally, higher q_{max} was obtained in higher pH condition. pH value was considered a critical factor in obtaining the maximum capacity. Th and U are bound to the sorbent through an ion exchange reaction [28] and reducing the pH should break this weak bonding due to ligand protonation [29], which in turn decreasing the maximum sorbent capacity at lower pH. The examination of the sorbent ability to fixate Th and

U in acidic conditions would be advantageous because Th and U are generally associated with acidic matrix samples, e.g., mine wastewater and nuclear industry wastewater [30].

2.3.5 Adsorption kinetics

Fig 2.6 shows that within 15 min the metal removals generally had reach 75% of equilibrium condition. To describe the kinetic of adsorption process, the experimental data in Fig 2.6 would be treated with pseudo-first order (5), pseudo-second order (6) and intra particle diffusion model (7) [28, 31]:

$$q_t = q_E(1 - e^{-k_1 t}) \tag{5}$$

$$q_t = \frac{k_2 q_E^2 t}{1 + k_2 q_E t} \tag{6}$$

$$q_{\mathrm{t}} = k_{\mathrm{i}}\sqrt{t} + I \tag{7}$$

$$H = k_2 q_{\mathrm{E}}^2 \tag{8}$$

$$t_{1/2} = \frac{q_{\mathrm{E}}}{H} \tag{9}$$

$$dq\ (\%) = \ 100\sqrt{\frac{1}{n-1}\sum_{i=1}^{n}\left(\frac{q_{\mathrm{t\ exp}} - q_{\mathrm{t\ cal}}}{q_{\mathrm{t\ exp}}}\right)^2} \tag{10}$$

$$ARE\ (\%) = \frac{100}{n-1}\sum_{i=1}^{n}\left(\frac{q_{\mathrm{t\ exp}} - q_{\mathrm{t\ cal}}}{q_{\mathrm{t\ exp}}}\right)^2 \tag{11}$$

Table 2.3 Comparison of Th and/or U adsorption capability of sorbents reported in the literatures and this study.

Sorbent material (Reference no.)	Optimum pH	q_{max} (mg g^{-1})		Equilibrium time (min)	Reference
		Th	U		
humic acid immobilized on zirconium pillared clay	6		132.7	180	[7]
crystalline tin oxide nanoparticle	6	62.5	66.7	240	[15]
bicine-amberlite XAD 4	6	58.0	90.5	30	[32]
calixarene semicarbazone polymer supported	6		3.0	45	[33]
o-vaniline semicarbazone polymer supported	6		2.9	120	[34]
o-phenylene dioxyacetic acid-amberlite XAD resin	5.5	26.2	28.8	15	[35]
tiron-amberlite XAD 2	5		7.7	30	[36]
amine modified silica gel	4.5		90.3	120	[9]
catechol modified silica gel	4.5		14.0		[37]
PAN-zeolite composite	4	9.3		45	[14]
MTTZ modified clay	4	24.3	30.4	1440	[11]
manganese oxide coated zeolite	4		15.1	180	[12]
humic acid-amberlite XAD-4	4	35.0		60	[38]
calixarene semicarbazone polymer supported	3.5	2.8		45	[33]
o-vaniline semicarbazone polymer supported	3.5	3.2		120	[34]
polyhydroxyethylmethachrylate-pumice composite	3	84.2	74.7	1440	[28]
Humic acid modified silica gel	3	28.0	43.9	180	present study

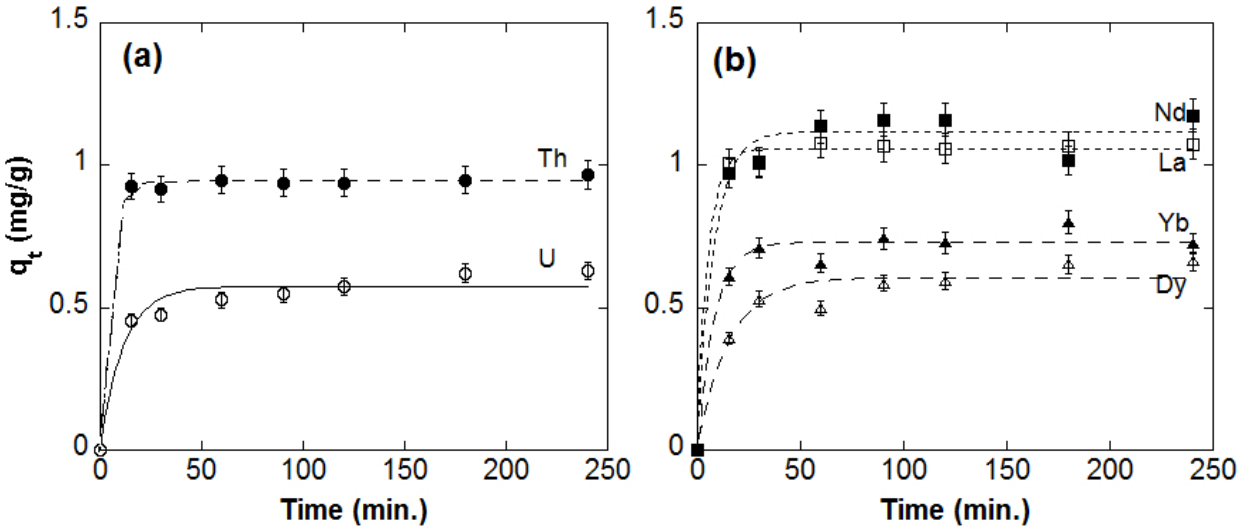

Fig 2.6 Effect of contact time on (a) Th, U and (b) lanthanides adsorption with initial concentration 2 mg L^{-1} , pH 3 (Th and U) or pH 6 (lanthanides) at 25°C.

q_{texp} and q_{tcal} are the sorption capacity based on the experimental data and the modeling at a given time *t*, respectively, while *n* is the number of observations. k_1 (min^{-1}), k_2 (g mg^{-1} min^{-1}) and k_i (mg g^{-1} $min^{0.5}$) are the rate constant of pseudo-first order, pseudo-second order and intra particle diffusion rate constant respectively while *H* (8) (mg g^{-1} min^{-1}) and $t_{1/2}$ (9) (min) are initial adsorption rate and time required to absorb the half of initial concentration for the pseudo-second order reaction. Normalized standard deviation (*dq*) and average relative error (*ARE*) were used to evaluate the model compatibility to the experimental data. *dq* and *ARE* given in Eq. (10) and (11) [39].

Table 2.4 summarizes the adsorption kinetics parameter based on pseudo-first order, pseudo-second order and intra particle diffusion model. Based on the normalized standard deviation and average relative error of Th, U and lanthanides suggested the adsorption process proceeded based on pseudo second order kinetics. It was evident that q_E from modeling is satisfactorily agree with q_E from experimental data. This implied that the adsorption process is

concentration dependent [40]. The value of k_2 for Th was larger compare to that of U. The result conformed to the results of isotherm studies, which indicated higher binding constant of Th compared to U (Table 2.2). The results of initial adsorption rate (H) shown the similar trend which in turn caused the adsorption of U by Si-HA requires longer period to remove half of initial concentration ($t_{1/2}$).

In modeling the kinetic data of Th, U and lanthanides by intra particle diffusion model generally resulted in the linear curve which did not intercept the origin point. This suggested that the rate of adsorption was influenced by intra particle diffusion [41]. Based on Table 2.4, U has higher k_i value than that of Th, which implies the adsorption process of U was influenced by intra particle diffusion process which also rate-limiting step [38].

2.3.6 Separation studies by batch method

Fig 2.7 shows that the distribution coefficient of each metal after a mixture of Th, U and lanthanides was subjected to adsorption by the batch method. The result was consistent with the data in Fig 2.2, and it confirmed the favorable of acidic condition for the separation of Th and U from lanthanides. The adsorption process at acidic pH retained Th and U while leaving lanthanides in the aqueous phase. At higher pH, the sorbent selectivity would decrease because at this range lanthanides began to be absorbed by the sorbent. pH 3 was the optimum pH to separate Th and U from lanthanides. The separation factors of Th-La, Th-Yb, U-La, and U-Yb were 3890, 2930, 50, and 38, respectively, in the pH.

Table 2.4 Kinetic parameters of Th, U and lanthanides adsorption after fitting with pseudo-first order, pseudo-second order and intra particle diffusion model with their normalized standard deviation (*dq*) and average relative error (*ARE*) for compatibilities.

Parameters	C_0 Th (mg L^{-1})		C_0 U (mg L^{-1})		C_0 La (mg L^{-1})		C_0 Nd (mg L^{-1})		C_0 Dy (mg L^{-1})		C_0 Yb (mg L^{-1})	
	2	**10**	**2**	**10**	**2**	**10**	**2**	**10**	**2**	**10**	**2**	**10**
Pseudo-first-order												
k_1 (min^{-1})	0.27	0.15	0.09	0.49	1.00	1.00	0.14	1.00	0.11	1.00	1.00	1.00
q_E model (mg g^{-1})	0.94	3.40	0.57	2.50	1.05	4.57	1.11	5.67	0.70	3.49	0.83	4.36
q_E experimental (mg g^{-1})	0.97	3.70	0.63	3.10	1.07	4.79	1.17	5.73	0.74	3.61	0.85	4.36
dq (%)	1.55	4.56	8.40	14.25	3.10	6.67	5.79	2.29	3.95	2.84	7.11	2.74
ARE (%)	0.024	0.208	0.706	2.032	0.096	0.446	0.336	0.053	0.156	0.081	0.506	0.075
Pseudo-second-order												
k_2 (g mg^{-1} min^{-1})	2.03	0.09	0.27	0.05	0.76	0.07	0.35	0.95	0.34	0.37	0.43	0.44
q_E model (mg g^{-1})	0.95	3.54	0.61	2.89	1.08	4.88	1.14	5.69	0.73	3.55	0.88	4.41
q_E experimental (mg g^{-1})	0.97	3.70	0.63	3.10	1.07	4.79	1.17	5.73	0.74	3.61	0.85	4.36
H (mg g^{-1} min^{-1})	1.83	1.12	0.10	0.43	0.88	1.61	0.46	30.67	0.18	4.65	0.33	8.59
$t_{1/2}$ (min)	0.52	3.16	6.20	6.78	1.23	3.03	2.49	0.19	3.99	0.76	2.66	0.51
dq (%)	1.23	4.55	5.26	8.03	1.59	1.91	5.47	2.26	2.51	2.31	4.33	2.48
ARE (%)	0.015	0.207	0.277	0.645	0.025	0.036	0.300	0.051	0.063	0.054	0.187	0.061
Intra-particle diffusion												
k_i (mg g^{-1} $min^{0.5}$)	0.003	0.063	0.016	0.087	0.006	0.056	0.011	0.011	0.012	0.020	0.010	0.004
I (mg g^{-1})	0.910	2.722	0.396	1.772	0.995	4.072	0.995	5.566	0.564	3.302	0.744	4.334
dq (%)	0.864	6.434	1.495	3.486	1.959	3.735	6.482	2.159	3.262	1.561	4.806	2.708
ARE (%)	0.007	0.414	0.022	0.122	0.038	0.140	0.420	0.047	0.106	0.024	0.231	0.073

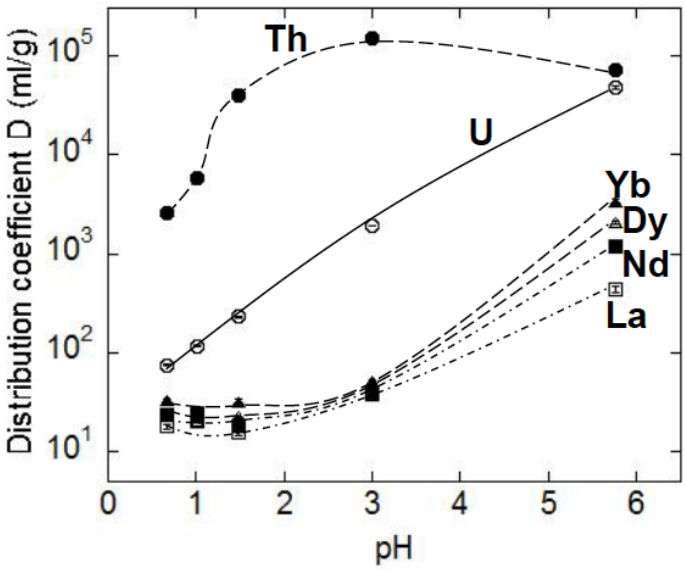

Fig 2.7 Distribution coefficients of Th, U and lanthanides for Si-HA adsorbent as a function of pH from the equilibration of 25 ml Th, U and lanthanides mixture solution (each metal concentration 2 mg L^{-1}) with 50 mg Si-HA sorbent.

Fig 2.8 illustrates the distribution coefficients of each metal ion between Si-HA and each leaching agent in (a) 0.1- 4 M hydrochloric acid, (b) 0.1-10 M EDTA, and (c) 1-10 mM citric acid. In Fig. 2.8a, the low separation factor among the metal ion species (0.6 – 38) indicates that hydrochloric acid solution as leaching agent was not very useful for the separation of Th, U and lanthanides. EDTA could be used to separate lanthanides from Th and U as shown in Figure 2.8b. The high separation factors, 3900 and 195 for Th-La and U-La pairs, respectively were obtained by using 0.1 mM EDTA as leaching agent.

Fig 2.8c shows that citric acid was an effective leaching agent to separate U from Th exemplified by the high separation factor between both elements (1.2×10^5 in 1 mM citric acid). The high distribution coefficient of Th onto Si-HA in the three leaching agents (Fig 2.8a-c)

suggested that the three solutions did not effectively recover Th. However, it was found that 1 M nitric acid could desorb Th quantitatively from the Si-HA sorbent.

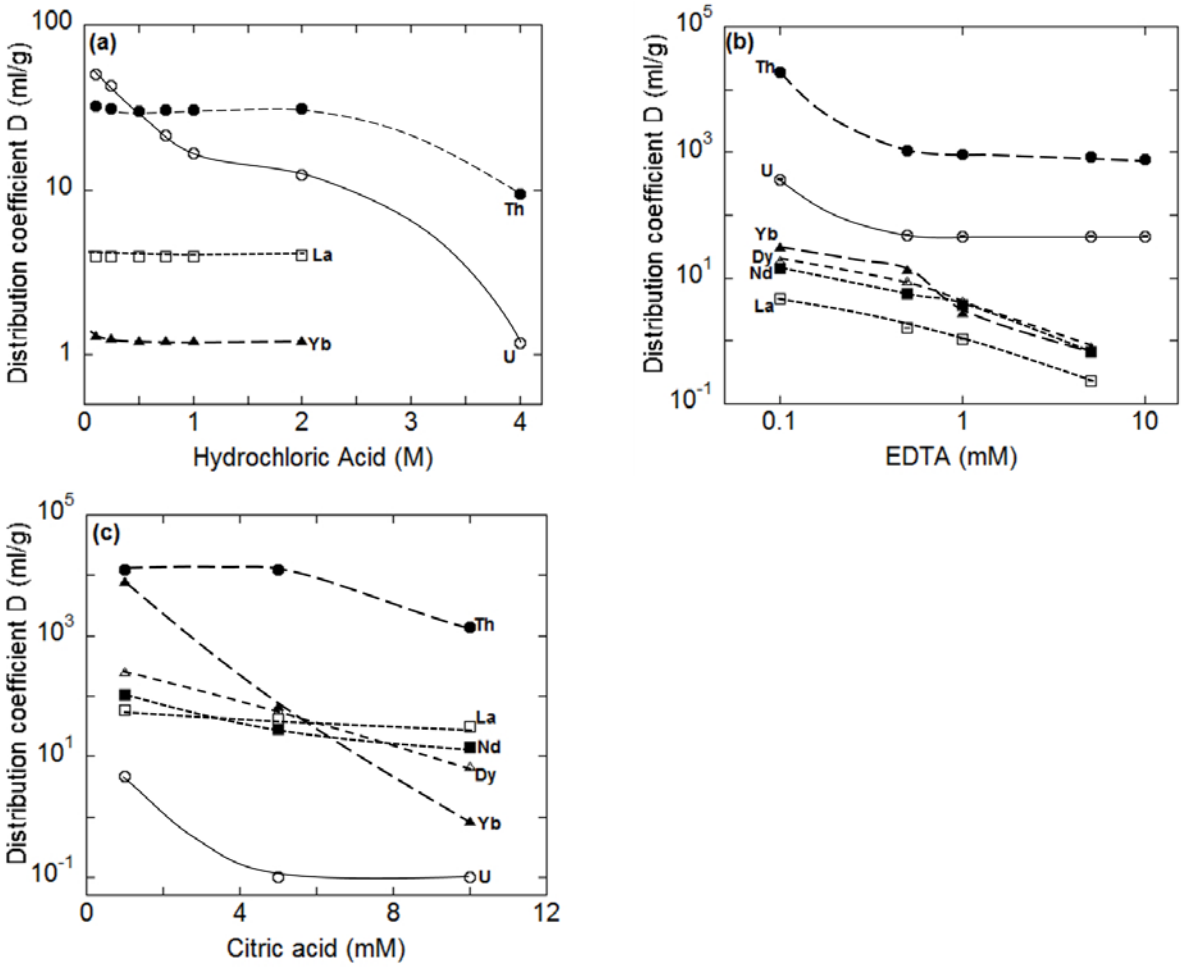

Fig 2.8 Distribution coefficients for Th, U and lanthanides desorption as function of leaching agent concentration: (a) hydrochloric acid, (b) EDTA and (c) citric acid by equilibrating 25 ml leaching agent with 50 mg Si-HA sorbent contained 1 mg g^{-1} for each metal.

2.3.7 Effect of salinity

Figure 2.9 shows the distribution coefficient of Th, U and lanthanides adsorption in sodium chloride solution varied between 0.05 – 2 M. Based on the results, Th and U adsorptions

were insignificantly influenced by salinity while the lanthanide adsorption were considerably affected.

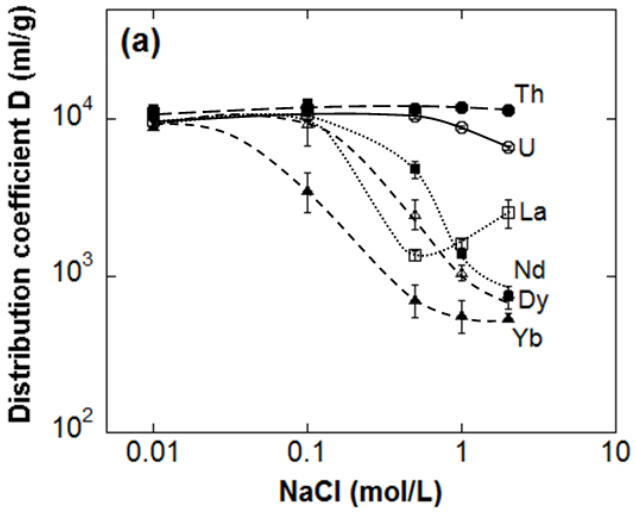

Fig 2.9 Distribution coefficient of Th, U and lanthanides adsorption as function of (a) salinity and (b) ionic strength. 10 mg Si-HA sorbent equilibrated with 5 ml metal solution (2 mg L^{-1}).

There was trend the salinity effect correlated positively with atomic number of lanthanides (Yb was the most influenced). The results show that beside pH, salinity also contributed to the selectivity of sorbent toward Th and U. The adsorption availability also evaluated in high salinity since many Th, U deposits are associated with beach (placer) deposits and the possibility of Th and U pollution in this environment.

2.3.8 Sorbent reusability

Reusability is an important factor in the economic value of sorbent. This characteristic involves a desorption process to regenerate used sorbent to reuse it to the next cycle of metal adsorption. The regeneration efficiency is the ratio of metal uptake between the first and the last runs [9]. After 4 cycles of regeneration using 1 M nitric acid, the regeneration efficiency for Th

and U was found to be 99.6±1.6% and 93.8±5.6%, respectively. Using 2 M nitric acid yielded regeneration efficiencies of 99.1 ± 0.9% Th and 92.6 ± 1.8% U. No difference was observed in the regeneration using 1 M or 2 M nitric acid. Therefore, 1 M nitric acid was adopted as the last leaching agent. The constant regeneration efficiency indicates the stability of sorbent in sequential reactions, which is comparable to that of the previously studied sorbents listed in Table 2.3.

2.4 Conclusions

This study demonstrated that humic acid attached to silica gel (Si-HA) is suitable adsorbent to recover and separate Th, U and lanthanides. The variation on humic acid played minor role on the adsorbent properties. The recovery of Th and U was confirmed in acidic conditions (pH 3), while lanthanides required slightly neutral conditions (pH 6). The maximum sorbent capacity (pH 3) of Th and U was 28.0 and 43.9 mg g^{-1}, respectively. The isotherm parameters in this study denoted that the adsorption of Th, U, and lanthanide ions was favorable, and its optimum was attained within 90 min. The difference in the pH requirements might assist this sorbent to separate Th and U from lanthanides, which was advantageous compared to other sorbents. The proposed separation method was based on the favored adsorption of Th and U at pH 3 and the differences in the distribution ratio of each metal in EDTA or citric acid. Salinity only slightly affected the sorbent ability to remove Th and U while ionic strength had influence to certain extent. The sorbent showed good stability in strong acid and was reusable for at least 4 cycles. The results affirmed the suitability of Si-HA sorbent as an alternative lower-cost sorbent to remove Th and U, including their separation from lanthanides.

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CHAPTER 3

SOL-GEL SYNTHESIS OF A HUMIC ACID-SILICA GEL COMPOSITE MATERIAL AS A LOW-COST ADSORBENT FOR THORIUM AND URANIUM REMOVAL

Abstract

A new humic acid-silica gel composite (HASi) to serve as an adsorbent was synthesized via a single-pot method, and its formation via the sol-gel process was confirmed by FTIR and SEM-EDS characterization. The adsorbent effectively removed Th and U at low pH (2.5–3), and the Langmuir model yielded a maximum sorption capacity of 32.3 and 33.2 mg g^{-1} for Th and U respectively. The removal process was rapid (85% removal within 5 min) and followed a pseudo-second-order model. The salinity of the solution had little effect on the removal efficiency, which continued throughout the adsorbent's repeated use up to nine times.

Keywords: adsorption, humic acid, silica gel, thorium, uranium, sol-gel

3.1 Introduction

Because of its important role in future energy use, radioactive material, such as thorium (Th) and uranium (U) will be in high demand. This in turn will encourage mining activities and nuclear energy programs that will generate waste to which both humans and the environment will be exposed [1]. The recovery of these elements from the waste is mandatory prior to release of the waste into the environment. Various techniques are used in Th and U recovery, e.g., chemical precipitation, liquid-liquid separation, electrochemical treatment and membranes. However, these techniques are not considered to be cost effective [2]. In contrast, solid-liquid separation (adsorption) possesses advantages in terms of being relatively cost effective, convenient to use and applicable to a low concentrations of pollutant, making it suitable for radioactive waste treatment [3].

Various adsorbents have been synthesized and tested for the recovery and pre-concentration of Th and U from aqueous solutions, yet many of these adsorbent materials are not considered cost-effective because of complicated procedures and special chemicals used in their preparation. One inexpensive and widely available material for adsorbent synthesis is humic acid, which possesses a high ability to bind metal elements [4, 5] because of the presence of carboxylic, phenolic and mixed ligands [6]. Previous study had demonstrated that humic acid, attached to silica gel, is suitable functional group to recover Th and U from acidic or high saline solution including their separation from the lanthanides.

Silica gel, compared to other reported support materials e. g. zirconium pillared clay [7], resin polymer [8] for humic acid based adsorbent synthesis, has advantages due to its stability, physical strength and easily controlled structural parameters [9]. One of the most common schemes for attaching a functional group, including humic acid, to the silica gel surface is

silylation [10], which has been addressed in numerous publications [4, 13-16]. Silylation is considered expensive and complicated procedure, which involve hazardous chemicals and generate additional waste as shown in previous chapter in producing Si-HA adsorbent. Due to persisting difficult and expensive procedure, in this chapter, sol-gel method is proposed to produce an organic-hybrid material. This method has advantages, as the material can be prepared through a simple single-pot reaction wherein the functional moieties or molecules can be doped directly into a sol of the inorganic host matrix prior to gelation [17]. Most investigators have used organosilane derivatives (e.g., tetraethylorthosilicate) as a silica sol precursor [18], but in this research, sodium silicate was chosen for the sol-gel synthesis because it is economical and widely available.

Therefore, the main motive of this chapter is to describe an easier and cheaper alternative method to attach humic acid as a functional group to silica gel. Using the sol-gel method, a humic acid-silica gel composite material (HASi) was synthesized by incorporating humic acid into a silica matrix. The low-cost material was be further investigated in terms of its characterization and its performance in Th and U removal from an aqueous solution.

3.2 Experimental

3.2.1 Materials

All of the chemicals, including sodium silicate, were purchased from Kanto Chemicals and Wako Chemicals Japan and used as received. A single lot of humic acid was provided by Across Organics (No. A013566901) and purified according to Koopal et al (1999) [19]. It was used throughout the experiment to keep the composite properties uniform. The dilution and

solution preparations were carried out using Milli Q water (Milli Q system, Millipore). The solution pH was adjusted by hydrochloric acid and sodium hydroxide.

3.2.2 Instrumentation and characterization

Th and U in solutions were analyzed spectrophotometrically using a Jasco V-530 UV/Vis spectrophotometer based on the colored complex these elements form with Arsenazo III, while mixture solutions were analyzed using ICP-AES (SPS-7700, Seiko Instrument Co). The solution pH was measured using an F-52 Horiba pH meter. FT-IR spectra, which were used to distinguish the frequency difference between undoped and humic-acid-doped silica matrices, were obtained using a Jasco FT/IR 4100 spectrometer by the KBr method with a wavelength range of 400 to 4000 cm^{-1}. The surface morphology of the adsorbent was observed using a Hitachi S-2400 scanning electron microscope operated at 15 kV after coating the samples with gold. In addition to the surface morphology, the elemental distribution on the adsorbent surface was detected and mapped using a JEOL JSM-5310 scanning microscope-energy dispersive X-Ray spectroscope (SEM-EDS) operated at 15 kV. In elemental analysis, total carbon, hydrogen and nitrogen were determined using CHN analyzer CE440, Exeter Analytical Inc. The zeta potentials were determined by Delsa^{TM} Nano HC Zeta Particle Analyzer, equipped with DelsaTM Nano AT Autotitrator (Backman Coulter, USA). All analysis was performed in Graduate School of Environmental Science, Hokkaido University, except SEM-EDS (Graduate School of Science, Hokkaido University), elemental analysis and zeta potentials (Open Facility, Hokkaido University, Sousei Hall).

3.2.3 Silica gel-humic acid composite preparation

The HASi was prepared by the sol-gel method. A typical procedure is as follows: Purified humic acid was dissolved in 10 ml of 6% sodium silicate solution. The sodium silicate-humic acid mixture solution around pH 12, while vigorously stirred, was titrated by a 2 mol L^{-1} nitric acid solution to around pH 10, and the stirring was continued until gelation occurred. The gel was dried at room temperature, ground using a mortar and sieved to < 64 μm size. The HASi powder was washed with Milli Q water to remove unbound humic acid. After being protonated by washing with 1 mmol L^{-1} hydrochloric acid, the adsorbent was dried at 50°C and stored in a cool and dry place to prevent any alterations.

Table 3.1 The sorption capacity (q, mg g^{-1}) of four types of HASi adsorbents based on a preliminary capacity test (solid-liquid ratio 2 mg ml^{-1}, pH 3, 12 h equilibrium), including the result of elemental analysis.

Adsorbent	q (mg g^{-1})		Elemental Analysis (%)		
	Th	U	C	H	N
HASi0	7.2 ± 1.8	1.2 ± 0.9	na	na	na
HASi1	27.0 ± 3.8	35.6 ± 0.9	0.79	0.61	< 0.3
HASi2	28.2 ± 2.0	31.9 ± 3.2	3.10	0.82	< 0.3
HASi3	30.0 ± 1.9	35.6 ± 0.8	4.44	0.93	< 0.3

Four types of HASi adsorbent materials were prepared, namely, HASi0, HASi1, HASi2 and HASi3, that corresponded to the amount of humic acid added to 10 ml of a 6% sodium silicate solution, i.e., 0, 100, 200 and 300 mg, respectively. To determine the amount of humic acid immobilized in the composite material, the carbon content of each adsorbent was determined (Table 3.1), showing the carbon content in adsorbent correlate positively with the

amount of humic acid added in the sol-gel synthesis. Based on a preliminary capacity test in Table 3.1, it is clear that the humic acid content (C content) did not correlate positively to the capacity of composite material to remove Th and U from the solution. In this case, HASi1 was chosen for further sorption studies.

3.2.4 Batch adsorption experiments

Sorption studies were carried out by batch experiments to determine the optimum condition in terms of pH, solid-liquid ratio, metal concentration, contact time, cation concentration, desorption, regeneration and reusability of the HASi adsorbent. The general procedure in a batch method was to equilibrate the HASi adsorbent with a Th or U solution in a centrifuge tube by mixing at 100 rpm at room temperature. The supernatant solution was separated by centrifugation at 3500 rpm for 30 min. The metal concentration in the supernatant solution was then determined using a UV-Vis spectrophotometer (Arsenazo III method) or ICP-AES. The adsorbent capacity (q, mg g^{-1}) and recovery (R, %) were calculated based on Eqs. (1) and (2).

$$q = \frac{(C_o - C_E)V}{m} \quad (1)$$

$$R = \frac{(C_o - C_E) \times 100}{C_o} \quad (2)$$

where C_o and C_E are the initial and equilibrium metal concentrations (mg L^{-1}), respectively, V (ml) is the volume of the liquid phase, and m (mg) is the mass of adsorbent added.

3.3 Results and discussion

3.3.1 Adsorbent characterization

FT-IR analysis was carried out to confirm the formation of HASi hybrid material by comparing the spectrum of the synthesized material to those of its precursors (Fig 3.1). The silica adsorbent, which was synthesized by the sol-gel process without humic acid (HASi0), exhibits broad bands at 460 and 1080 cm^{-1}, which are assigned to Si-O-Si and the silicate ion. The peak related to the tetrahedral silica matrix is occurs at 796 cm^{-1}, while the sharp peak at 1400 cm^{-1} is probably caused by the nitrate ion residue that was introduced during the gelation process. The sorption band at 954 cm^{-1} represents the terminal group of the silanol group (Si-OH).

The purified humic acid spectrum exhibits a sorption peak at 3400 – 3800 cm^{-1}, indicating the presence of the hydroxy group of a carboxyl group [20], while peaks at 1650 – 1700 cm^{-1} are contribut ions from oxygen functional groups, e.g., carbonyl group of carboxylate, and aldehyde and ketone groups [21]. Polyphenol is characterized by peaks at 600 and 900 cm^{-1}.

The modified material (HASi1) retains the characteristics of both precursors (HASi0 and purified humic acid), which confirms that HASi1 is a hybrid material. Fig 3.1 shows the shared characteristics between HASi0 and HASi1 (wavenumbers in italics), e.g., broad bands at 460 and 1080 cm^{-1} (Si-O-Si), the peak at 796 cm^{-1} (tetrahedral matrix silica) and the silanol functional group at 954 cm^{-1}. The purified humic acid characteristics retained by HASi1 include an oxygen functional group at 1650 – 1700 cm^{-1} and a carboxylic group at 3500 – 3800 cm^{-1} (wavenumbers in bold).

Fig 3.2 shows SEM images of HASi0 and HASi1 adsorbents, revealing the surface texture and morphology of both adsorbents and suggesting that there is no remarkable difference between the unmodified silica gel (HASi0) and the humic acid-silica gel adsorbent (HASi1).

Both pictures exhibit similar surface characteristics in which minute particles encrust the adsorbent surface along with larger flake-like particles, causing an unsmooth surface. This result indicates that humic acid was evenly dispersed inside the silica matrix during the hybrid material synthesis.

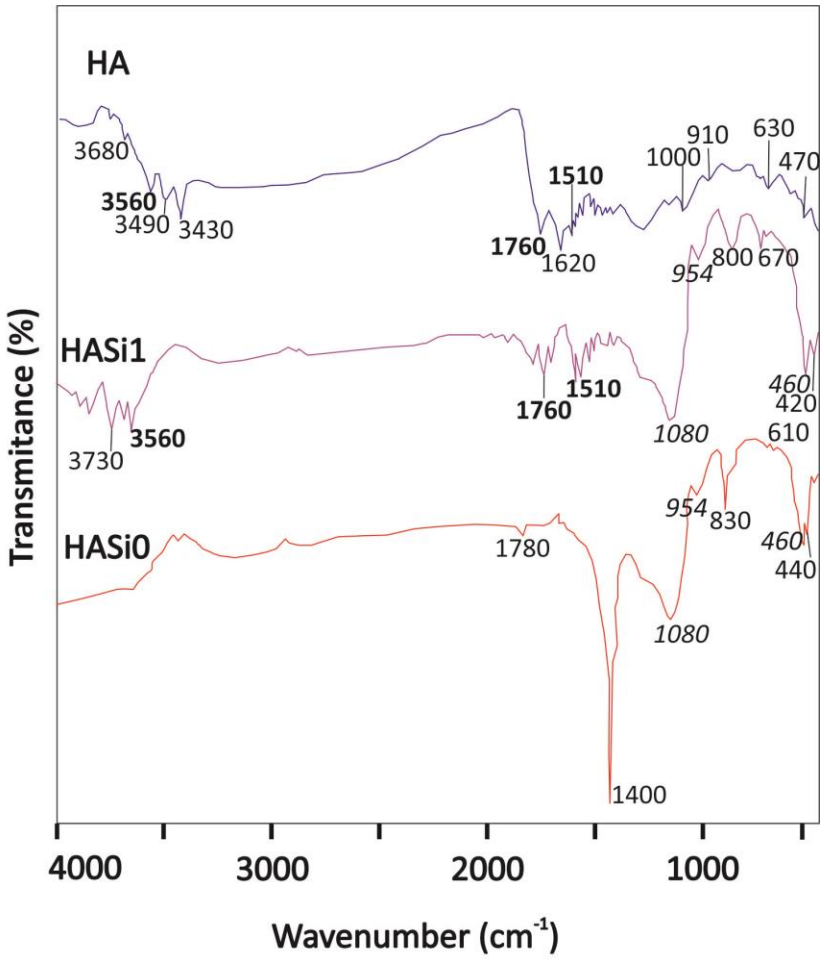

Fig 3.1 FT-IR spectra of the silica adsorbent synthesized without humic acid (HASi0), the humic acid-silica gel hybrid material (HASi1) and purified humic acid (HA). Italic and bold wavenumbers indicate shared characteristics of HASi1 as the modified material, with purified humic acid and HASi0, as precursors.

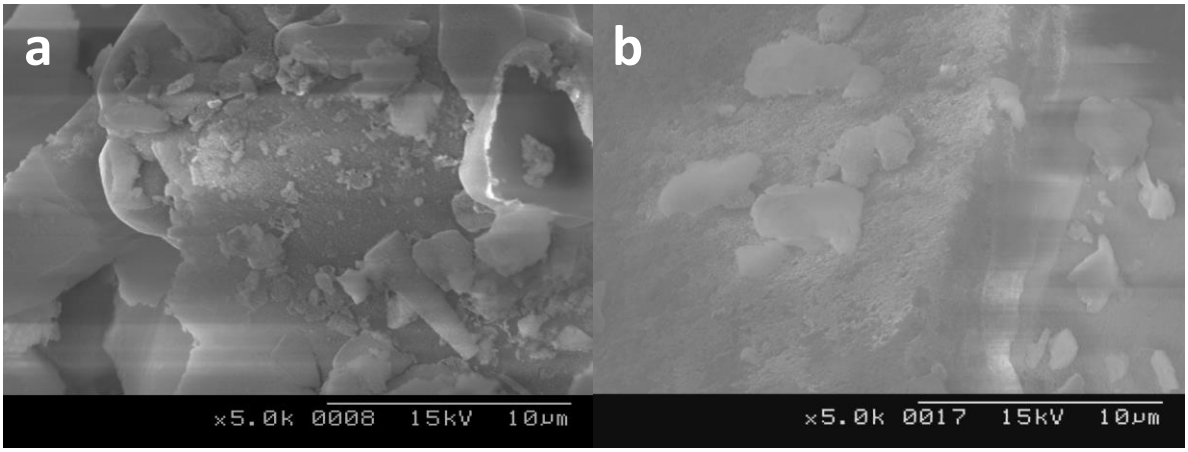

Fig 3.2 Surface morphologies of (a) HASi0 and (b) HASi1 observed with a scanning electron microscope.

The presence of humic acid was also ascertained by SEM-EDS analysis (Figs 3.3a and b). In the figures, both materials present strong signals for Si and O, which are the major components of silica gel, and sodium as a precursor in silica gel synthesis (sodium silicate). C (carbon), as a major component in humic acid, is almost undetected in the pristine material (HASi0), while in the modified material (HASi1), the presence of C is confirmed.

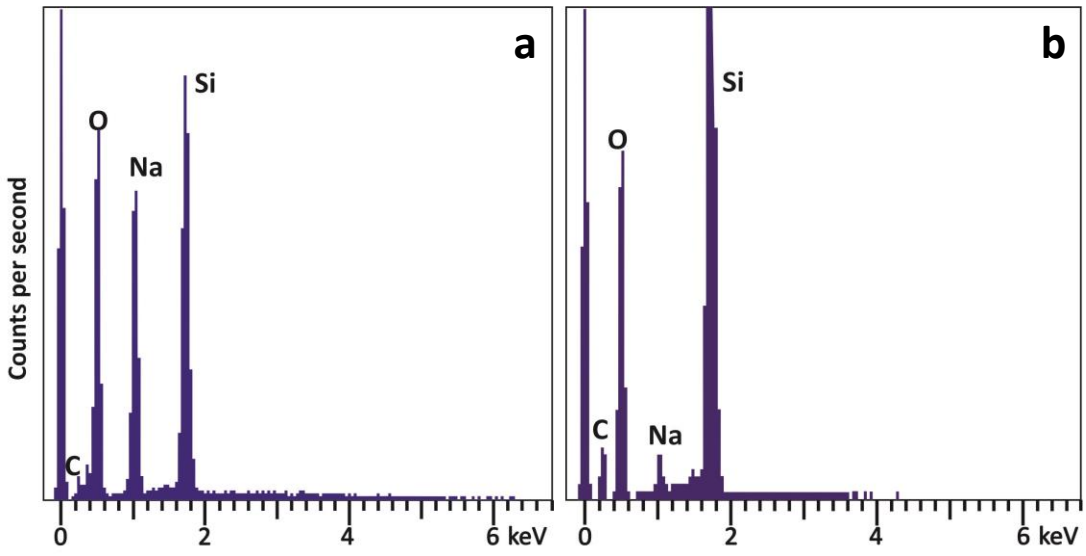

Fig 3.3 Elemental signals based on the SEM-EDS of (a) HASi0 and (b) HASi1.

In addition, carbon mapping (Fig 3.4) verifies the even distribution of carbon on the surface of the HASi1 adsorbent. As shown in Fig 3.3, the significant decrease in the amount of sodium after modification is caused by the presence of humic acid, which would cause a decrease in surface potential [22], which was elucidated by zeta potential analysis (Fig 3.5) The decrease in turn stimulates the desorption of sodium on the surface of silicate materials [23]. Additionally, during the adsorbent washing, unbound and washed humic acid would desorb the sodium on the surface of HASi1.

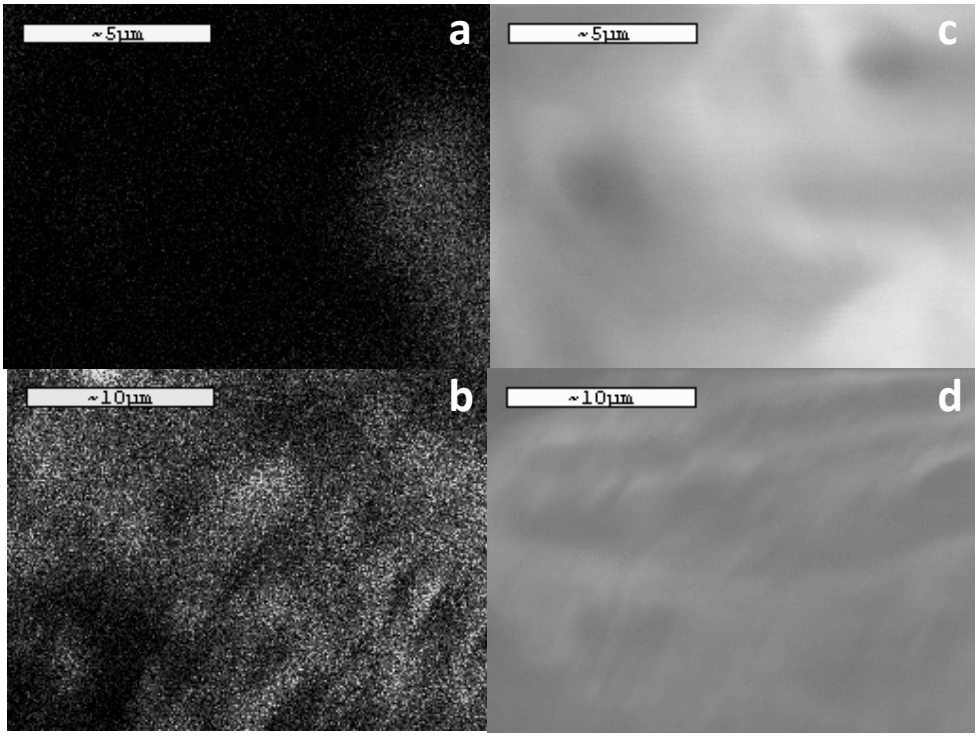

Fig 3.4 Carbon mapping using energy dispersive X-ray spectroscopy of the surfaces of (a) HASi0 and (b) HASi1 with corresponding surface images for (c) HASi0 and (d) HASi1.

Surface zeta potential of adsorbent HASi0 and HASi1 as function of pH is shown in Fig 3.5. Based on the figure, the pH at zero charge potential (pHzpc) for unmodified material is pH 2. Humic acid decrease the surface potential (HASi1) causing negative surface potential, which is beneficial to attract cationic species from aqueous phase.

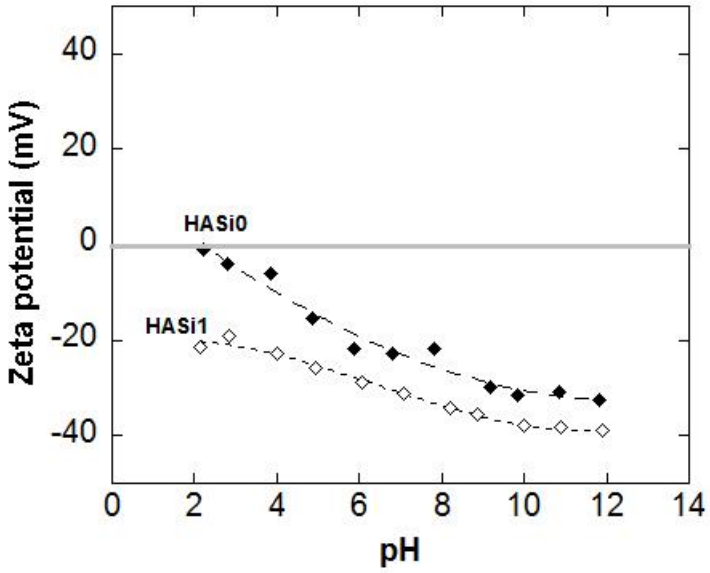

Fig 3.5 Zeta potential of HASi0 and HASi1 as function of pH.

3.3.2 Effect of pH on adsorption

The effect of pH on the Th and U sorption of HASi1 from an aqueous solution was studied at pH 1 – 5 by equilibrating 10 mg of the HASi1 adsorbent with 5 ml of a 10 mg L^{-1} Th or U solution for 3 h, which is based on previous studies using silica gel-humic acid adsorbent and is considered sufficient to attain the equilibrium. Fig 3.6 shows that the maximum sorption capacity is attained at pH 2.5 and 3 for Th and U, respectively. The adsorbent possesses a high sorption capacity for Th compared with that for U at the same pH (pH 3), indicating that humic acid as a functional group has a higher affinity toward Th. The result agrees with several previous reports [8, 24] and might be due to ionic radii and charge factors. Another factor is

hydration energy, whereby hydrated species would tend to be in the aqueous phase to satisfy their hydration requirement [24].

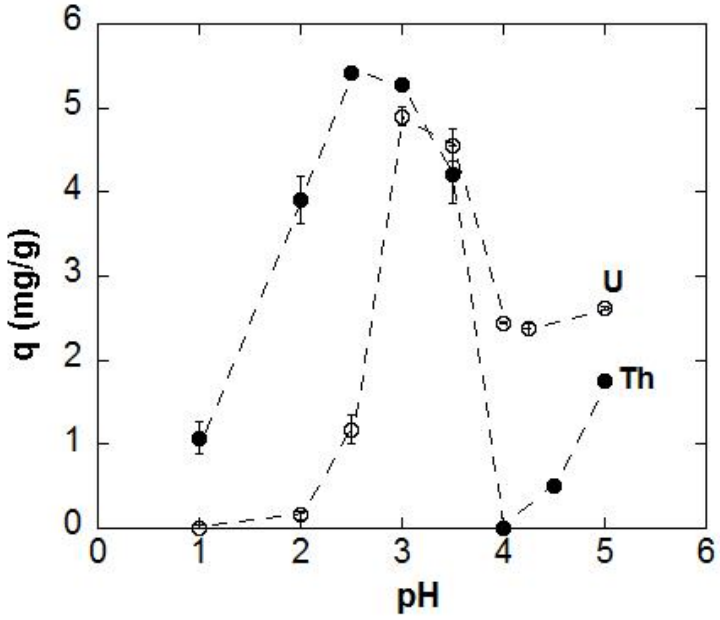

Fig 3.6 Effect of pH on the Th and U adsorption capacity of HASi1.

The adsorption mechanism is shown in Fig 3.7. At acidic pH, lower adsorption capacity values is partially due to the competition between the uranyl or thorium ion and the hydronium ion to occupy the ligand on the adsorbent surface [25]. When the pH increase the ligand site become dissociated to form negative charged group which would attract cationic species in aqueous phase. The decrease of sorption capacity when the pH is increasing is probably caused by the release of humic acid from silicate matrix and further forming complex with target cations. This was confirmed by performing batch studies using blank solution at pH 4 – 6. In this pH range, the release of humic acid could reach 5% of the total humic acid contained in the adsorbent based on UV-Vis analysis. Other reason is the formation of lower charged species e.g., $UO_2(OH)^+$, and $(UO_2)_3(OH)_5^+$, and Th^{4+} and $ThOH^{3+}$ replacing high charged species UO_2^{2+} and

Th^{4+} [26, 27], which possess a lower complex strength and a weaker affinity for the ligand. The increase in the sorption capacity at pH values higher than 4 is partially due to the dissociation of silanol group at pH 4 – 4.3 [28].

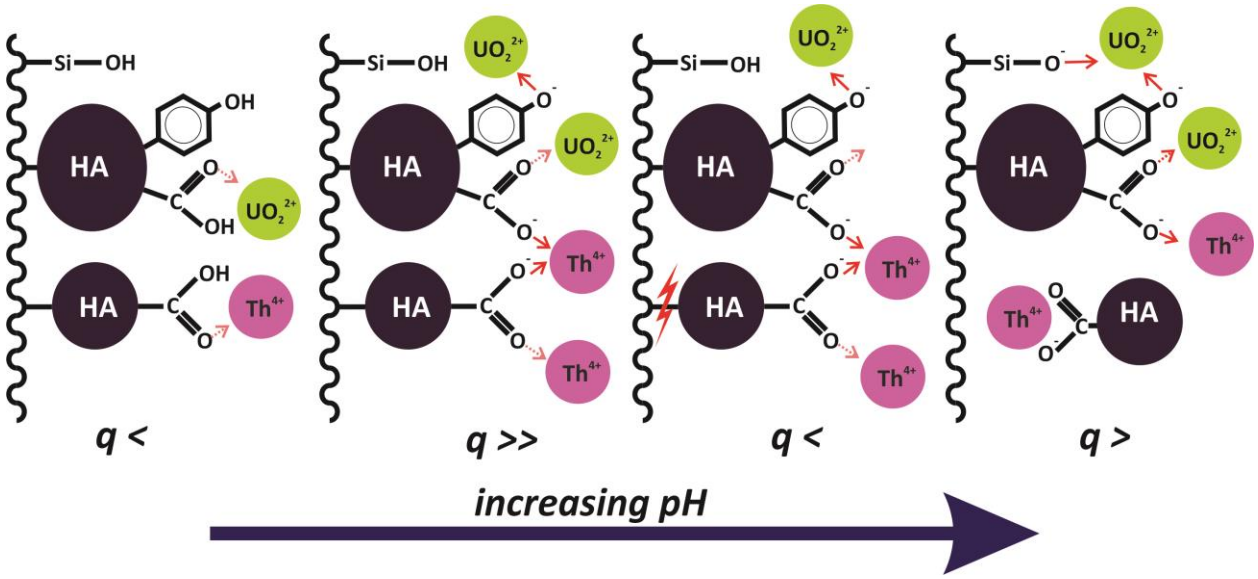

Fig 3.7 Adsorption mechanism by HASi1 adsorbent. Ligand site of humic acid (HA) shown are carboxylic and phenolic.

3.3.3 Effect of the solid-liquid ratio

The effect of the solid-liquid ratio was investigated from 0.5 to 3 mg ml^{-1} with an initial concentration of 10 mg L^{-1} for 3 h at the optimum pH for Th (2.5) and U (3). Fig 3.8 shows that the sorption efficiency depends on the adsorbent dose because the number of active ligand sites is proportional to the amount of adsorbent added. Quantitative Th and U removal was attained with a minimum dose of 1.5 mg ml^{-1}, and a further increase in the solid-liquid ratio would not significantly increase the recoveries.

Moreover, the objective of the studying the solid-liquid ratio effect is to ascertain the optimum dose for further experiments, i.e., the adsorption kinetics, salinity effect, lanthanide

effect and regeneration studies. Based on Fig 3.8, with an initial concentration of 10 mg L^{-1} as typical of the content of radioactive elements in nuclear industry wastewater [29], a solid-liquid dosage of 2 mg ml^{-1} was chosen for subsequent experiments.

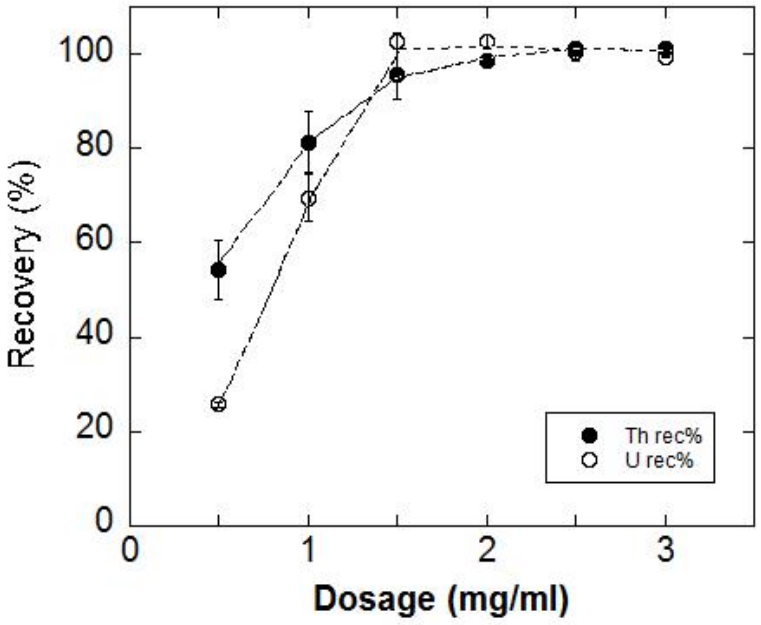

Fig 3.8 Effect of adsorbent dose on the adsorption of Th and U on HASi1.

3.3.4 Effect of the initial concentration (sorption isotherm)

To study the influence of the initial concentration of Th and U on the sorption process, 10 mg of HASi1 was equilibrated for 3 h with 5 ml of a Th and U solution that had a concentration from 10 – 500 mg L^{-1} at room temperature. To describe the experimental data at a constant temperature, the isotherm models of Langmuir and Freundlich were used. The Langmuir model (3) is based on the assumption that the adsorption process occurs as a monolayer system on the surface of the adsorbent. If the ligand sites are fully occupied, the sorption process would halt. In addition, the intramolecular force decreases as the distance to the adsorbent surface increases. The Freundlich model (4), in contrast, is based on the assumption that the sorption process could

occur on the surface with a heterogeneous functional group to form multilayer coverage, suggesting that adsorption is proportional to the initial sorbate concentration [24].

$$q_E = \frac{QKC_E}{1 + KC_E} \tag{3}$$

$$q_E = K_F C_E^{1/p} \tag{4}$$

where q_E (mg g^{-1}) and C_E (mg L^{-1}) are the sorption capacity and the metal concentration at equilibrium, respectively, while Q (mg g^{-1}) and K (ml mg^{-1}) are the theoretical maximum sorption capacity and binding constant, respectively. K_F is the Freundlich constant, and $1/p$ is the sorption intensity.

The root mean square error (*RMSE*) is used to evaluate the compatibility of the models, as in Eq. (5) [30]. q_{Eexp} and q_{Ecal} are the sorption capacity based on the experimental data and modeling at equilibrium, respectively, while n is the number of observations (data).

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(q_{E\,exp} - q_{E\,cal}\right)^2} \tag{5}$$

$$q_E = \frac{QKC_E^{1/p}}{1 + KC_E^{1/p}} \tag{6}$$

Based on Fig 3.9, the experimental saturation capacity could be visually estimated to be 31 and 30 mg g^{-1} for Th and U, respectively. Based on RMSE values (Table 3.2), the Freundlich model is better model and is in line with the heterogeneous characteristics of the functional groups on the surface of the adsorbent. However, to evaluate the maximum theoretical sorption

capacity Q (mg g^{-1}), the conventional Langmuir model was applied [31]. In the Freundlich model, the Q value could be estimated based on a constant initial concentration C_o (mg L^{-1}) with varied sorbent doses [32], which yielded the values 16.05 and 10.16 mg g^{-1} for Th and U, respectively. These values are much lower than the experimental saturation capacity previously mentioned. Several reports have mentioned an error when estimating the maximum sorption capacity by the Freundlich model. The results tend to be overestimated [33] or underestimated [34], and in the latter case, the authors have also shown that the Freundlich model is better than the Langmuir model in the case of fitting because of a lower error value.

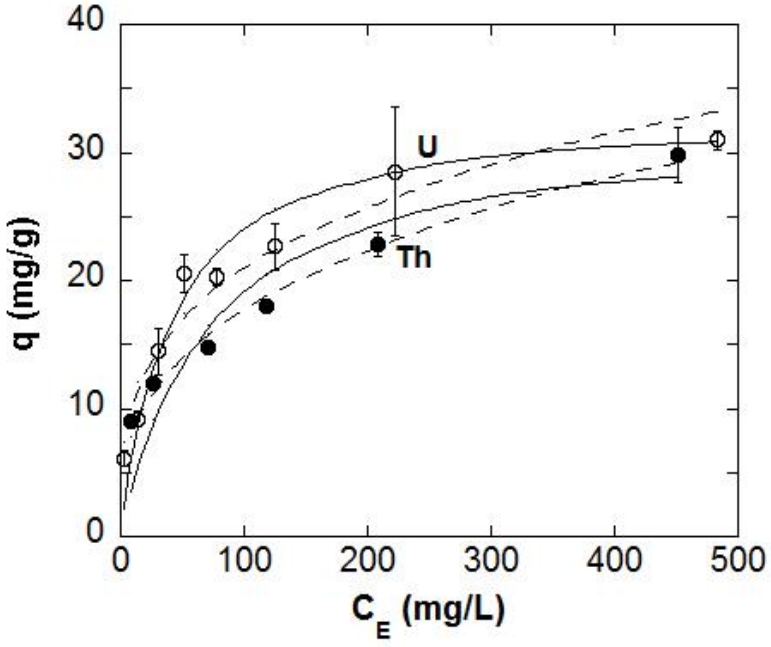

Fig 3.9 Experimental isotherm adsorptions of Th (closed circles) and U (open circles) for HASi1, as fitted by the Langmuir model (solid lines) and Freundlich model (dashed lines).

The determination of the maximum sorption capacity using the Sips model (6), which combines the Langmuir and Freundlich models [35], resulted in maximum sorption capacities of 214.93 mg g^{-1} (*RMSE* 0.80) and 54.02 mg g^{-1} (*RMSE* 1.86) for Th and U, respectively. Based on

the *RMSE* values, the Sips model is a better model than Langmuir model, and in the case of Th, it is better than the others. However, the model overestimates the value for the maximum sorption capacity. Thus, in this case, the Langmuir model was chosen because of the least error between the estimated value and the experimental value (Table 3.2). Based on the sorption intensity values, *1/p*, for Th and U, which are higher than 0 and less than 1 (0.33 and 0.29), it is assumed that the adsorption process is physical and favorable [36], which is demonstrated by the Th and U removal with the HASi1 adsorbent.

Table 3.2 Estimated isotherm parameters of Th and U adsorptions by the HASi1 adsorbent.

Elements	pH	Langmuir			Freundlich		
		Q (mg g^{-1})	K (L mg^{-1})	*RMSE*	K_F (ml mg^{-1})	p	*RMSE*
Th	2.5	32.3	0.015	2.97	3.92	3.03	0.80
U	3	33.2	0.027	2.07	5.57	3.46	2.06

3.3.5 Adsorption kinetics studies

Sorption kinetics studies were carried out to examine the effect of contact time on the sorption process by the batch technique at pH 2.5 (Th) and 3 (U). The initial concentrations were 10 and 25 mg L^{-1}, while the contact time was varied from 1 to 240 min, and the solid-liquid ratio was 2 mg ml^{-1}.

Three models (pseudo-first-order, pseudo-second-order and intra-particle diffusion) were applied to describe the experimental kinetics data. The pseudo-first-order model is based on the assumption that the adsorption rate at any given time (t, min) depends on the difference between the equilibrium sorption capacity (q_E, mg g^{-1}) and the sorption capacity at time t (q_t, mg g^{-1}), as formulated in Eq. (7). In the pseudo-second-order model, it is postulated that the sorption process

is a pseudo-chemical reaction process and that the sorption rate increases proportionally to the square of the driving force. The driving force in this case is the difference between the equilibrium sorption capacity (q_E) and the sorption capacity at any given time t (q_t), as described in Eq. (8). Based on the pseudo-second-order model, the initial adsorption rate (H, mg g^{-1} min^{-1}) and time required to adsorb half of the initial concentration ($t_{1/2}$, min) could be computed by Eqs. (9) and (10) [26]. The intra-particle diffusion model is based on the hypothesis that the adsorption process is controlled by the diffusion process (11). k_i (mg g^{-1} $min^{0.5}$) is the intra-particle diffusion rate constant, and I is the intra-particle diffusion constant, which is proportional to the boundary layer.

$$q_t = q_E(1 - e^{-k_1 t}) \tag{7}$$

$$q_t = \frac{k_2 q_E^2 t}{1 + k_2 q_E t} \tag{8}$$

$$H = k_2 q_E^2 \tag{9}$$

$$t_{1/2} = \frac{q_E}{H} \tag{10}$$

$$q_t = k_i \sqrt{t} + I \tag{11}$$

$$dq\ (\%) = 100 \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} \left(\frac{q_{t\,exp} - q_{t\,cal}}{q_{t\,exp}} \right)^2} \tag{12}$$

$$ARE\ (\%) = \frac{100}{n-1} \sum_{i=1}^{n} \left(\frac{q_{t\,exp} - q_{t\,cal}}{q_{t\,exp}} \right)^2 \tag{13}$$

Normalized standard deviation (*dq*) and average relative error (*ARE*) were used to evaluate the model compatibility to the experimental data. *dq* and *ARE* given in Eq. (12) and (13) [37]. q_{texp} and q_{tcal} are the sorption capacity based on the experimental data and the modeling at a given time *t*, respectively, while *n* is the number of observations.

Fig 3.10 shows that all models could fit better to the experimental data, which are also supported by the statistical analysis results of normalized standard error (*dq*) and the average relative error (*ARE*) values, as shown in Table 3.3. The table shows that based on both values, the pseudo-second-order model generally fits better to the experimental data than the pseudo-first-order model. Additionally, the pseudo-second-order model predicts the maximum sorption capacity better than the pseudo-first-order model. Generally, the k_2 value of the pseudo-second order model for U is greater than that of Th, which is probably caused by a higher binding for U than Th (Table 3.2).

The calculated initial adsorption rate (*H*) and time required to adsorb half of the initial concentration ($t_{1/2}$) for both Th and U suggest a rapid adsorption process. There is an agreement between the value of the equilibrium sorption capacity from the experimental data (q_{Eexp}) and that from the modeling (q_{Emodel}), indicating that the adsorption process is concentration dependent [38].

The fitting of the experimental kinetic data by the intra-particle diffusion model results in a linear curve that does not intercept the origin point. This result indicates that the adsorption rate is affected by the intra-particle diffusion process [39]. However, the intra-particle diffusion coefficient (k_i) value denotes that the diffusion process is not a rate-limiting step. The larger intra-particle diffusion constant (*I*) for U signifies an improvement in the sorption rate and a

better sorption mechanism because of the stronger bonding between the uranyl ion and the ligand site on the adsorbent surface [40], corresponding to its higher binding constant.

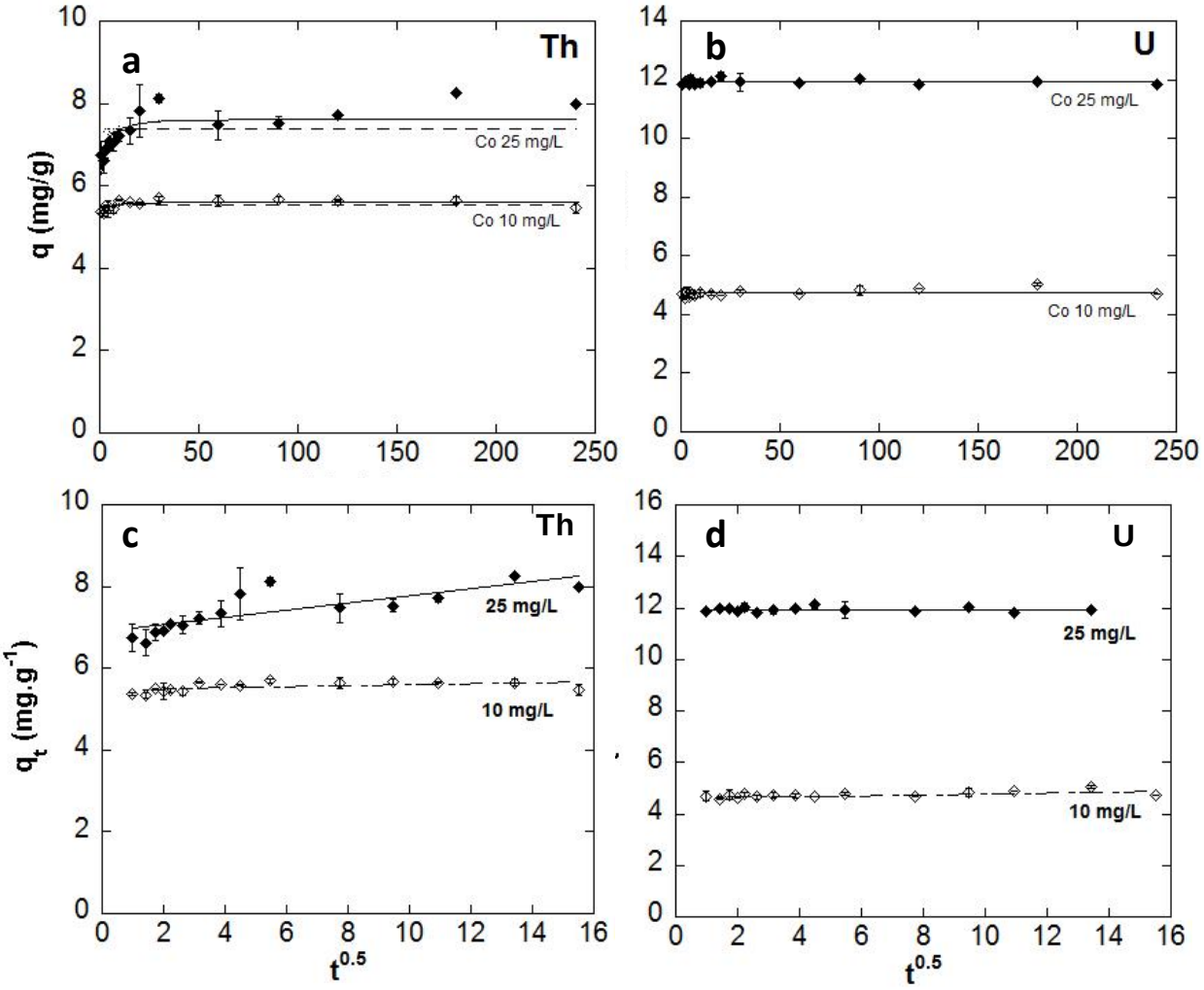

Fig 3.10 Fittings of the experimental kinetic data by the pseudo-first-order (dashed line) and pseudo-second-order (solid line) models for (a) Th and (b) U, and the intra-particle diffusion model: (c) Th and (d) U.

Table 3.3 Kinetic parameters of Th and U removal by the HASi1 adsorbent estimated based on modeling by the pseudo-first-order, pseudo-second-order and intra-particle diffusion models.

	C_o Th (mg L^{-1})		C_o U (mg L^{-1})	
Parameters	**10**	**25**	**10**	**25**
Pseudo-first-order				
k_1 (min^{-1}) × 10^{-3}	3.35	2.19	4.42	4.99
q_E model (mg g^{-1})	5.55	7.39	4.73	11.93
q_E experimental (mg g^{-1})	5.70	8.26	5.04	12.16
dq (%)	1.99	6.31	2.35	0.64
ARE (%)	0.04	0.40	0.06	0.00
Pseudo-second-order				
k_2 (g mg^{-1} min^{-1})	2.94	0.60	5.66	6.60
q_E model (mg g^{-1})	5.60	7.62	4.76	11.96
q_E experimental (mg g^{-1})	5.70	8.26	5.04	12.16
H (mg g^{-1} min^{-1})	92.18	35.10	128.36	943.26
$t_{1/2}$ (min)	0.06	0.22	0.04	0.01
dq (%)	1.50	4.58	2.16	0.69
ARE (%)	0.02	0.21	0.05	0.01
Intra-particle diffusion				
k_i (mg g^{-1} $min^{0.5}$)	0.088	0.013	0.001	0.016
I (mg g^{-1})	6.89	5.47	11.93	4.65
dq (%)	1.9	4.0	1.0	0.7
ARE (%)	0.04	0.16	0.01	0.01

3.3.6 Effect of salinity and lanthanide concentration

To evaluate the capability of the HASi1 adsorbent to remove Th and U in a highly saline environment, batch studies were performed by equilibrating 10 mg of the adsorbent with 5 ml of 10 mg L^{-1} Th or U in a sodium chloride solution at a concentration from 0 to 1 mol L^{-1}. This evaluation is considered to be important because many Th and U occurrences in nature are associated with marine beach placer deposits and are susceptible to Th and U pollutions. Fig 3.11a shows that salinity decreases the sorption capacity. In the case of Th, the sorption capacity decreases to 75% (NaCl 0.75 M) of the initial sorption capacity (NaCl 0 M), while that of U is reduced to 70% of the initial sorption capacity for the same sodium chloride concentration. The sorption capacity decrease due to the increasing salinity could be explained by the tendency of Th and U to form neutral and less charged chloro complexes [41], which decrease the electrostatic interaction between ion target and ligand site (Figure 3.12).

Fig 3.11b depicts the effect of the lanthanide concentration (Ln) on the HASi1 sorption capacity for Th and U removals. In batch studies, lanthanides were represented by La and Ce, which were used at the same amount to constitute the total lanthanide concentration, [Ln]. Typically, 10 mg of the HASi adsorbent was equilibrated with 5 ml of a Ln-Th or an Ln-U mixture solution, in which the total lanthanides ratio to the Th or U, [Ln/X], varied between 5 and 75. This study considers the close association between lanthanides and Th-U in nature, e.g., monazite sand. The results suggest that lanthanide concentration suppresses the Th and U removal capacities by up to 80% when the Th/U – Ln ratio reaches 1:75. In addition, U is more affected by the Ln concentration, probably because of the small difference in ionic charged species (UO_2^{2+} to Ln^{3+}) compared with Th (Th^{4+} to Ln^{3+}).

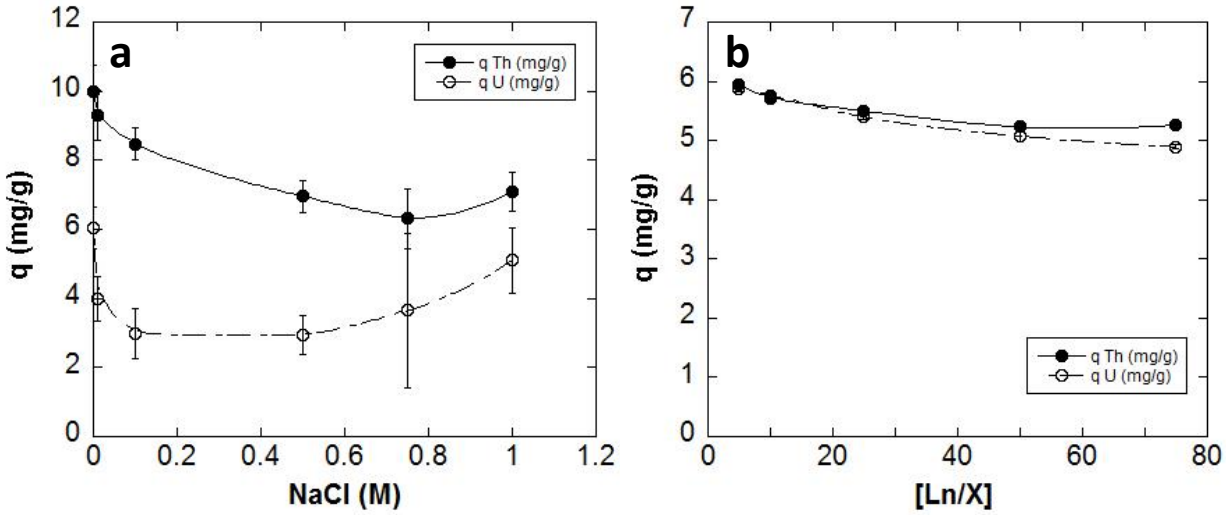

Fig 3.11 Sorption capacities of the HASi1 adsorbent for Th and U as function of (a) salinity and (b) the ratio of their concentration to the total lanthanide concentration, [Ln/X].

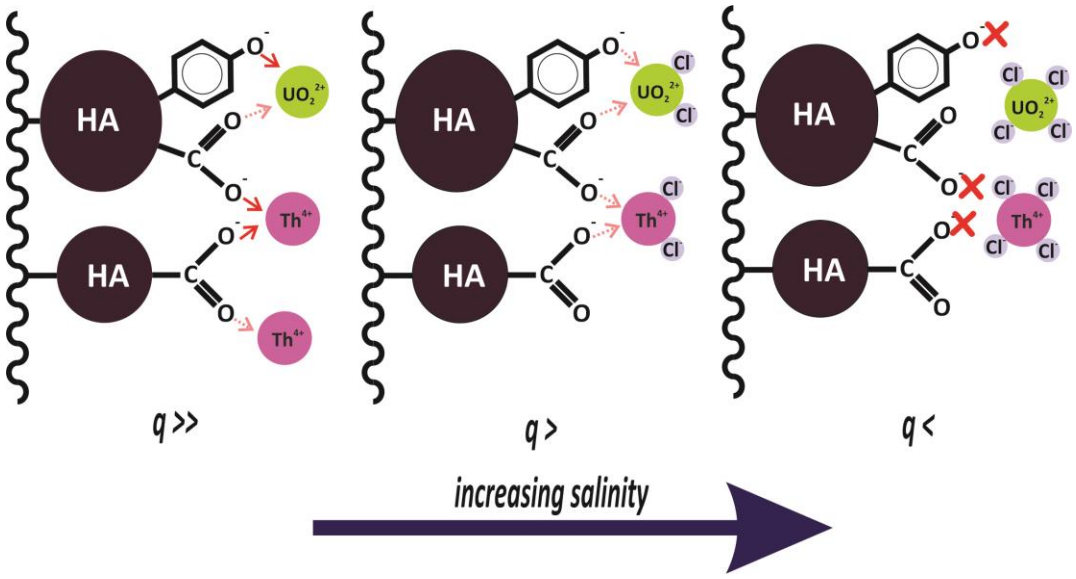

Fig 3.12 Effect of increasing salinity in adsorption by HASi. The electrostatic interaction is weakened due to less-charged chloride complex formation.

3.3.7 Desorption and reusability studies

Desorption and reusability studies were carried out to determine the regeneration capability of the HASi1 adsorbent and the viability of recovering Th and U for further use. In the desorption experiment, 10 mg of the HASi1 adsorbent containing Th or U at a concentration of 5 or 12 mg g^{-1} was leached by 1 ml of nitric acid or 5 ml of ammonium citrate for 5 min. The results of the leaching experiment for different concentrations of nitric acid and ammonium citrate are presented in Fig 3.13.

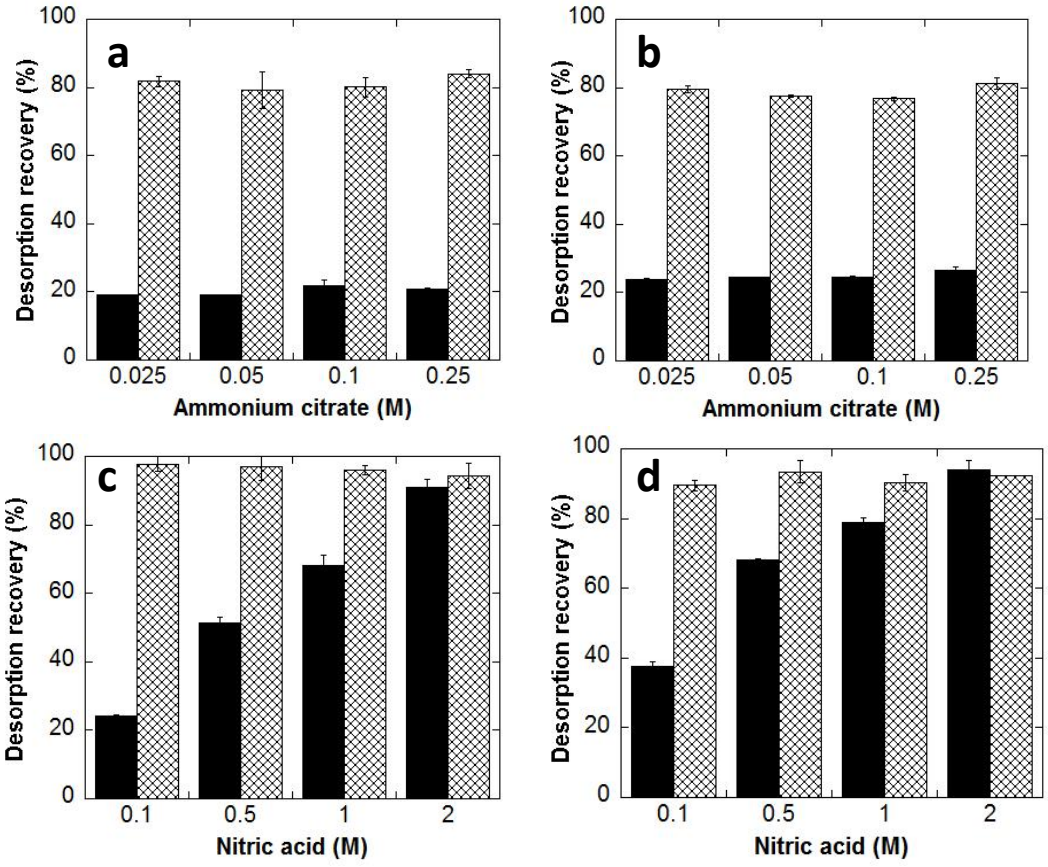

Fig 3.13 Desorption of Th (solid black column) and U (mesh column) by ammonium citrate with a metal content in the HASi1 adsorbent of (a) 5 mg g^{-1} and (b) 12 mg g^{-1}. The desorption by nitric acid with a metal content of (c) 5 mg g^{-1} and (d) 12 mg g^{-1}.

The concentration of ammonium citrate did not affect the recovery rate for either Th or U. In addition, U has a stronger affinity toward citrate, as demonstrated by the higher recovery leaching value (80%). This result suggests that ammonium citrate is a suitable leaching reagent to recover U from HASi1, including its regeneration and possible separation from Th. In the case of nitric acid, the concentration strongly affects the Th recovery. Th is quantitatively recovered by 2 M nitric acid, while quantitative U recovery is attained at a lower concentration. Based on a leaching experiment using different Th and U contents (5 or 12 mg g^{-1}) both with ammonium citrate and nitric acid, there is no significant difference regarding recovery, indicating the possibility of quantitatively recovering Th and U using a larger volume of leaching agent at a lower concentration.

The reusabilty studies included the sorption and desorption phases for each cycle. In these studies, 20 mg of the HASi adsorbent was equilibrated with 20 ml of a 10 mg L^{-1} Th or U solution (a solid-liquid ratio of 1 mg ml^{-1}). After Th and U were adsorbed, the supernatant solution was separated by centrifugation, and the HASi1 containing Th or U was then leached by 5 ml of 1 M nitric acid to recover Th and U (desorption). Following 5 min of agitation, the nitric acid containing Th or U was separated by centrifugation, and HASi1 was washed with Milli Q water, dried at 30°C and used for the next sorption-desorption cycle.

The results in Fig 3.14 show that the sorption capacity (q, mg g^{-1}) is relatively constant after nine regeneration cycles, demonstrating the stability of the HASi1 adsorbent and its suitability for repeated use. Table 3.4 compares the characteristics of several humic-acid-based adsorbents that have been reported to remove Th and U from an aqueous solution with respect to the optimum pH, maximum sorption capacity Q (mg g^{-1}), equilibrium time and reusability.

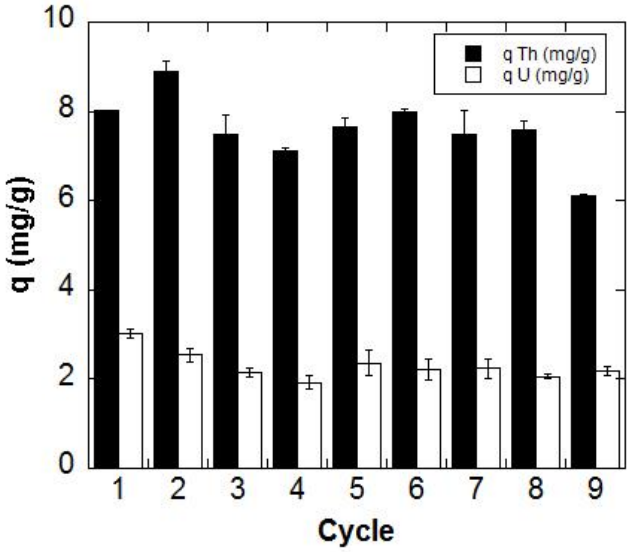

Fig 3.14 Sorption capacity of the HASi1 adsorbent after nine cycles of Th and U removal and regenerated using 1 M nitric acid.

Table 3.4 Comparison of the Th and U sorption capabilities of the humic-acid-based adsorbents from previous reports and this study.

Adsorbent material	pH	*Q* (mg g^{-1})		Equilibrium time (min)	Reusability (cycles)	Ref.
		Th	U			
1. Humic acid immobilized on zirconium pillared clay	6		132.7	180	4	[7]
2. Humic acid-Amberlite XAD-4	4	35.0		60		[8]
3. Insolubilized humic acid	3	20.0	17.0	360		[42]
4. Humic acid modified silica gel (silylation)	3	28.0	43.9	180	4	Chapter 2
5. Humic acid - silica sol gel composite	3		33.2	180	9	This chapter
6. Humic acid - silica sol gel composite	2.5	32.3		180	9	This chapter

3.4 Conclusions

The results clearly demonstrate that the sol-gel method is a suitable method to attach humic acid as a functional group to silica gel. The success of humic acid mobilization in the silica gel matrix was confirmed by FT-IR and SEM-EDS characterization. The performance of HASi1 for Th and U removal from an aqueous solution was best attained under acidic conditions (pH 2.5 – 3). The isotherm adsorption studies showed that the sorption process is concentration dependent because of the heterogeneous nature of the functional groups present. The maximum monolayer sorption capacity is found to be 32.3 and 33.2 mg g^{-1} for Th and U, respectively. Kinetics studies reveal that the pseudo-second-order model is best for describing the rapid adsorption process, of which 85% removal could be attained within 5 min. Conversely, the intra-particle diffusion model suggests that the diffusion process affected the adsorption process. Based on the ion competition studies, HASi1 is suitable to remove Th and U from a high-saline environment and to separate them from lanthanides, as their closest associated elements in nature. HASi1 could be regenerated using nitric acid, and its performance is relatively stable after nine regeneration cycles. Furthermore, the results in terms of adsorbent performance for Th and U removal signify the viability of HASi as an inexpensive alternative adsorbent compared with the previously reported materials and highlight the importance of the sol-gel method as an underdeveloped yet versatile method to produce hybrid materials applicable to environmental remediation.

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CHAPTER 4

HUMIC ACID-CHITOSAN-SILICA GEL – AN EFFICIENT AND ECONOMIC ADSORBENT FOR THORIUM AND URANIUM REMOVAL

Abstract

A novel and low-cost adsorbent was prepared by immobilization of humic acid on silica gel surface coated with cross-linked chitosan (SiChiHA), which was developed for Th and U removal from aqueous solution. The method is very simple and eco-friendly compared to previous reports on humic acid based adsorbents. The adsorbent was characterized by SEM-EDS method to describe the chitosan coating and humic acid immobilization on silica gel surface. The performance of adsorbent in Th and U removal was investigated in terms of pH, solid-liquid ratio, contact time, ionic strength and isotherm capacity. The optimum pHs for Th and U removal were 3.5 and 5, and Langmuir adsorption model showed the maximum sorption capacities were 30.6 and 75.4 mg g^{-1} for Th and U, respectively. The adsorption process was best described by pseudo-second order equation and correspondingly the times required to adsorb half of its initial concentration (50 mg L^{-1}) was less than 10 min both for Th and U. In solution, sodium concentration up to 2 mol L^{-1} and lanthanides concentration up to 100 times did not significantly affect the removal efficiency of Th. These results show that SiChiHA can be employed as an effective low-cost adsorbent for Th and U removal.

Keywords: Silica gel, humic acid, chitosan, adsorbent, Thorium, Uranium

4.1 Introduction

Thorium (Th) and Uranium (U) are the most important natural radioactive elements which productions tend to increase recently to supply the demands in energy sector and other applications [1-2]. The exploitation and extraction activities in turn would cause the release of these elements to the environment. The effect of exposure of these elements to the human health is well documented [3-4]. Therefore, the recovery of these radioactive elements from the waste is mandatory before its release to the environment.

Several techniques had been addressed to recover both elements including precipitation, liquid-liquid separation (solvent extraction), electrochemical and membranes. However, solid phase extraction has advantages compared to the others since this method does not generate additional waste (safer), cost effective and the most important feature is the capability to deal with very low concentration pollutant i. e. radioactive waste [5].

Silica gel is one of the most widely applied materials in solid phase extraction as adsorbent due to its physical strength and easily controlled structures (surface area, pore size, particle shape etc.) and stability [6]. In spite of these, low adsorption capacity becomes the major drawback of silica gel adsorbent due to weak binding ability of silanol or siloxane ligands as electron pair donor on the surface of silica gel to attract metal ions [7]. To increase the capacity of silica gel adsorbent, surface modification is deemed necessary.

Previous chapter reports the success in silica gel modification by humic acid through simple sol-gel method (HASi). The results show that HASi posseses almost same sorption capacity compared to that of humic-acid silica gel produced by conventional silylation method (SiHA) reported in Chapter 1. The advantages of HASi include selectivity to remove Th and U from lanthanides, reusability and applicability in Th and U recovery and separation. However,

HASi has limitation in terms of narrow effective pH range (2.5 – 3). At lower pH the adsorption efficiency would decrease due to ligand protonation while at higher pH adsorption capacity also decrease due to humic acid instability. Other limitation is the decreasing capacity of HASi at high salinity condition due to neutral or anionic chloro complex formation (Chapter 3 Section 3.3.6).

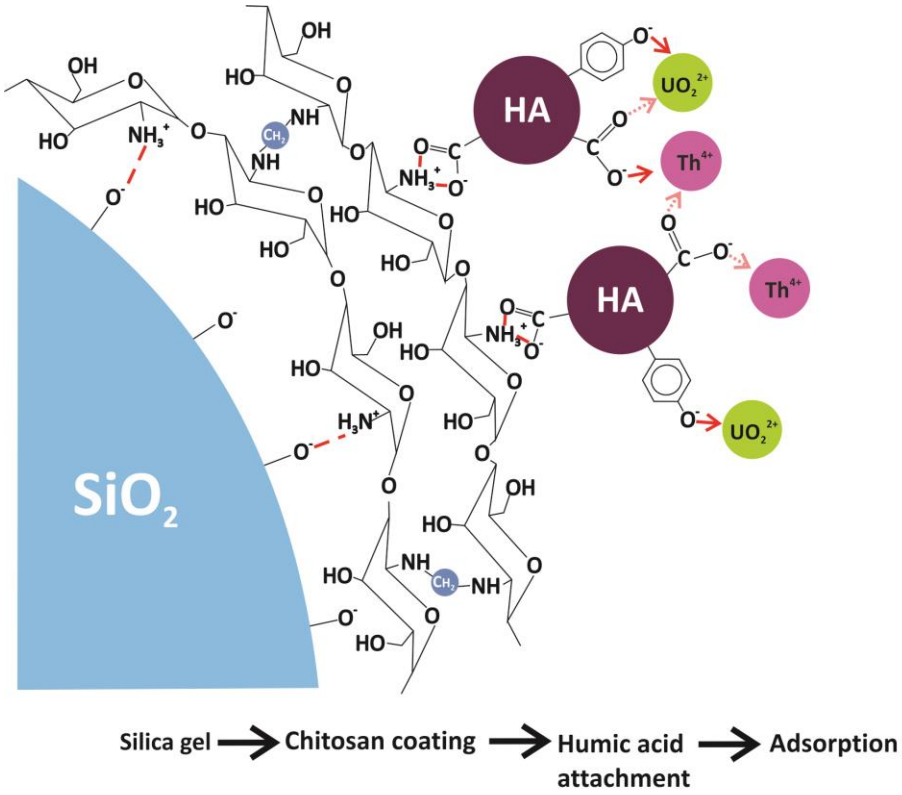

Fig 4.1 Proposed method in adsorbent synthesis.

To address the problems encountered in previous research, in this chapter it would be proposed a method to modify silica gel surface by humic acid using cross-linked chitosan coating. Chitosan is proposed based on several considerations. First, chitosan contains amine group, like aminoalkyltrimethoxysilane compound, which would be expected as template for functional group modifier i.e. humic acid through amine-carboxylic bonding (Fig 4.1). Second, cross-linked

chitosan is stable at a wide range pH, which is advantageous to stabilize humic acid in high pH condition. Third, it is hypothesized that amine group would act as basic functional group. In high saline condition, the presence of amine would be advantageous to attract neutral or anionic Th or U chloro complex and keep the adsorption efficiency high. Further, the objectives of this chapter are to confirm the successful of silica gel modification process by characterizations and to investigate its performance in Th and U removal from aqueous media.

4.2 Materials and method

4.2.1 Reagents and instrumentation

All chemicals including chitosan were purchased from Kanto Chemicals and Wako Chemicals Japan and used as received, while silica gel (for chromatography, size 40 – 63 μm) was obtained from Merck, Darmstadt. Humic acid was supplied by Acros Organics and purified according to Koopal et al. [8]. All solution and dilution were carried out using Milli Q water (Milli Q system, Millipore). Solution pH was adjusted using hydrochloric acid or sodium hydroxide and determined by Horriba pH meter F-52. Thorium or uranium in single solution was determined spectrophotometrically based on their colored complex with Arsenazo III by Jasco V-530 UV/Vis spectrophotometer. Th or U in mixture solution with other metals on the other hand was measured using ICP-AES (SPS-7700, Seiko Instrument Co).

Surface morphology of synthesized adsorbent was observed using Hitachi S-2400 Scanning Electron Microscope operated at 15 kV after gold coating of adsorbent particle. Beside the morphology, the element distribution on the surface of the sorbent was also mapped using JEOL JSM-5310 Scanning Microscope-Energy Dispersive X-Ray Spectroscope (SEM-EDS), operated at 15 kV. The zeta potentials of synthesized adsorbents were determined by Delsa™

Nano HC Zeta Particle Analyzer, equipped with DelsaTM Nano AT Autotitrator (Backman Coulter, USA). FT-IR spectra were obtained using a Jasco FT/IR 660 Plus spectrometer by the KBr method with a wavelength range of 400 to 4000 cm^{-1}. All analysis was performed in Graduate School of Environmental Science, Hokkaido University, except SEM-EDS (Graduate School of Science, Hokkaido University), FT-IR and zeta potentials (Open Facility, Hokkaido University, Sousei Hall).

4.2.2 Adsorbent preparation

Silica gel was activated by heating in oven at temperature 150℃ for 24 hours. A 1 gr activated silica gel was dispersed in 20 ml of 1% chitosan solution which was prepared by dissolving chitosan in 2% acetic acid. The slurry was then vigorously stirred and after 24 hours 2 ml formaldehyde 37% as cross-linking agent was added dropwise into the suspension and stirring was continued until gel formed on the surface of silica gel. The product was then dried at 40℃ and sticked particles were separated by crushing and sieving (< 64 µm) to produce chitosan-silica gel (SiChi) powder. A 1 g SiChi powder was added into 30 ml humic acid solution, prepared by dissolving 1 g purified humic acid in 30 ml sodium hydroxide 0.1 M. After SiChi addition, the pH of mixture solution was adjusted to 7.5 by using hydrochloric acid and then stirred for 24 hours at room temperature. After that, the solid phase was separated by centrifugation and washed with 0.2 M sodium chloride pH 10 to remove unbound humic acid and subsequently by 1 mM hydrochloric acid to protonate the functional group on the surface of the sorbent. Finally, the sorbent was dried at 40° C to produce humic acid-chitosan-silica gel (SiChiHA) sorbent.

4.2.3 Batch adsorption experiments

The performance of SiChiHA adsorbent in Th and U removal was studied by batch method to determine the optimum condition in terms of pH, sorbent dose, initial metal concentration, contact time, salt effect, metal recovery and regeneration. Typically, in batch method 10 mg SiChiHA adsorbent was equilibrated with 5 ml of thorium or uranium solution at room temperature. After equilibrium, liquid phase was separated by centrifugation and metal concentration in supernatant solution was analyzed spectrophotometrically or by using ICP-AES.

Adsorption capacity (q, mg g^{-1}) of SiChiHA adsorbent after Th or U removal was calculated using equation (1):

$$q = (C_o - C_E)\frac{V}{m} \quad (1)$$

Recovery (R,%) of the Th and U removal was calculated using equation (2):

$$R = \frac{100 \times (C_o - C_E)}{C_o} \quad (2)$$

C_o and C_E are initial and equilibrium concentration of metal ion (mg L^{-1}) respectively, V is volume of aqueos phase (ml) and m is adsorbent added (mg).

4.3 Results and discussions

4.3.1 Adsorbent characterization

Fig 4.2 shows the surface morphology observed by scanning electron microscopy. In Fig 4.2a, activated commercial silica gel as unmodified material exhibits smooth surface and the

coating process to modify the surface by chitosan cross-linking results (SiChi) in encrustation of chitosan on the silica gel surface (Fig 4.2b).

Further, there is no difference in terms of surface morphology of SiChi after it was modified by humic acid to form SiChiHA (Fig 4.2c). This suggest that the bounding of humic acid to the SiChi surface was not achieved by impregnation process which in this case would be indicated by the presence of humic acid as inclusions on the surface of SiChi and would cause different surface morphology.

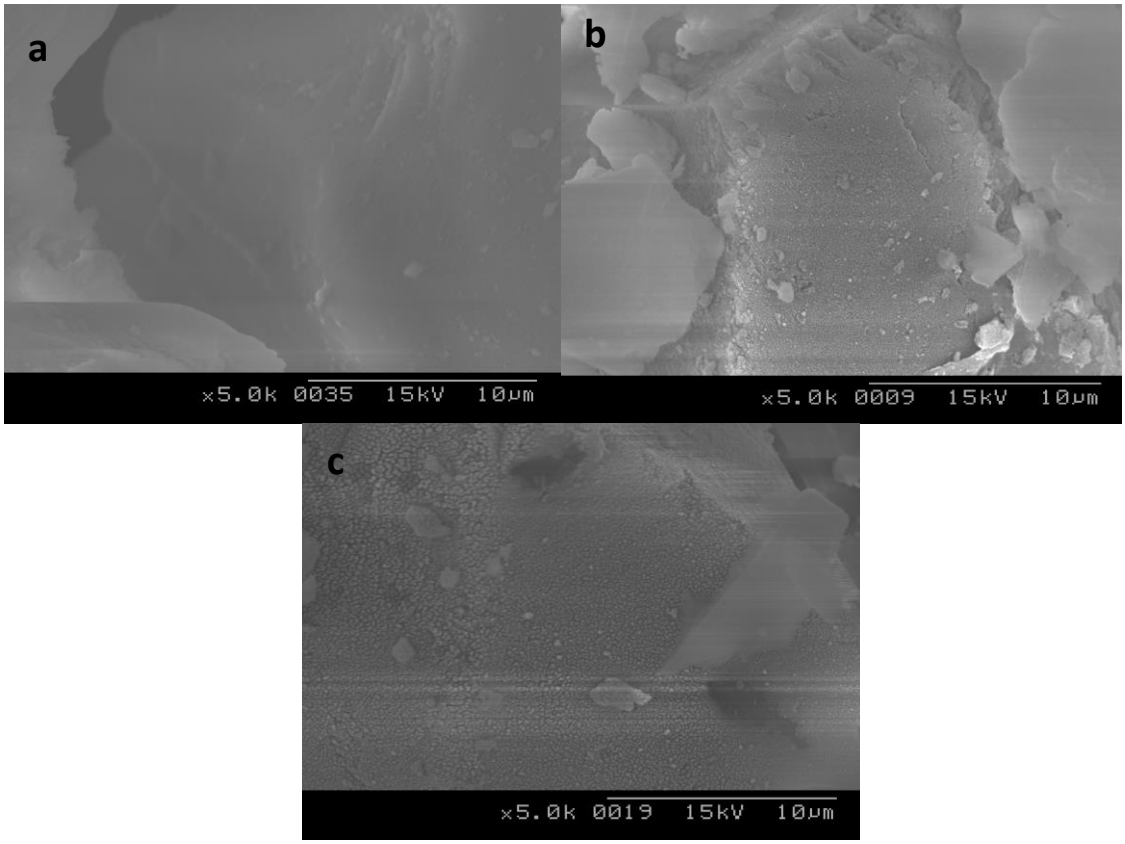

Fig 4.2 Scanning electromicrograph of a. Silica gel (commercial, Merck) b. Chitosan coated silica gel (SiChi) c. Humic acid-chitosan-silica gel (SiChiHA).

The coating process by chitosan and humic attachment were confirmed based on the results of scanning SEM-EDX (Fig 4.3). Fig 4.3a – 4.3c exhibits strong signal for Si and O which are the major component of silica gel. After coating by cross-linked chitosan, carbon (C) signal appears which is the major component of chitosan (Fig 4.3b). The C signal becomes more obvious after humic acid attachment to the adsorbent surface (Fig 4.3c). Besides, Fig 4.4 displays the mapping of C element on the adsorbent surface which suggest the even distribution of cross-linked chitosan and humic acid as surface modifiers.

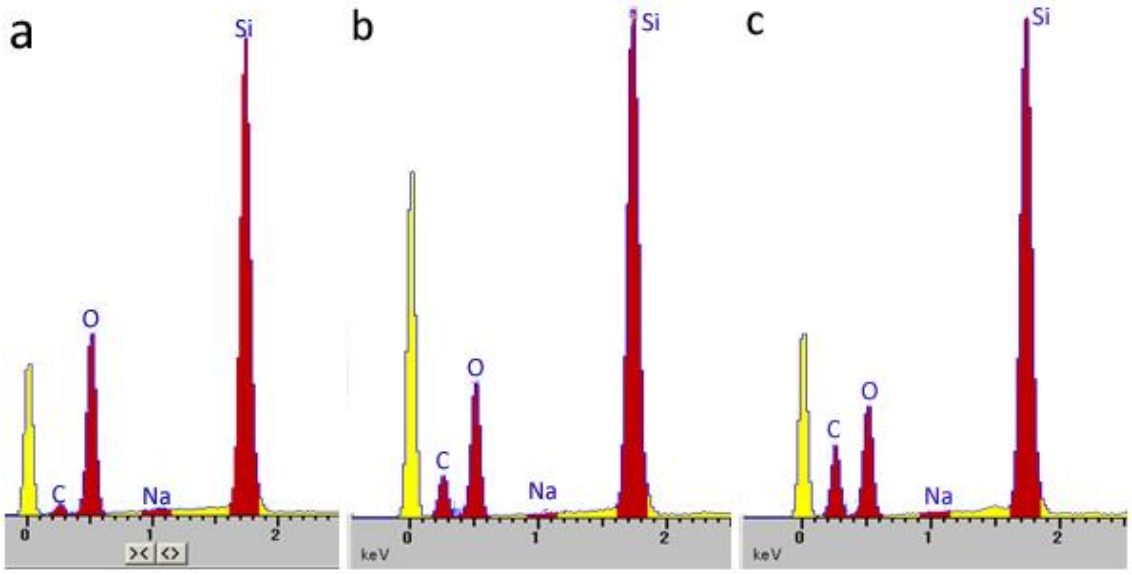

Fig 4.3 EDX profile of a. Silica gel, b. SiChi, c. SiChiHA.

FT-IR analysis was carried out to elucidate the presence of functional group on the adsorbent surface and to confirm the surface modification i.e. cross-linked chitosan coating and humic acid immobilization. The results is shown in Fig 4.5 Commercial silica gel (SiO_2) shown adsorption band of silanol at 954 cm^{-1} and Si-O-Si as broad band at 1080 cm^{-1}. Peak at 796 cm^{-1} is assigned as tetrahedral silica matrix. After chitosan coating (SiChi), the peak appears at 1539 cm^{-1} which confirm the presence of amine group. Humic acid attachment (SiChiHA) caused the

peak at 3500 – 3800 cm^{-1}, which is assigned for carboxylic functional group and 1650 cm^{-1} for oxygen functional group. The presence of amine is still detected on SiChiHA surface as peak at 1539 cm^{-1}.

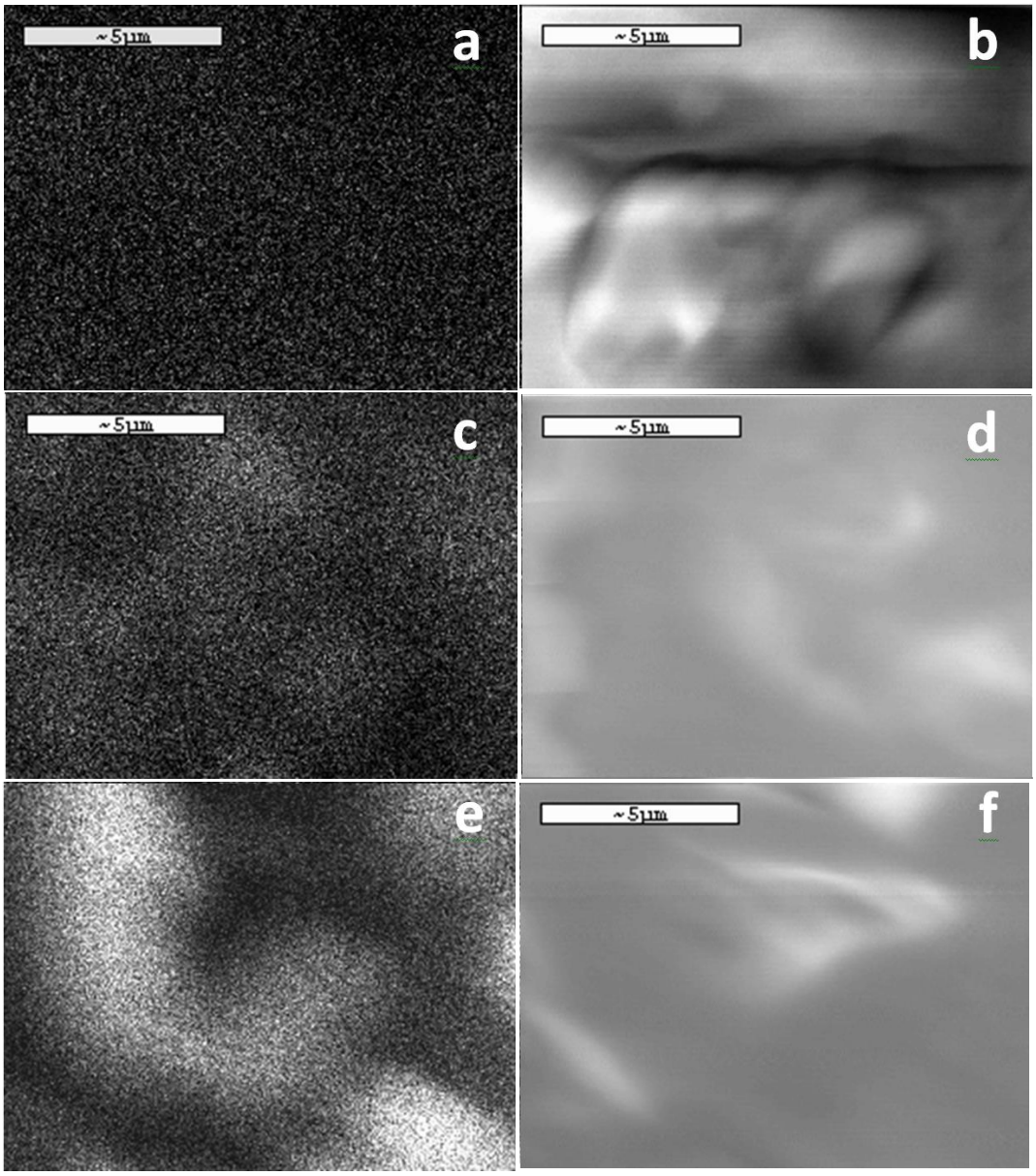

Fig 4.4 SEM-EDX of carbon mapping on sorbent surface with corresponding surface image a-b. silica gel, c-d. SiChi, e-f. SiChiHA.

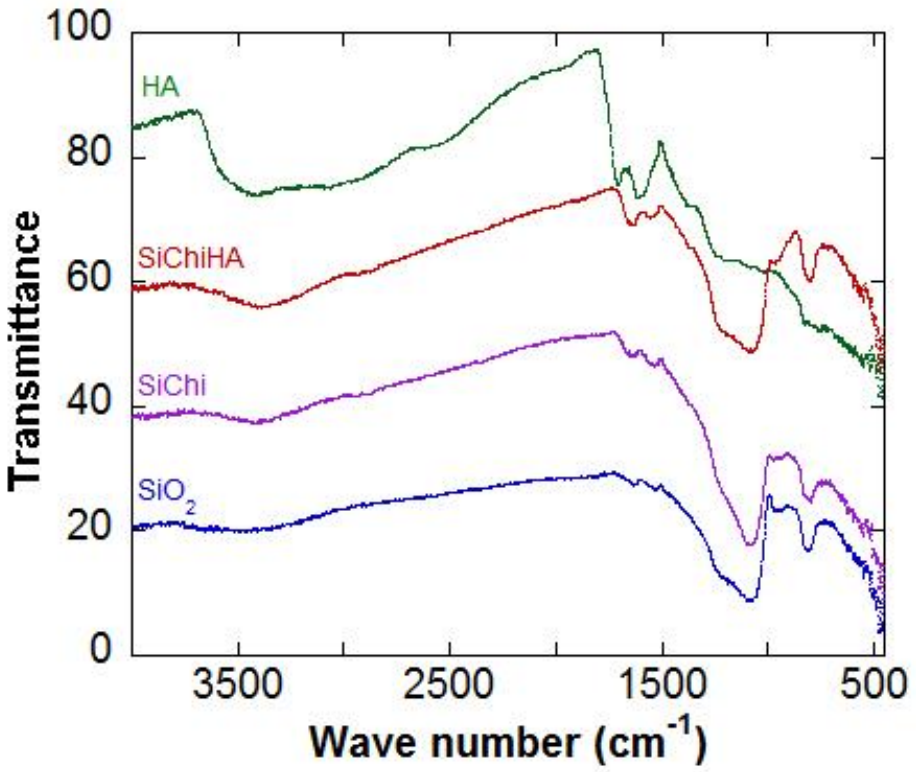

Fig 4.5 FT-IR spectra of commercial silica gel (SiO2), SiChi and SiChiHA.

Surface zeta potential of adsorbent SiO_2, SiChi and SiChiHA as function of pH is shown in Fig 4.6. Based on the figure, the pH at zero charge potential (pHzpc) untuk commercial silica gel (SiO_2) adalah 4.0. This value is higher compared to literatures [9-10], which mentioned the value to be around 3.0. Modification of silica gel surface by chitosan (SiChi) increases pHzpc value to 8.0. This was due to the presence of amine group, as basic functional group tends to form positively charged group $–NH_3^+$ [11]. Further modification by attachment of humic acid through the interaction of carboxylic group humic acid and amine group of chitosan decreased the pHzpc value of SiChiHA value to 4.6.

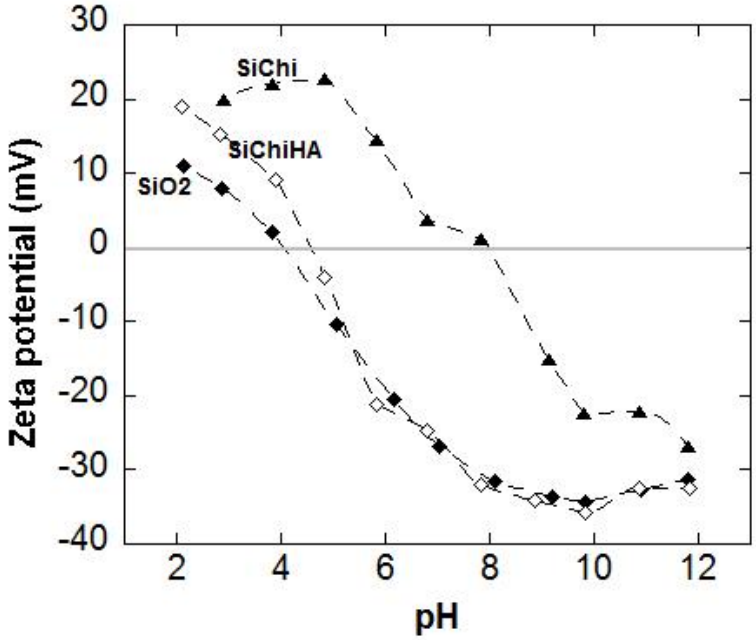

Fig 4.6 Zeta potential of silica gel, SiChi and SiChiHA as function of pH.

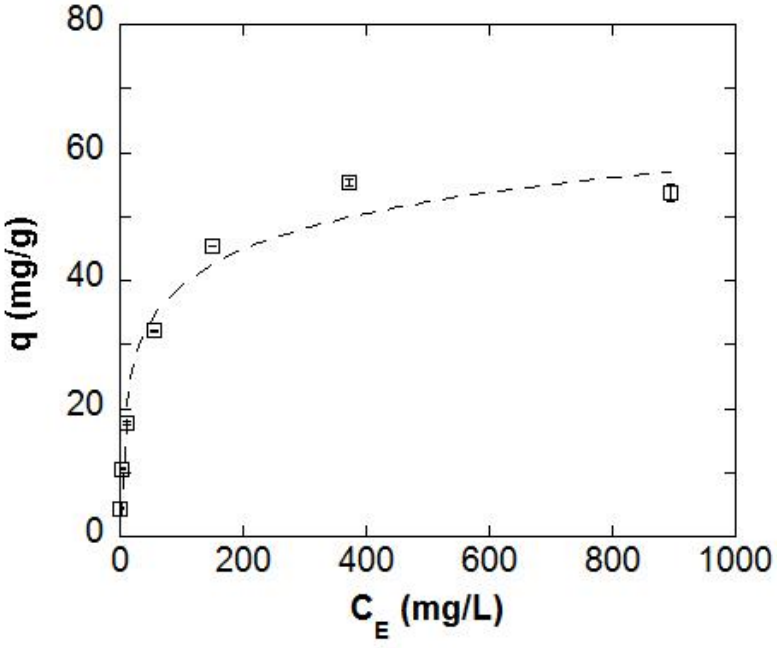

Fig 4.7 Isotherm adsorption in immobilizing humic acid onto SiChi surface.

In surface modification of SiChi by humic acid, it is important to determine the adsorption capacity of SiChi. Isotherm plot in humic acid immobilization by SiChi is shown in Fig 4.7, which was based on batch studies at room temperature, solid-liquid ratio 2 mg ml^{-1}, pH 7.5 and 24 h equilibrium. The figure shows the steep slope at low equilibrium humic acid concentration, which became plateau at higher concentration indicating the saturation in humic acid adsorption by SiChi. The maximum saturation capacity of humic acid by SiChi is 52 mg g^{-1}.

4.3.2 Effect of pH on the adsorption

pH variable on the Th and U removal by SiChiHA was studied in the range 0 – 5 at room temperature and initial concentration 10 mg L^{-1} by 3 hour equilibration which results are presented in Fig 4.8. Based on the figure, sorption capacity is positively correlated with the pH. The optimum removal of Th and U were attained at pH 3.5 and 5 respectively. Observations at higher pH were not performed due to the possibility of Th and U precipitation. The effect of pH on the sorption capacity could be explained based on speciation mechanism of ligan site on the surface of adsorbent and the speciation of metal ion (Th^{4+} and UO_2^{2+}) as sorbate (Fig 4.9). At low pH, higher concentration of hydronium tend to protonate the ligand sites into neutral or positive charged group, which in turn decrease the electrostatic affinities between the ligand site and positive charged metal ion. The decrease of hydronium concentration at higher pH causes the ligand dissociation into negative charged group e.g. $–COO^-$ and $–CO^-$. Different charge would increase the electrostatic affinities between the ligand site and ion target [12], which in turn would enhance the sorption capacity.

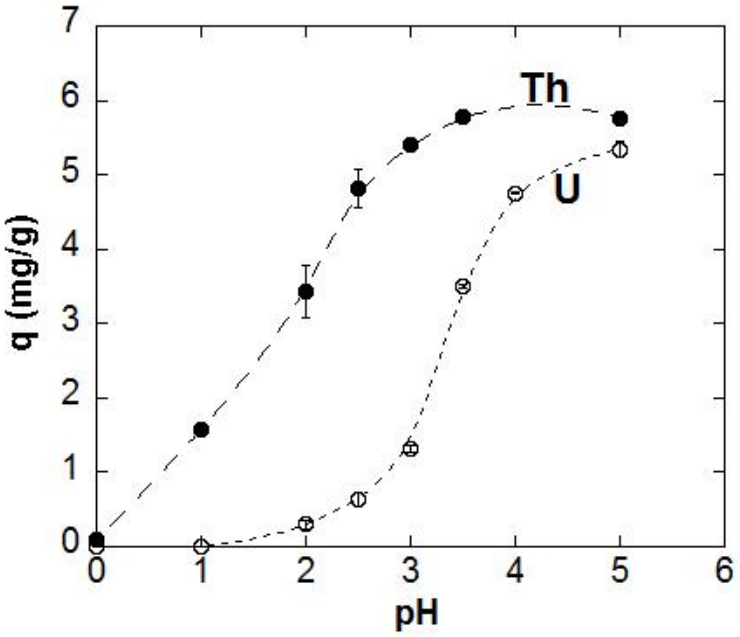

Fig 4.8 Effect of pH on the Th and U adsorption on SiChiHA.

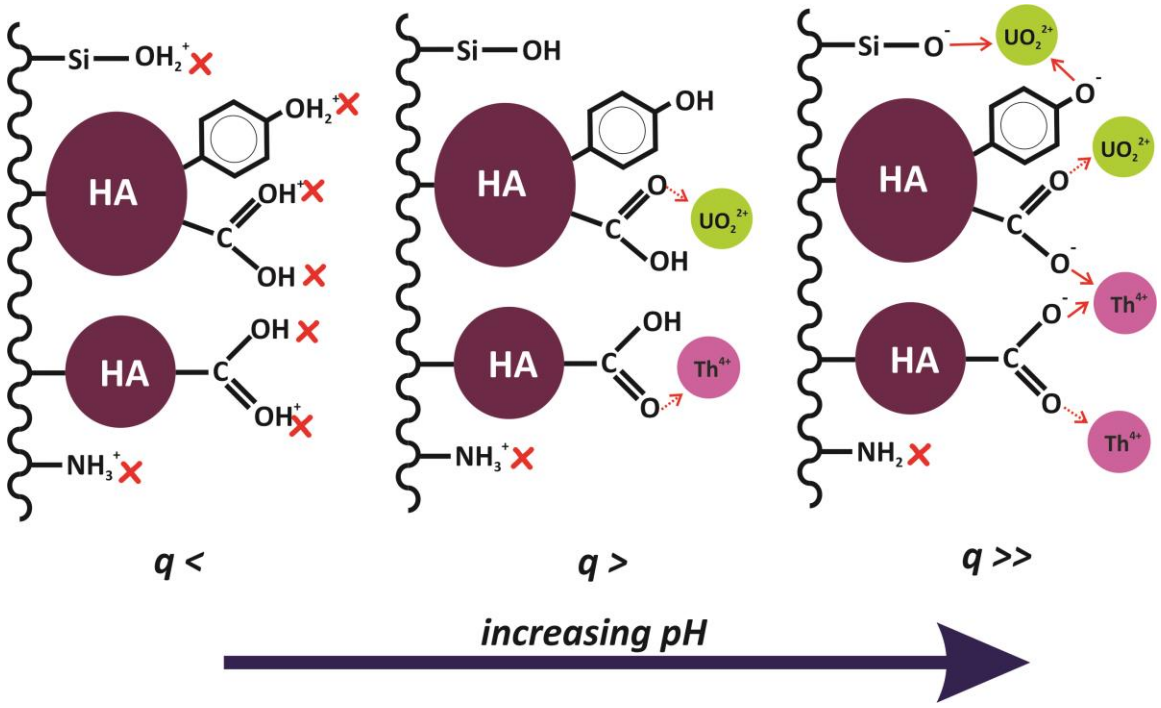

Fig 4.9 Adsorption mechanism by SiChiHA adsorbent. Ligand site of humic acid (HA) shown are carboxylic and phenolic, amine group as basic ligand and silanol are contributed by cross-linked chitosan and silica gel respectively.

There are differences in optimum pH for Th and U adsorption between humic acid modified silica gel (HASi) reported in previous chapter (pH 3) with these obtained by SiChiHA adsorbent (3.5 and 5 for Th and U respectively). This is probably due to the presence of amine group in adsorbent surface and secondary amine (confirmed by FT-IR analysis, Fig 4.5), which would act as basic functional group. This functional group would hinder the transformation of charge potential of adsorbent surface to negative charged when the pH increased, which is supported by surface zero charge potential results (Fig 4.6).

4.3.3 Effect of sorbent dose

Effect of solid-liquid ratio to the Th and U adsorption was carried out at ratio 0.5 – 3 mg ml^{-1} by 3 hour equilibration at room temperature at optimum pH: 3.5 and 5 for Th and U respectively with initial concentration 10 mg L^{-1}. The results in Fig 3.11 demonstrate the sorption efficiency correlates positively to the solid-liquid ratio until certain value in which the addition of adsorbent did not increase further the recovery, 1 and 1.5 mg ml^{-1} for Th and U respectively. Based on the results in Fig 4.10, considering the recovery efficiency and effective dose, solid-liquid ratio 2 mg ml^{-1} was chosen for further experiments.

4.3.4 Effect of initial concentration (Sorption isotherm)

To study the effect of initial concentration to adsorption process, 10 mg SiChiHA adsorbent was equilibrated with 5 ml Th or U solution which concentration varied between 10 and 500 mg L^{-1} for 3 hours at optimum pH. To describe the experimental data of Th and U adsorption by SiChiHA, Langmuir and Freundlich isotherm models would be used (Fig 4.11).

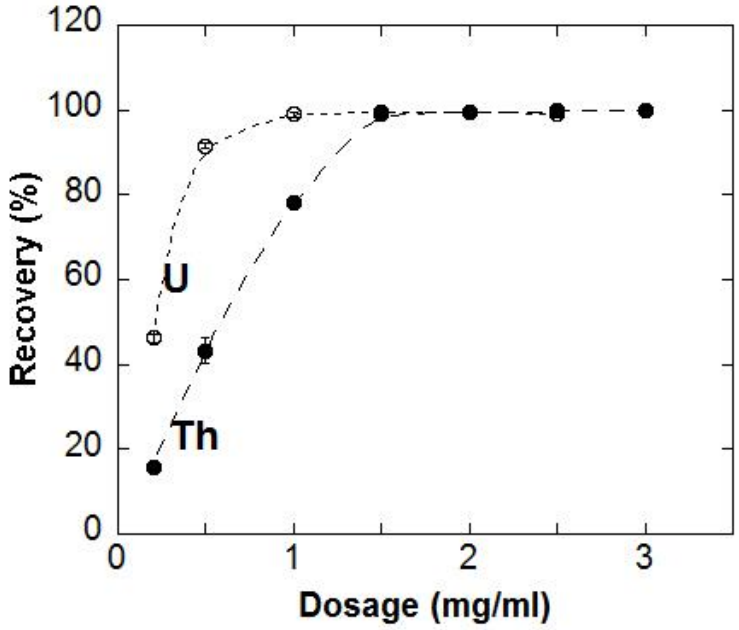

Fig 4.10 Effect of sorbent dose on the adsorption of Th and U onto SiChiHA.

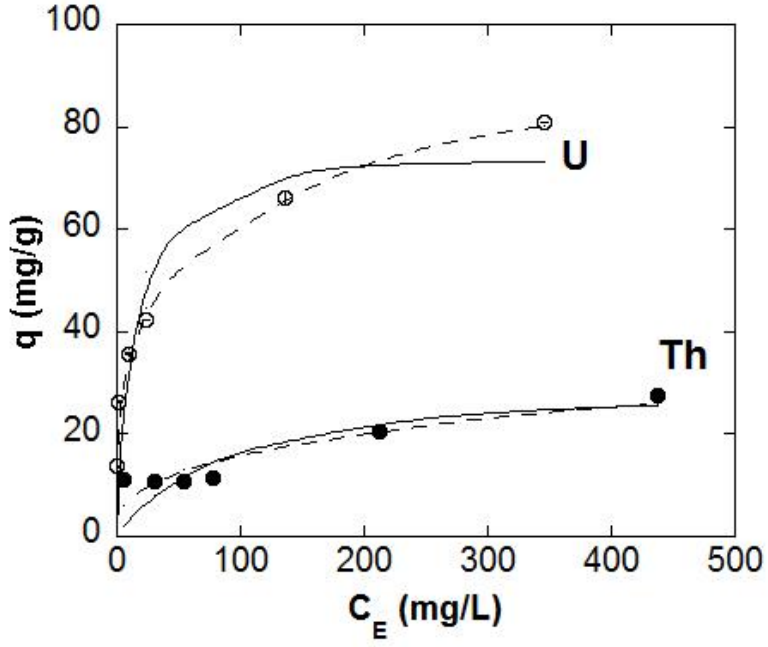

Fig 4.11 Experimental isotherm adsorption of Th and U by SiChiHA fitting by the Langmuir model (solid lines) and Freundlich model (dashed lines).

Langmuir model is based on the assumption that the adsorption process would form monolayer system on the surface of adsorbent. When all ligan sites had been occupied, the adsorption process would be halted. Besides the intermolecular force would decrease if the distance to adsorbent surface increase. On the other hand, Freundlich model is based on the assumption that the adsorption could occur on the surface with heterogenous functional group by forming multilayer coverage [13], which signifies the adsorption process correlates positively with the initial concentration of target ions. The Langmuir and Freundlich model are described by equation 3 and 4.

$$q_E = \frac{QKC_E}{(1 + KC_E)} \tag{3}$$

$$q_E = K_F C_E^{1/n} \tag{4}$$

q_E (mg g^{-1}) is adsorption capacity at equilibrium, C_E (mg L^{-1}) is equilibrium concentration of target ion, Q (mg g^{-1}) is theoretical maximum sorption capacity and K is binding constant (ml mg^{-1}). K_F and $1/n$ are Freundlich constant and sorption intensity respectively.

To evaluate the compatibility of Langmuir and Freundlich model to the experimental data, root mean square (*RMSE*, equation 5) would be used [14]. $q_{E\ exp}$ and $q_{E\ cal}$ are equilibrium sorption capacity based on experimental data and modeling respectively, while n is the number of observation.

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(q_{E\ exp} - q_{E\ cal}\right)^2} \tag{5}$$

Table 4.1 resumes the parameters of isotherm adsorption of Th and U by SiChiHA. The value of sorption intensity varies between 1 – 10, indicating the adsorption process to be physical. Based on *RMSE* value it is apparent that the adsorption process described better by Freundlich model which suggests the adsorption process to be concentration dependent [15] due to heterogenous functional group present on the adsorbent surface.

Table 4.1 Estimated isotherm parameters for the adsorption of Th and U by SiChiHA.

Metal ion	**pH**	**Langmuir**			**Freundlich**		
		***Q* mg g^{-1}**	***K* (L mg^{-1})**	***RMSE***	***K_F***	***n***	***RMSE***
Th	3.5	30.6	0.012	4.255	3.43	3.00	2.652
U	5	75.4	0.094	9.632	22.61	4.62	1.929

Based on preliminary studies on the sorption capacity, by equilibrating 10 mg SiChiHA with 5 ml Th or U solution 250 mg L^{-1} at pH 3 for 12 hours, the sorption capacities are 33.53 and 19.15 mg/g for Th and U respectively. The studies were done in order to compare the sorption capacity of SiChiHA with humic acid modified silica gel obtained by silylation process (24.75 and 18.00 for Th and U respectively) at the same pH (3). These figures demonstrate that cross-linked chitosan could be used as low cost substitute for silylation process in modifying silica gel surface.

One important parameter in Langmuir isotherm is dimensionless constant of equilibrium parameter R_L (6). K (L mg^{-1}) and C_o (mg L^{-1}) are binding constant and initial concentration respectively. Favorable and reversible condition is attained if $0 < R_L < 1$. R_L in adsorption by

SiChiHA varied between 0.15 – 0.75 for Th and 0.02 – 0.28 for U which suggest the adsorption of Th and U by SiChiHA is favorable and reversible.

$$R_L = \frac{1}{(1 + KC_o)} \quad (6)$$

4.3.5 Sorption kinetic studies

Adsorption kinetic studies were performed to describe the effect of contact time in the Th and U removal by SiChiHA adsorbent. In these studies batch technique was used with initial concentration 10, 25 and 50 mg L^{-1} at optimum pH and contact time varied between 1 – 240 minutes. The value of sorption capacity (q) for Th and U based on contact time is depicted in Fig 4.12.

To describe the experimental kinetic data several model would be employed: pseudo-first order, pseudo-second order and intra particle diffusion model [14]. Pseudo-first order is based on the hypotheses that the kinetic of Th and U removal at any given time (t, min) is proportional to the difference between the equilibrium sorption capacity (q_E, mg g^{-1}) and the sorption capacity at time t (q_t, mg/g) as formulated in equation 7. In the pseudo-second order model, it is assumed that the sorption process is a pseudo-chemical reaction process and the sorption rate positively correlates to the square value of the driving force. In this case driving force is the difference between the equilibrium sorption capacity (q_E) and the sorption capacity at time t (q_t) as formulated in equation 8.

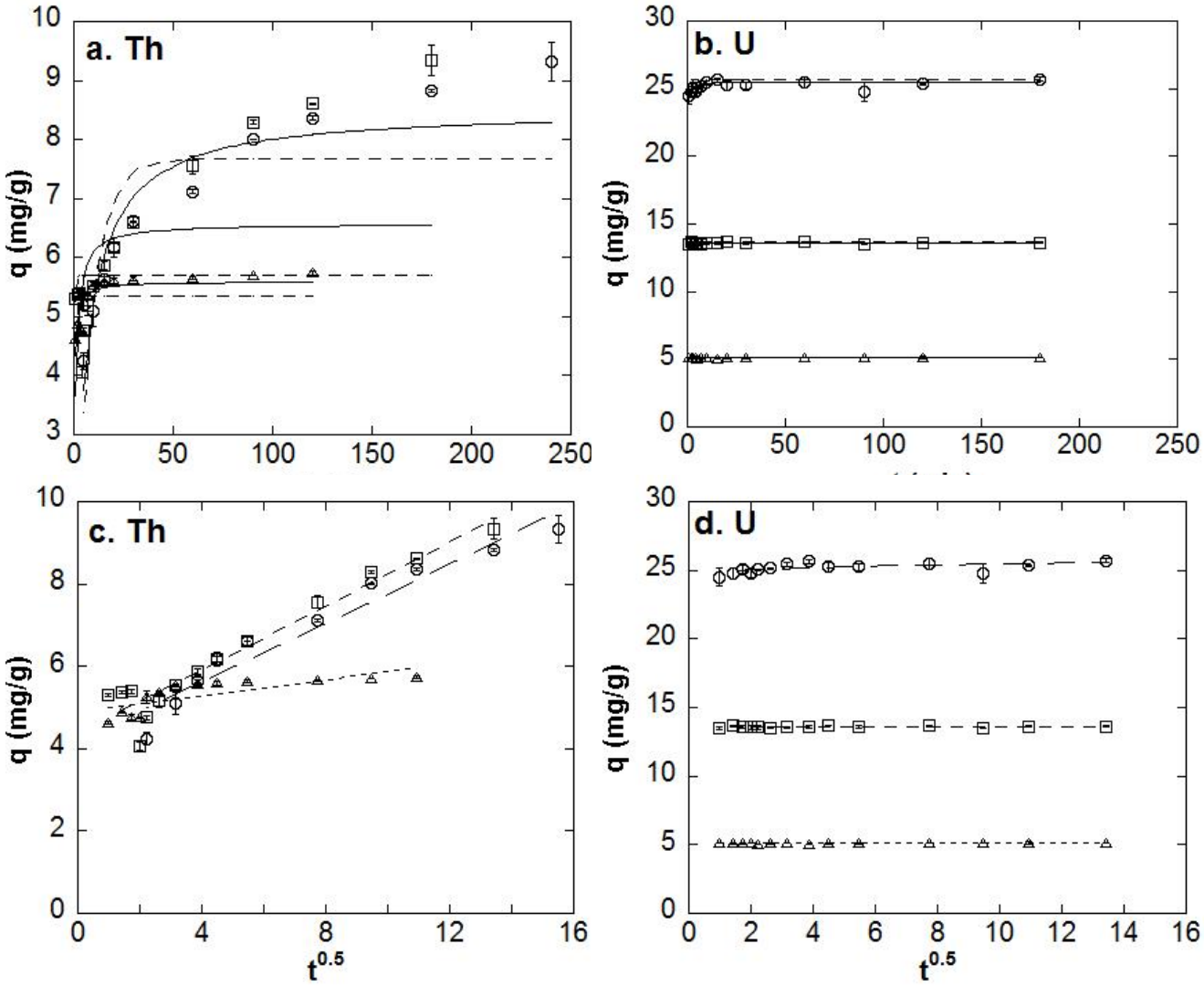

Fig 4.12 Experimental data of contact time effect on Th and U removal with initial concentration 10 (triangle), 25 (square) and 50 mg L^{-1} (circle). (a) Th and (b) U data, fitted by pseudo-first order (dashed line) and pseudo-second order (solid line). (c) Th and (d) U data, fitted by intra-particle diffusion model.

Based on the pseudo-second order model, initial adsorption rate (H, mg g^{-1} min^{-1}) and time required to adsorb half of the initial concentration ($t_{1/2}$, min) could be estimated by equation 9 and 10 [16]. The intra particle diffusion model is proposed based on hypotheses that the

adsorption process is controlled by diffusion process (11). k_i (mg g^{-1} $min^{0.5}$) is the rate constant of intra particle diffusion and *I* is the intra particle diffusion constant which is proportional to the boundary layer.

$$q_t = q_E(1 - e^{-k_1 t}) \tag{7}$$

$$q_t = \frac{k_2 q_E^2 t}{1 + k_2 q_E t} \tag{8}$$

$$H = k_2 q_{\mathrm{E}}^2 \tag{9}$$

$$t_{1/2} = \frac{q_{\mathrm{E}}}{H} \tag{10}$$

$$q_{\mathrm{t}} = k_{\mathrm{i}}\sqrt{t} + I \tag{11}$$

Coefficient correlation (r^2), normalized standard deviation (*dq*) and average relative error (*ARE*) were used to evaluate the compatibility of a model to describe the experimental data. Normalized standard deviation (*dq*) and average relative error (*ARE*) are calculated based on equation 12 and 13 [17]. q_{texp} and q_{tcal} are the experimental and modeled sorption capacity at *t* respectively while n is the number of observation.

$$dq\ (\%) = 100\sqrt{\frac{1}{n-1}\sum_{i=1}^{n}\left(\frac{q_{t\,exp} - q_{t\,cal}}{q_{t\,exp}}\right)^2} \tag{12}$$

$$ARE\ (\%) = \frac{100}{n-1}\sum_{i=1}^{n}\left(\frac{q_{t\,exp} - q_{t\,cal}}{q_{t\,exp}}\right)^2 \tag{13}$$

Table 4.2 Kinetic parameters of Th and U removal by SiChiHA based on pseudo-first, pseudo second and intra particle diffusion modeling.

Parameters	C_o Th (mg L^{-1})			C_o U (mg L^{-1})		
	10	25	50	10	25	50
Pseudo first order						
k_1 (min^{-1})	1.81	2.51	0.12	9.61	4.09	2.99
q_E model (mg g^{-1})	5.36	5.71	7.68	5.15	13.69	25.72
q_E experimental (mg g^{-1})	5.74	9.34	9.32	5.12	13.65	25.72
dq (%)	6.739	22.672	5.847	0.793	0.785	2.361
ARE (%)	0.454	5.14	0.237	0.006	0.006	0.056
Pseudo second order						
k_2 (g mg^{-1} min^{-1})	0.62	0.19	0.019	12.7	6.7	0.774
q_E model (mg g^{-1})	5.59	6.57	8.51	5.12	13.62	25.51
q_E experimental (mg g^{-1})	5.74	9.34	9.32	5.12	13.65	25.72
H (mg g^{-1} min^{-1})	19.37	8.20	1.38	332.92	1242.88	503.69
$t_{1/2}$ (min)	0.30	1.14	6.77	0.02	0.01	0.05
dq (%)	4.212	20.034	3.671	0.673	0.4	1.152
ARE (%)	0.177	4.014	0.093	0.005	0.002	0.013
Intra particle diffusion						
k_i (mg g^{-1} min^{-1})	0.10	0.43	0.36	0.00	0.01	0.05
I (mg g^{-1})	4.89	3.99	4.20	5.11	13.56	24.92
r^2	0.600	0.960	0.944	0.034	0.130	0.278
dq (%)	4.698	8.976	5.931	0.370	0.408	1.161
ARE (%)	0.221	0.806	0.352	0.001	0.002	0.013

Based on Fig 4.12, it is apparent that all models are compatible to the experimental data of kinetic studies. However, based on statistical results in Table 4.2, in terms of normalized standard error, average relative error and coefficient correlation, pseudo-second order fits better to the experimental data compared to pseudo-first model. Generally, pseudo-second order

coefficient k_2 for U is larger than of Th for different initial concentration 10, 25 and 50 mg L^{-1}, which is probably due to its higher binding constant (Table 4.1). Initial adsorption rate (H) and time required to adsorb half of the initial concentration ($t_{1/2}$) suggest that the Th and U removal to be rapid while the process become slower as the initial concentration increase. However, in general 10 minutes are sufficient to absorb half of initial concentration 50 mg L^{-1} for Th and U. Stastical analysis demonstrate that modeled sorption capacity could fit well with experimental sorption capacity data. This implies that the adsorption is concentration dependent [18]. The fitting result of experimental data by intra particle diffusion model results in linear curve which does not intercept the origin point. This indicates that the adsorption rate is affected by intra particle diffusion [19] while based on coefficient correlation value, the diffusion process is not rate limiting step. Larger intra particle diffusion constant of U suggest the improvement in the adsorption rate due to stronger bonding between uranyl ion to the ligand site.

4.3.6 Effect of salinity and lanthanides concentration

To evaluate the effect of salinity to the SiChiHA capacity in Th and U removal, 10 mg sorbent was equilibrated with 5 ml 10 mg L^{-1} Th or U solution in sodium chloride which concentration varied between 0 – 2 M. The evaluation is considered important since many Th and U deposits in nature are associated with coastal-marine environment. Fig 4.13a demonstrate that the effect of salinity on Th removal is not significant, while in the case of U the removal efficiency decrease to 90% when salinity reach 2 M. Insignificant decrease of sorption capacity in high saline condition is caused by the presence of amine group, which would function as basic functional group to attract neutral or negative chaeged thorium or uranyl chloro complex (Fig 4.14.

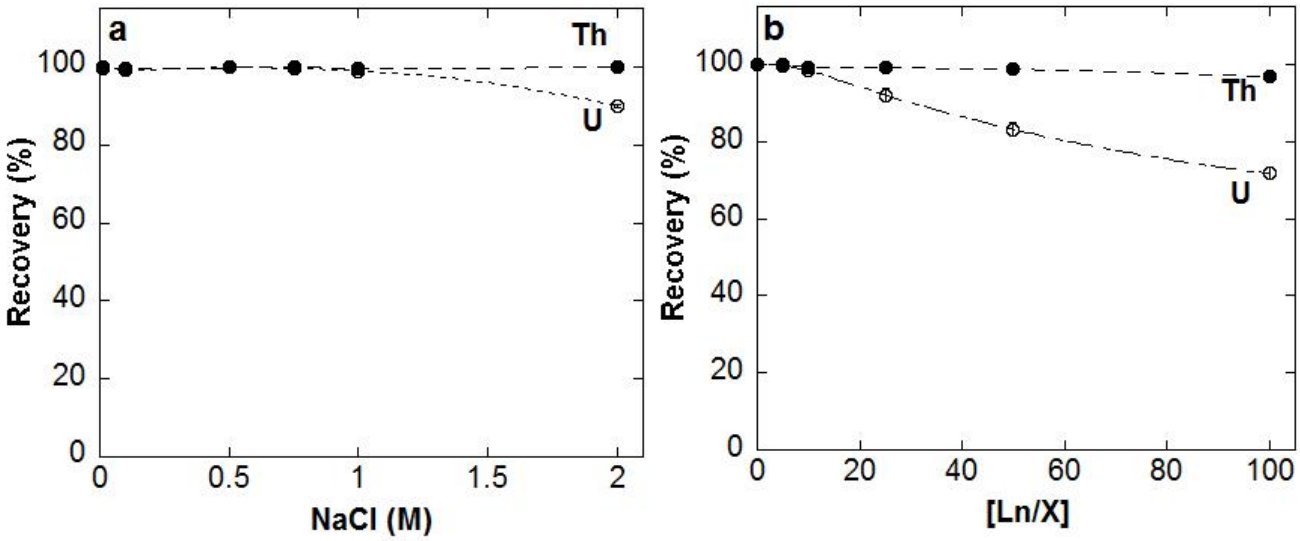

Fig 4.13 Recovery of Th and U removal from aqueous solution by SiChiHA adsorbent as function of a. salinity/sodium chloride concentration and b. the ratio of their concentration to total lanthanide concentration [Ln/X].

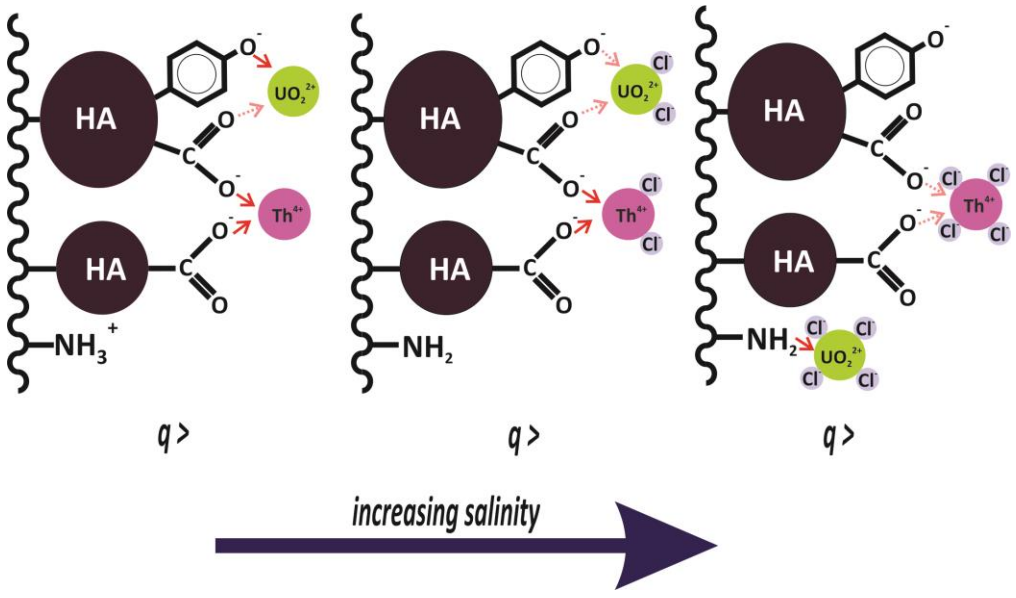

Fig 4.14 Effect of increasing salinity in adsorption by SiChiHA.

Fig 4.13b illustrates the effect of lanthanides in Th and U removal. In batch studies, lanthanum and cerium in equal amount were used to constitute the total lanthanides (Ln). Typically, 10 mg adsorbent was equilibrated with 5 ml Th-Ln or U-Ln mixture solution which ratio between Th or U (x) with total lanthanides [Ln/X] varied between 0 – 100. The studies were carried out considering the close association of Th and U with lanthanides in nature e. g. monazite sand, and decontamination of lanthanides is deemed important due to major role of these elements in modern green technology. The results show that lanthanides concentration up to 100 times higher did not affect the sorption efficiency of Th by SiChiHA adsorbent while in the case of U at the same lanthanide concentration, the efficiency decrease to 75%. U is more susceptible to the lanthanide concentration, which is probably caused by lower charged species of U compared to Th and lanthanides (UO_2^{2+} compared to Th^{4+} and Ln^{3+}).

4.3.7 Desorption and reusability studies

Desorption studies were carried out to ascertain the regeneration possibility of SiChiHA adsorbent and the viability to recover Th and U for further use which is important in considering the economical merit of adsorbent. In desorption experiment, 10 mg SiChiHA sorbent containing 5 or 10 mg g^{-1} Th or U was leached by 1 ml nitric acid or 2.5 ml ammonium citrate which concentration varied. The results illustrated in Fig 4.15 demonstrated that the desorption recovery was not dictated by the initial content of Th or U in the adsorbent both in the case of ammonium citrate and nitric acid at the same concentration. In the cose of nitric acid leaching, U was quantitaively recovered using low concentration of nitric acid (0.1 M). Th recovery correlates positively to the nitric acid concentration which quantitative recovery was attained at nitric acid concentration 1 M. In the case of ammonium citrate leaching there is significant

difference between Th and U in which U shows strong affinity to the ammonium citrate. This demonstrates that ammonium citrate could be applied as leaching agent to recover U from SiChiHA and probably the separation of U from Th.

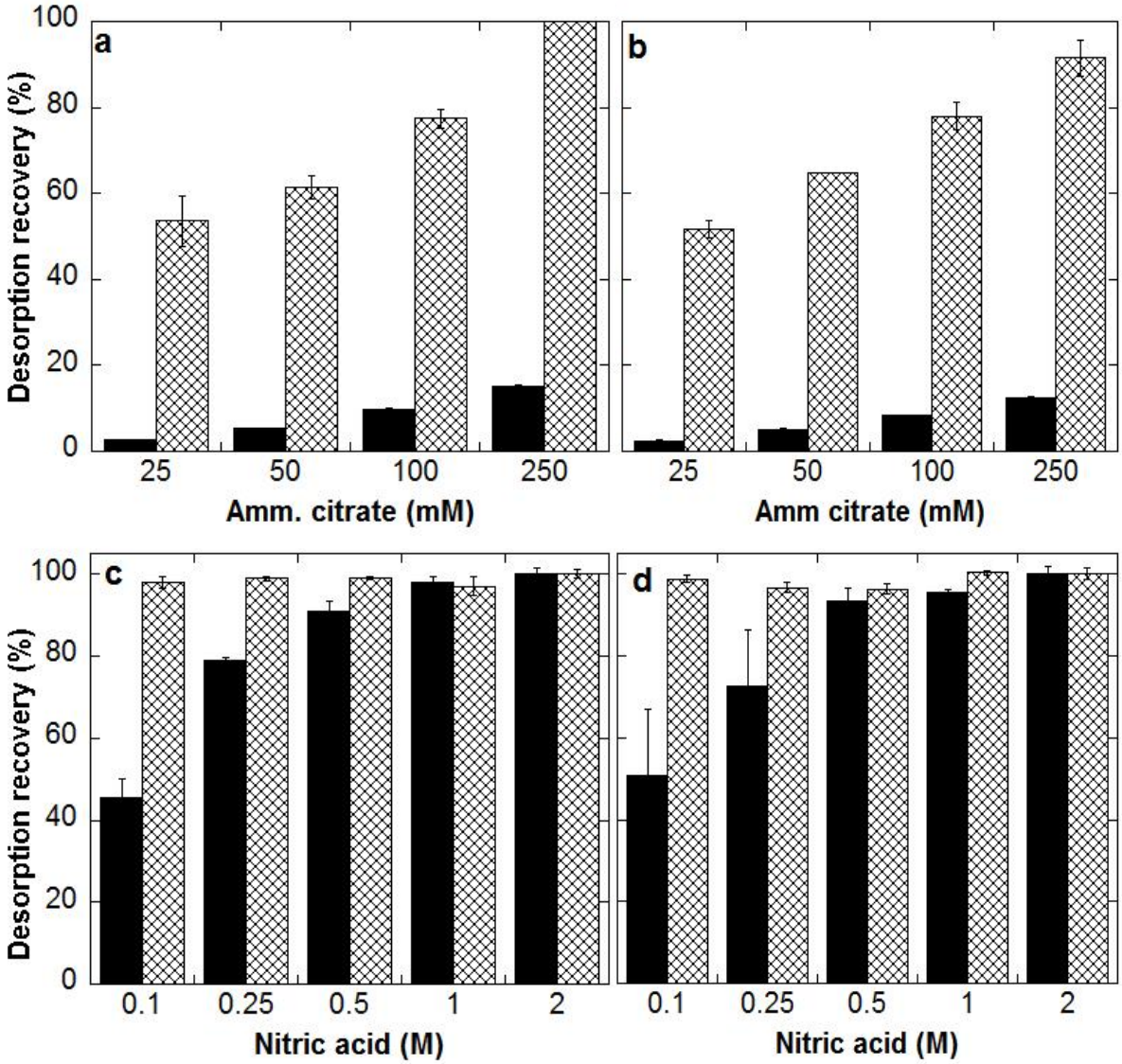

Fig 4.15 Desorption of Th (solid black column) and U (mesh column) by ammonium citrate (a and b) and nitric acid (c and d) with initial metal content in SiChiHA sorbent (a and c) 5 mg/g (b and d) 10 mg g^{-1}.

Regeneration study was carried out batch experiment, 15 mg adsorbent was equilibrated with 15 ml 10 mg L^{-1} Th or U solution. After the equilibration, solid phase was separated by centrifugation and its Th or U content was leached using 1 M nitric acid. Nitric acid containing Th and U was separated and the used adsorbent was washed with Milli Q water, dried and used for next sorption-desorption cycle. Fig 4.16 demonstrated that the sorption capacity of SiChiHA adsorbent was stable and colud be reused for at least 5 cycles. Table 4.3 resumes several humic acid based adsorbent previously reported to remove Th and U from aqueous solution in term of pH condition, theoretical maximum capacity, equilibrium time and reusability.

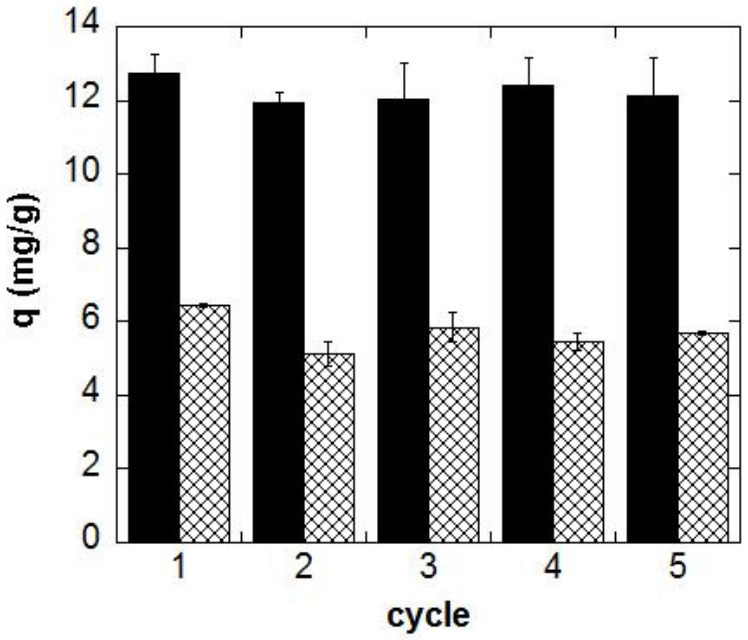

Fig 4.16 Sorption capacity of SiChiHA adsorbent in Th and U removal after 5 cycles of regeneration using 1 M nitric acid.

Table 4.3 Comparison of several humic acid based adsorbent in Th and U removal from previous reports and from this study.

Sorbent material	pH	*Q* (mg/g)		Equilib time (minute)	Reuse (cycles)	Reference
		Th	U			
1. Humic acid immobilized on zirconium pillared clay	6		132.7	180	4	[20]
2. humic acid-amberlite XAD-4	4	35.0		60		[21]
3. Insolubilized humic acid	3	20.0	17.0	360		[12]
4. Humic acid modified silica gel (silylation)	3	28.0	43.9	180	4	Chapter 2
5. Humic acid - silica sol gel composite	3		33.2	180	9	Chapter 3
6. Humic acid - silica sol gel composite	2.5	32.3		180	9	Chapter 3
7. Silica gel-chitosan-humic acid	3.5	30.6		180	5	This chapter
8. Silica gel-chitosan-humic acid	5		82.0	180	5	This chapter

4.4 Conclusions

The results demonstrated that cross-linked chitosan could be served as a substitute of silylation in attaching humic acid to the surface of silica gel through simple and eco-friendly coating process. The success in silica gel-chitosan-humic acid (SiChiHA) adsorbent synthesis was confirmed by characterization results. Further, SiChiHA address the weakness of adsorbent previously synthesized by sol-gel method i.e. adsorption in high pH and saline solution. The best ability of SiChiHA for removal is attained at pH 3.5 for Th (maximum sorption capacity 30.6 mg g^{-1}) and pH 5 for U (maximum sorption capacity 75.4 mg g^{-1}). Contact time studies revealed the adsorption kinetic was rapid and obeyed pseudo-second order model, which indicated the effect of Th and U concentration. The fitting also indicated that the adsorption was affected by intra particle diffusion process. The test on Th and U removal from saline and lanthanide contained solution showed that the efficiency of SiChiHA in Th removal was not influenced by salinity up

to 2 M and lanthanides concentration up to 100 times. Desorption studies suggested that SiChiHA is suitable in Th and U preconcentration and separation using ammonium citrate and nitric acid as leaching agents. Further, five cycle of regeneration along with simple synthesis method using natural materials signified the economical merit of SiChiHA adsorbent.

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CHAPTER 5

GENERAL CONCLUSIONS

In general, the studies signified the importance of developing humic acid-silica gel as economic adsorbent, not only in terms of low cost starting material but also the facile synthesis process. Th and U removal from aqueous solution have been successfully carried out using humic acid-silica gel based adsorbent. The study on Th and U removal by humic acid attached covalently to silica gel by conventional silylation method (Si-HA) showed that humic acid and silica gel were suitable functional group and support material respectively. Both materials have advantages in terms of economy (wide availability and cost effective). Besides, since both of them are derived from natural products, they are environmental friendly and could minimize the waste produced during adsorbent synthesis or as spent adsorbent. Further, based on the study results, the combination of humic acid and silica gel to produce adsorbent could be developed by several schemes in order to increase its economical merit i.e. sol-gel process (HASi) and chitosan coating process (SiChiHA). The success in each process was confirmed by the characterization results. Each scheme produces adsorbent with its own advantage and limitation, as shown in Table 5.1. Notably, HASi offers advantage in applicability to remove Th and U from acidic solution and high lanthanide concentration, while SiChiHA is applicable at wider pH range and high saline solution.

The optimum condition of Th removal occurred in acidic pH (2.5 – 3) while U required slightly higher pH condition (3 – 5). The adsorption process was considered physical and reversible, which occurred as electrostatic interaction. In isotherm adsorption studies, it was shown that the process obeyed Freundlich model, which confirm the heterogenous nature of

ligand site present in humic acid. The adsorption process proceed rapidly (50% adsorption achieved in less than 10 min) and followed pseudo-second order based on contact time studies. It was also indicated that intra-particle diffusion played role in the adsorption process.

Table 5.1 Comparison of humic acid based adsorbent synthesized in this study in terms of performance in Th and U removal. Circle and cross signify availability and limitation respectively. ○○ very favourable, ○ favourable, △ limited, × not available.

Adsorbent		Acidic pH (2 - 3)	Weak acidic pH (3 - 5)	Saline matrix	Lanthanides matrix	Separation (Th-U)	Synthesis
SiHA	Th	○	○○	○○	○○	○	Expensive/ Complicated
	U	○	○○	○	○	○	
HASi	Th	○	×	×	○○	○	Cheap/simple (single step)
	U	○	×	×	○	○	
SiChiHA	Th	○	○○	○○	○○	○	Cheap/simple
	U	△	○	○	△	○	

The study demonstrated that the humic acid-silica gel adsorbent were suitable for Th and U removal from high saline environment especially SiChiHA adsorbent. Besides, the efficiency of adsorbent was insignificantly influenced by the presence of lanthanides until certain concentration, which indicated the suitability of adsorbent for Th-U and lanthanides separation or lanthanides decontamination due to close association of these elements in nature. Based on desorption studies on the used humic acid-silica gel adsorbent, there is possibility to separate Th and U by using ammonium citrate to recover U and separate it from Th which retained by the adsorbent. Th could be further recovered quantitatively by using nitric acid. Nitric acid also was served to regenerate the adsorbent in order to use it up to several cycles.

The studies confirm the applicability of humic acid-silica gel as economic adsorbent for Th and U removal, and there is possibility to develop these adsorbent for an application not only

for environmental restoration but also for other fields such as separation and purification. To reach that goal there are several recommendation should be considered to increase the value and applicability of adsorbent, which include: 1. Studies to corroborate the detail adsorption mechanism, metal ion speciation, ligand-metal ion coordination structure and adsorption thermodynamics, 2. Availability of adsorbent to deal with very low concentration (sub mg L^{-1}). 3. Applicability of adsorbent for column method and 4. Availability of Th and U from waste water with more complex chemical composition with diverse ion compositions.

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Sol–gel synthesis of a humic acid-silica gel composite material as low-cost adsorbent for thorium and uranium removal

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Abstract A new humic acid-silica gel composite (HASi) to serve as an adsorbent was synthesized via a single-pot method, and its formation via the sol–gel process was confirmed by FTIR and SEM-EDS characterization. The adsorbent effectively removed Th and U at low pH (2.5–3), and the Langmuir model yielded a maximum sorption capacity of 32.3 and 33.2 mg/g for Th and U, respectively. The removal process was rapid (85 % removal within 5 min) and followed a pseudo-second-order model. The salinity of the solution had little effect on the removal efficiency, which continued throughout the adsorbent's repeated use up to nine times.

Keywords Adsorption · Humic acid · Silica gel · Thorium · Uranium · Sol–gel

Introduction

Because of its important role in future energy use, radioactive material, such as thorium (Th) and uranium (U) will be in high demand. This in turn will encourage mining activities and nuclear energy programs that will generate waste to which both humans and the environment will be exposed [1]. The recovery of these elements from the waste is mandatory prior to release of the waste into the environment. Various techniques are used in Th and U recovery, e.g., chemical precipitation, liquid–liquid separation, electrochemical treatment and membranes. However, these techniques are not considered to be cost effective [2]. In contrast, solid–liquid separation (adsorption) possesses advantages in terms of being relatively cost effective, convenient to use and applicable to a low concentrations of pollutant, making it suitable for radioactive waste treatment [3].

Various adsorbents have been synthesized and tested for the recovery and pre-concentration of Th and U from aqueous solutions, yet many of these adsorbent materials are not considered cost-effective because of complicated procedures and special chemicals used in their preparation. One inexpensive and widely available material for adsorbent synthesis is humic acid, which possesses a high ability to bind metal elements [4, 5] because of the presence of carboxylic, phenolic and mixed ligands [6]. Unfortunately, the applicability of humic acid is hindered by the difficulties in its separation from the liquid phase. This problem has been overcome by attaching humic acid molecules to larger inorganic or organic particles as a support, including zirconium pillared clay [7], resin polymer [8] and silica gel [9].

Silica gel is one of the most popular supports because of its advantages: stability, physical strength and easily controlled structural parameters [10]. One of the most common schemes for attaching a functional group, including humic acid, to the silica gel surface is silylation [11], which has been addressed in numerous publications [4, 9, 12–17]. Nevertheless, problems concerning difficult and expensive procedures persist. Thus, we propose to produce an organic-hybrid material by the sol–gel method. This method has advantages, as the material can be prepared

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through a simple single-pot reaction wherein the functional moieties or molecules can be doped directly into a sol of the inorganic host matrix prior to gelation [18]. Most investigators have used organosilicone derivatives (e.g., tetraethylorthosilicate) as a silica sol precursor [19], but in this research, sodium silicate was chosen for the sol–gel synthesis because it is economical and widely available.

Therefore, the main motive of this paper is to describe an easier and cheaper alternative method to attach humic acid as a functional group to silica gel. Using the sol–gel method, we synthesized a humic acid-silica gel composite material (HASi) by incorporating humic acid into a silica matrix. The low-cost material was be further investigated in terms of its characterization and its performance in Th and U removal from an aqueous solution.

Experimental

Materials

All of the chemicals, including sodium silicate, were purchased from Kanto Chemicals and Wako Chemicals Japan and used as received. A single lot of humic acid was provided by Across Organics (No. A013566901) and purified according to Koopal et al. [9]. It was used throughout the experiment to keep the composite properties uniform. The dilution and solution preparations were carried out using Milli Q water (Milli Q system, Millipore). The solution pH was adjusted by hydrochloric acid and sodium hydroxide.

Instrumentation and characterization

Th and U solutions were analyzed spectrophotometrically using a Jasco V-530 UV/Vis spectrophotometer based on the colored complex these elements form with Arsenazo III, while mixture solutions were analyzed using ICP-AES (SPS-7700, Seiko Instrument Co). The solution pH was measured using an F-52 Horiba pH meter. FT-IR spectra, which were used to distinguish the frequency difference between undoped and humic-acid-doped silica matrices, were obtained using a Jasco FT/IR 4100 spectrometer by the KBr method with a wavelength range of 400–4000 cm^{-1}. The surface morphology of the adsorbent was observed using a Hitachi S-2400 scanning electron microscope operated at 15 kV after coating the samples with gold. In addition to the surface morphology, the elemental distribution on the adsorbent surface was detected and mapped using a JEOL JSM-5310 scanning microscope-energy dispersive X-ray spectroscope (SEM-EDX) operated at 15 kV in Graduate School of Science, Hokkaido University.

Silica gel-humic acid composite preparation

The silica gel-humic acid composite (HASi) was prepared by the sol–gel method. A typical procedure is as follows: Purified humic acid was dissolved in 10 ml of 6 % sodium silicate solution. The sodium silicate-humic acid mixture solution (pH $\sim$12), while vigorously stirred, was titrated by a 2 mol L^{-1} nitric acid solution to pH $\sim$10, and the stirring was continued until gelation occurred. The gel was dried at room temperature, ground using a mortar and sieved to <64 μm size. The HASi powder was washed with Milli Q water to remove unbound humic acid. After being protonated by washing with 1 mmol L^{-1} hydrochloric acid, the adsorbent was dried at 50 °C and stored in a cool and dry place to prevent any alterations. Four types of HASi adsorbent materials were prepared, namely, HASi0, HASi1, HASi2 and HASi3, that corresponded to the amount of humic acid added to 10 ml of a 6 % sodium silicate solution, i.e., 0, 100, 200 and 300 mg, respectively. Based on a preliminary capacity test (Table 1), in which 10 mg of an adsorbent was equilibrated with 10 ml of a 250 mg L^{-1} Th or U solution at pH 3 for 12 h, HASi1 was chosen for further sorption studies.

Batch adsorption experiments

Sorption studies were carried out by batch experiments to determine the optimum condition in terms of pH, solid–liquid ratio, metal concentration, contact time, cation concentration, desorption, regeneration and reusability of the HASi adsorbent. The general procedure in a batch method was to equilibrate the HASi adsorbent with a Th or U solution in a centrifuge tube by mixing at 100 rpm at room temperature. The supernatant solution was separated by centrifugation at 3500 rpm for 30 min. The metal concentration in the supernatant solution was then determined using a spectrophotometer or ICP-AES. The adsorbent capacity (q, mg g^{-1}) and recovery (R, %) were calculated based on Eqs. (1) and (2).

$$q = \frac{(C_o - C_E)V}{m} \quad (1)$$

$$R = \frac{(C_o - C_E) \times 100}{C_o} \quad (2)$$

Table 1 The sorption capacity (q, mg g^{-1}) of four types of HASi adsorbents based on a preliminary capacity test (solid–liquid ratio 2 mg ml^{-1}, pH 3, 12 h equilibrium)

Elements	HASi0	HASi1	HASi2	HASi3
Th	7.2 ± 1.8	27.0 ± 3.8	28.2 ± 2.0	30.0 ± 1.9
U	1.2 ± 0.9	35.6 ± 0.9	31.9 ± 3.2	35.6 ± 0.8

where C_o and C_E are the initial and equilibrium metal concentrations (mg L^{-1}), respectively, V (ml) is the volume of the liquid phase, and m (mg) is the mass of adsorbent added.

Results and discussion

Adsorbent characterization

FT-IR analysis was carried out to confirm the formation of the humic acid-silica gel hybrid material by comparing the spectrum of the synthesized material to those of its precursors (Fig. 1). The silica adsorbent, which was synthesized by the sol–gel process without humic acid (HASi0), exhibits broad bands at 460 and 1080 cm^{-1}, which are assigned to Si–O–Si and the silicate ion. The peak related to the tetrahedral silica matrix is occurs at 796 cm^{-1}, while the sharp peak at 1400 cm^{-1} is probably caused by the nitrate ion residue that was introduced during the gelation process. The sorption band at 954 cm^{-1} represents the terminal group of the silanol group (Si–OH). The purified humic acid spectrum exhibits a sorption peak at 3400–3800 cm^{-1}, indicating the presence of the hydroxy group of a carboxyl group [20], while peaks at 1650 – 1700 cm^{-1} are contribute ions from oxygen functional groups, e.g., the carbonyl group of a carboxylate, and aldehyde and ketone groups [21]. Polyphenol is characterized by peaks at 600 and 900 cm^{-1}.

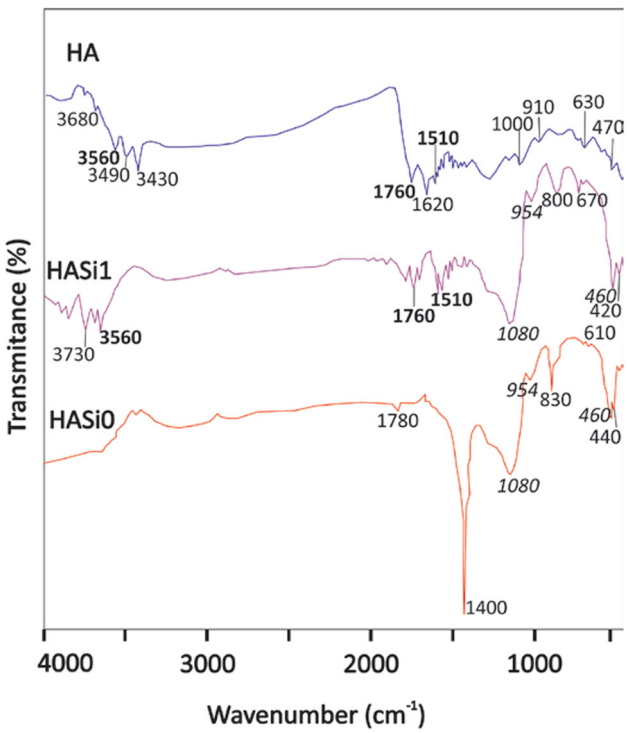

Fig. 1 FT-IR spectra of the silica adsorbent synthesized without humic acid (HASi0), the humic acid-silica gel hybrid material (HASi1) and purified humic acid (HA). *Italic* and *bold* wavenumbers indicate shared characteristics of HASi1 as the modified material, with purified humic acid and HASi0, as precursors

The modified material (HASi1) retains the characteristics of both precursors (HASi0 and purified humic acid), which confirms that HASi1 is a hybrid material. Figure 1 shows the shared characteristics between HASi0 and HASi1 (wavenumbers in italics), e.g., broad bands at 460 and 1080 cm^{-1} (Si–O–Si), the peak at 796 cm^{-1} (tetrahedral matrix silica) and the silanol functional group at 954 cm^{-1}. The purified humic acid characteristics retained by HASi1 include an oxygen functional group at 1650–1700 cm^{-1} and a carboxylic group at 3500–3800 cm^{-1} (wavenumbers in bold).

Figure 2 shows SEM images of HASi0 and HASi1 adsorbents, revealing the surface texture and morphology of both adsorbents and suggesting that there is no remarkable difference between the unmodified silica gel (HASi0) and the humic acid-silica gel adsorbent (HASi1). Both pictures exhibit similar surface characteristics in which minute particles encrust the adsorbent surface along with larger flake-like particles, causing an unsmooth surface. This result indicates that humic acid was evenly dispersed inside the silica matrix during the hybrid material synthesis.

The presence of humic acid was also ascertained by SEM-EDS analysis (Fig. 3). In the figures, both materials present strong signals for Si and O, which are the major components of silica gel, and sodium as a precursor in silica gel synthesis (sodium silicate). C (carbon), as a major component in humic acid, is almost undetected in the pristine material (HASi0), while in the modified material (HASi1), the presence of C is confirmed.

In addition, carbon mapping (Fig. 4) verifies the even distribution of carbon on the surface of the HASi1 adsorbent. As shown in Fig. 3, the significant decrease in the amount of sodium after modification is caused by the presence of humic acid, which would cause a decrease in surface potential [22]. The decrease in turn stimulates the desorption of sodium on the surface of silicate materials [23]. Additionally, during the adsorbent washing, unbound and washed humic acid would desorb the sodium on the surface of HASi1.

Effect of pH on adsorption

The effect of pH on the Th and U sorption of HASi1 from an aqueous solution was studied at pH 1–5 by equilibrating 10 mg of the HASi1 adsorbent with 5 ml of a 10 mg L^{-1} Th or U solution for 3 h, which is based on previous studies using silica gel-humic acid adsorbent and is considered

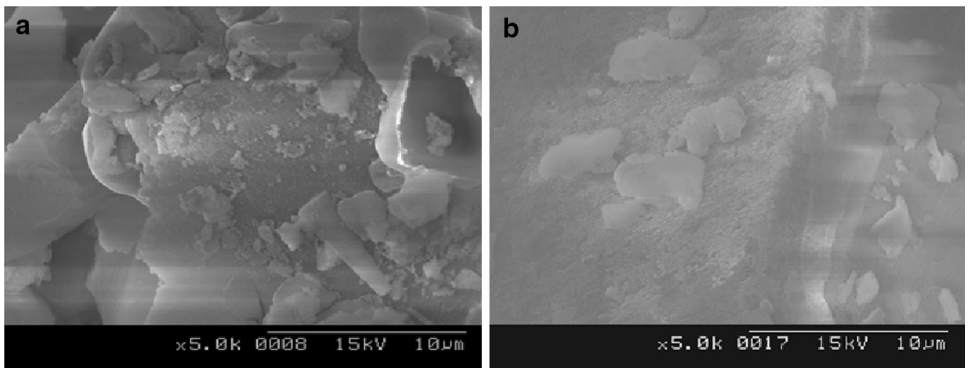

Fig. 2 Surface morphologies of **a** HASi0 and **b** HASi1 observed with a scanning electron microscope

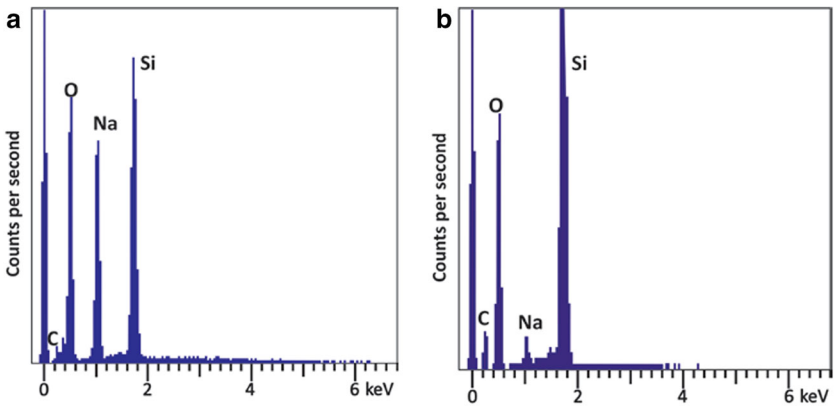

Fig. 3 Elemental signals based on the SEM-EDS of **a** HASi0 and **b** HASi1

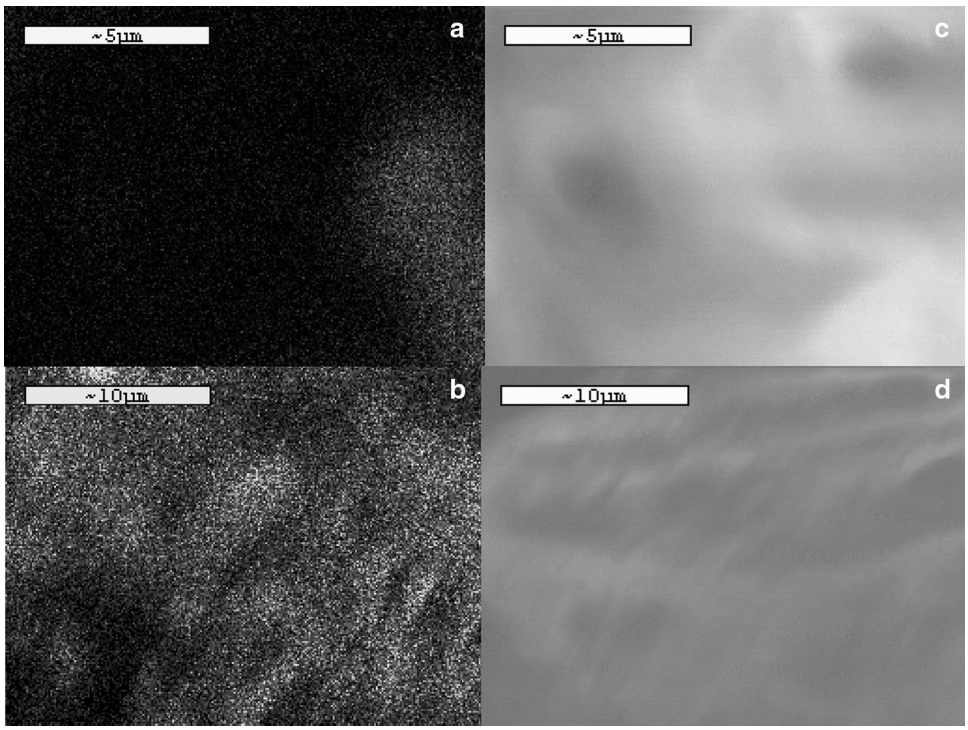

Fig. 4 Carbon mapping using energy dispersive X-ray spectroscopy of the surfaces of **a** HASi0 and **b** HASi1 with corresponding surface images for **c** HASi0 and **d** HASi1

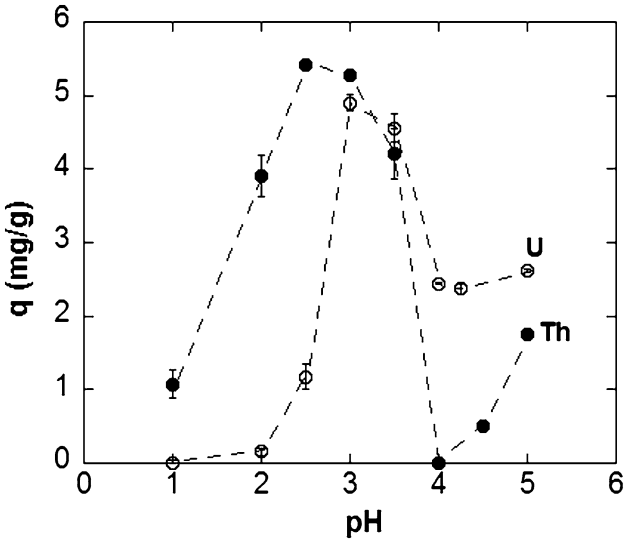

Fig. 5 Effect of pH on the Th and U adsorption capacity of HASi1

sufficient to attain the equilibrium. Figure 5 shows that the maximum sorption capacity is attained at pH 2.5 and 3 for Th and U, respectively. pH is an important parameter that influences the speciation of a metal ion in water by forming an aquo-hydroxo complex, e.g., $UO_2(OH)^+$, and $(UO_2)_3(OH)_5^+$, and Th^{4+} and $ThOH^{3+}$ [24]. UO_2^{2+} and Th^{4+} are dominant at a lower pH and are substituted by lower charged species, e.g., $UO_2(OH)^+$ or $Th(OH)_3^+$, when the pH is greater than 3 [25]. Species with lower charges possess a lower complex strength [26] and a weaker affinity for the ligand, which in turn decreases the sorption capacity at a higher pH. Conversely, the lower adsorption capacity at lower pH values is partially due to the competition between the uranyl or thorium ion and the hydronium ion to occupy the ligand on the adsorbent surface [27].

Based on Fig. 5, the adsorbent possesses a high sorption capacity for Th compared with that for U at the same pH (pH 3), indicating that humic acid as a functional group has a higher affinity toward Th. The result agrees with several previous reports [8, 28] and might be due to ionic radii and charge factors. Another factor is hydration energy, whereby hydrated species would tend to be in the aqueous phase to satisfy their hydration requirement [28].

The increase in the sorption capacity at pH values higher than 4 is partially due to the dissociation of functional groups on the surface of the adsorbent into negatively charged groups, i.e., the carboxylic group of humic acid at pH 4.28 [29] and the silanol group (pH 4–4.3) [30]. A negatively charged functional group would have a higher affinity toward positively charged thorium or uranium species in the aqueous phase, which in turn increases the removal efficiency and sorption capacity.

Effect of the solid–liquid ratio

The effect of the solid–liquid ratio was investigated from 0.5 to 3 mg ml^{-1} with an initial concentration of 10 mg L^{-1} for 3 h at the optimum pH for Th (2.5) and U (3). Figure 6 shows that the sorption efficiency depends on the adsorbent dose because the number of active ligand sites is proportional to the amount of adsorbent that is added. Quantitative Th and U removal was attained with a minimum dose of 1.5 mg ml^{-1}, and a further increase in the solid–liquid ratio would not significantly increase the recoveries.

Moreover, the objective of the studying the solid–liquid ratio effect is to ascertain the optimum dose for further experiments, i.e., the adsorption kinetics, salinity effect, lanthanide effect and regeneration studies. Based on Fig. 6, with an initial concentration of 10 mg L^{-1} as typical of the content of radioactive elements in nuclear industry wastewater [31], a solid–liquid dosage of 2 mg ml^{-1} was chosen for subsequent experiments.

Effect of the initial concentration (sorption isotherm of Th and U)

To study the influence of the initial concentration of Th and U on the sorption process, 10 mg of HASi1 was equilibrated for 3 h with 5 ml of a Th and U solution that had a concentration from 10 to 500 mg L^{-1} at room temperature. To describe the experimental data at a constant temperature, the isotherm models of Langmuir and Freundlich were used. The Langmuir model (3) is based on the assumption that the adsorption process occurs as a monolayer system on the surface of the adsorbent. If the ligand sites are fully

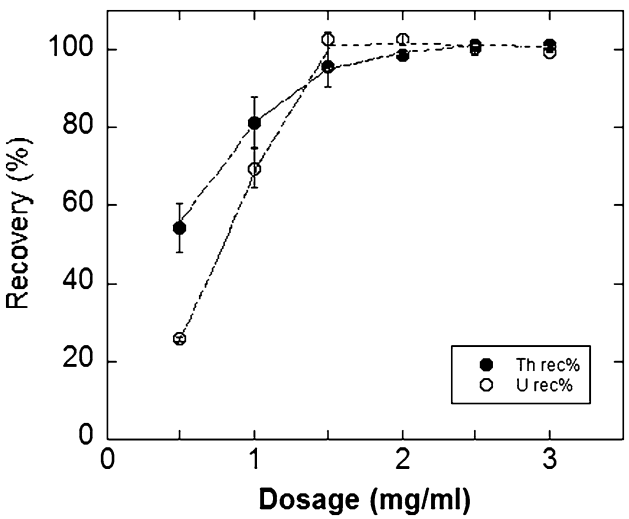

Fig. 6 Effect of adsorbent dose on the adsorption of Th and U on HASi1

occupied, the sorption process would halt. In addition, the intramolecular force decreases as the distance to the adsorbent surface increases. The Freundlich model (4), in contrast, is based on the assumption that the sorption process could occur on the surface with a heterogeneous functional group to form multilayer coverage, suggesting that adsorption is proportional to the initial sorbate concentration [32].

$$q_{\mathrm{E}} = \frac{QKC_{\mathrm{E}}}{1 + KC_{\mathrm{E}}} \tag{3}$$

$$q_{\mathrm{E}} = K_{\mathrm{F}} C_{\mathrm{E}}^{1/p} \tag{4}$$

where q_{E} (mg g^{-1}) and C_{E} (mg L^{-1}) are the sorption capacity and the metal concentration at equilibrium, respectively, while Q (mg g^{-1}) and K (ml mg^{-1}) are the theoretical maximum sorption capacity and binding constant, respectively. K_{F} is the Freundlich constant, and $1/p$ is the sorption intensity.

The root mean square error (RMSE) is used to evaluate the compatibility of the models, as in Eq. (5) [33]. $q_{\mathrm{E\ exp}}$ and $q_{\mathrm{E\ cal}}$ are the sorption capacity based on the experimental data and modeling at equilibrium, respectively, while n is the number of observations (data).

$$\mathrm{RMSE} = \sqrt{\frac{1}{n}\sum_{\mathrm{i}=1}^{n}\left(q_{\mathrm{E\ exp}} - q_{\mathrm{E\ cal}}\right)^2} \tag{5}$$

Based on Fig. 7, the experimental saturation capacity could be visually estimated to be 31 and 30 mg g^{-1} for Th and U, respectively. Based on RMSE values (Table 2), the Freundlich model is better model and is in line with the heterogeneous characteristics of the functional groups on the surface of the adsorbent. However, to evaluate the maximum theoretical sorption capacity Q (mg g^{-1}), the conventional Langmuir model was applied [34]. In the Freundlich model, the Q value could be estimated based on a constant initial concentration C_o (mg L^{-1}) with varied sorbent doses [35], which yielded the values 16.05 and 10.16 mg g^{-1} for Th and U, respectively. These values are much lower than the experimental saturation capacity previously mentioned. Several reports have mentioned an error when estimating the maximum sorption capacity by the Freundlich model. The results tend to be overestimated [36] or underestimated [37], and in the latter case, the authors have also shown that the Freundlich model is better than the Langmuir model in the case of fitting because of a lower error value.

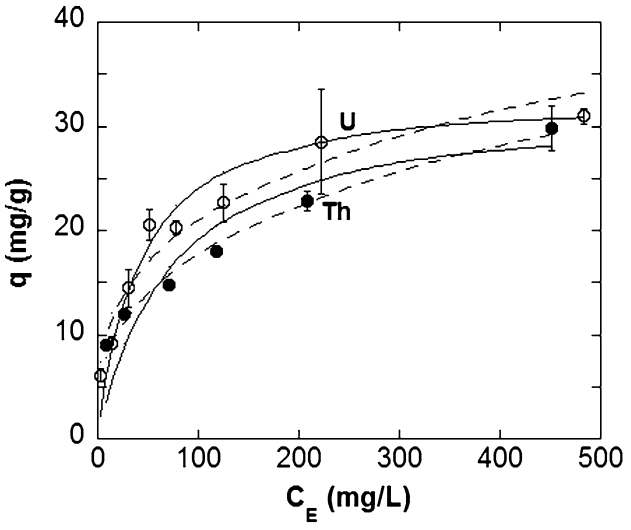

Fig. 7 Experimental isotherm adsorptions of Th (*closed circles*) and U (*open circles*) for HASi1, as fitted by the Langmuir model (*solid lines*) and Freundlich model (*dashed lines*)

The determination of the maximum sorption capacity using the Sips model, which combines the Langmuir and Freundlich models [38], resulted in maximum sorption capacities of 214.93 mg g^{-1} (RMSE 0.80) and 54.02 mg g^{-1} (RMSE 1.86) for Th and U, respectively. Based on the RMSE values, the Sips model is a better model than Langmuir model, and in the case of Th, it is better than the others. However, the model overestimates the value for the maximum sorption capacity. Thus, in this case, the Langmuir model was chosen because of the least error between the estimated value and the experimental value (Table 2). Based on the sorption intensity values, *1/p*, for Th and U, which are higher than 0 and less than 1 (0.33 and 0.29), it is assumed that the adsorption process is physical and favorable [39], which is demonstrated by the Th and U removal with the HASi1 adsorbent.

Adsorption kinetics studies

Sorption kinetics studies were carried out to examine the effect of contact time on the sorption process by the batch technique at pH 2.5 (Th) and 3 (U). The initial concentrations were 10 and 25 mg L^{-1}, while the contact time was varied from 1 to 240 min, and the solid–liquid ratio was 2 mg ml^{-1}.

Three models (pseudo-first-order, pseudo-second-order and intra-particle diffusion) were applied to describe the experimental kinetics data. The pseudo-first-order model is based on the assumption that the adsorption rate at any given time (t, min) depends on the difference between the equilibrium sorption capacity (q_{E}, mg g^{-1}) and the sorption capacity at time t (q_{t}, mg g^{-1}), as formulated in Eq. (6). In the pseudo-second-order model, it is postulated that the sorption process is a pseudo-chemical reaction process and that the sorption rate increases proportionally to the square of the driving force. The driving force in this case is the difference between the equilibrium sorption capacity (q_{E}) and the sorption capacity at any given time

Table 2 Estimated isotherm parameters of Th and U adsorptions by the HASi1 adsorbent

Elements	*p*H	Langmuir			Freundlich		
		Q (mg g^{-1})	K (L mg^{-1})	*RMSE*	K_F (ml mg^{-1})	p	RMSE
Th	2.5	32.3	0.015	2.97	3.92	3.03	0.80
U	3	33.2	0.027	2.07	5.57	3.46	2.06

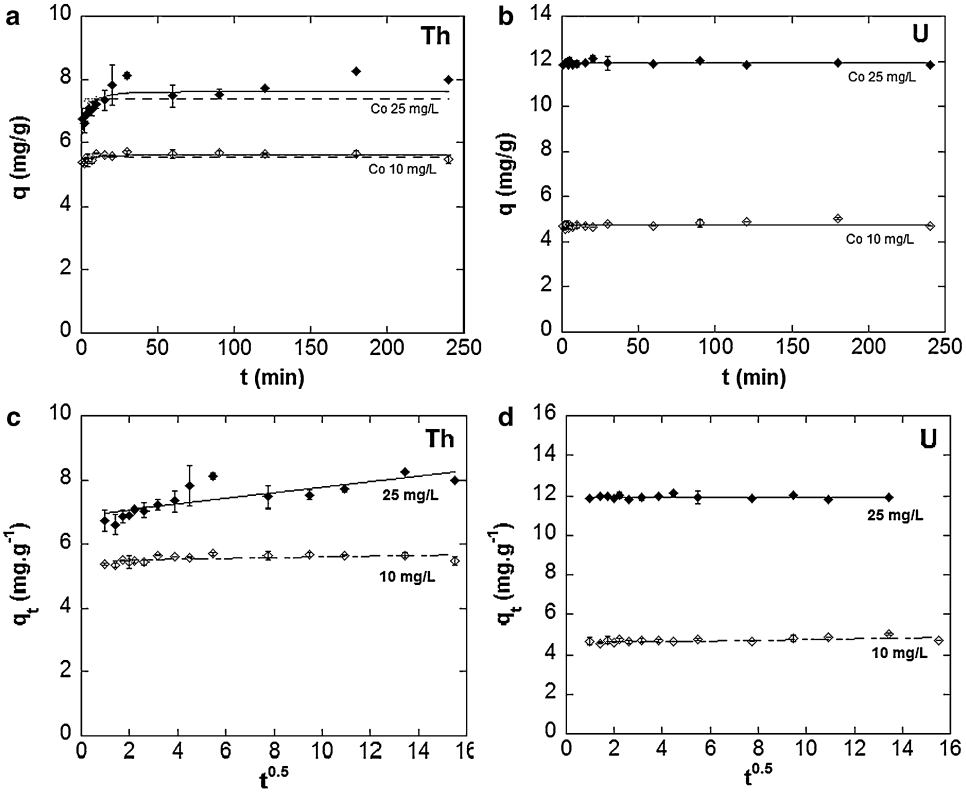

Fig. 8 Fittings of the experimental kinetic data by the pseudo-first-order (*dashed line*) and pseudo-second-order (*solid line*) models for **a** Th and **b** U, and the intra-particle diffusion model: **c** Th and **d** U

t (q_t), as described in Eq. (7). Based on the pseudo-second-order model, the initial adsorption rate (H, mg g^{-1} min^{-1}) and time required to adsorb half of the initial concentration ($t_{1/2}$, min) could be computed by Eqs. (8) and (9) [27]. The intra-particle diffusion model is based on the hypothesis that the adsorption process is controlled by the diffusion process (10). k_i (mg g^{-1} min$^{0.5}$) is the intra-particle diffusion rate constant, and I is the intra-particle diffusion constant, which is proportional to the boundary layer.

$$q_t = q_E(1 - e^{-k_1 t}) \tag{6}$$

$$q_t = \frac{k_2 q_E^2\, t}{1 + k_2 q_E\, t} \tag{7}$$

$$H = k_2 q_E^2 \tag{8}$$

$$t_{1/2} = \frac{q_E}{H} \tag{9}$$

$$q_t = k_i \sqrt{t} + I \tag{10}$$

$$dq(\%) = 100\sqrt{\frac{1}{n-1}\sum_{i=1}^{n}\left(\frac{q_{t\ exp} - q_{t\ cal}}{q_{t\ exp}}\right)^2} \tag{11}$$

$$\mathrm{ARE}(\%) = \frac{100}{n-1}\sum_{i=1}^{n}\left(\frac{q_{t\ exp} - q_{t\ cal}}{q_{t\ exp}}\right)^2 \tag{12}$$

The linear coefficient correlation (r^2), normalized standard deviation (dq) and average relative error (ARE) were used to evaluate the model compatibility to the experimental data. dq and ARE given in Eqs. (11) and (12) [40]. $q_{t\ exp}$ and $q_{t\ cal}$ are the sorption capacity based on the experimental data and the modeling at a given time t, respectively, while n is the number of observations.

Figure 8 shows that all models could fit to the experimental data, which is supported by the statistical analysis results of the linear coefficient correlation, the normalized standard error and the average relative error, as shown in Table 3. The table shows that based on the normalized

Table 3 Kinetic parameters of Th and U removal by the HASi1 adsorbent estimated based on modeling by the pseudo-first-order, pseudo-second-order and intra-particle diffusion models

Parameters	C_o Th (mg L^{-1})		C_o U (mg L^{-1})	
	10	25	10	25
Pseudo-first-order				
k_1 (min^{-1}) × 10^{-3}	3.35	2.19	4.42	4.99
q_E model (mg g^{-1})	5.55	7.39	4.73	11.93
q_E experimental (mg g^{-1})	5.70	8.26	5.04	12.16
dq (%)	1.99	6.31	2.35	0.64
ARE (%)	0.04	0.40	0.06	0.00
Pseudo-second-order				
k_2 (g mg^{-1} min^{-1})	2.94	0.60	5.66	6.60
q_E model (mg g^{-1})	5.60	7.62	4.76	11.96
q_E experimental (mg g^{-1})	5.70	8.26	5.04	12.16
H (mg g^{-1} min^{-1})	92.18	35.10	128.36	943.26
$t_{1/2}$ (min)	0.06	0.22	0.04	0.01
dq (%)	1.50	4.58	2.16	0.69
ARE (%)	0.02	0.21	0.05	0.01
Intra-particle diffusion				
k_i (mg g^{-1} $min^{0.5}$)	0.088	0.013	0.001	0.016
I (mg g^{-1})	6.89	5.47	11.93	4.65
r^2	0.645	0.255	0.002	0.410
dq (%)	1.90	4.00	1.00	0.70
ARE (%)	0.04	0.16	0.01	0.01

standard error (dq) and the ARE, the pseudo-second-order model generally fits better to the experimental data than the pseudo-first-order model.

Additionally, the pseudo-second-order model predicts the maximum sorption capacity better than the pseudo-first-order model. Generally, the k_2 value of the pseudo-second order model for U is greater than that of Th, which is probably caused by a higher binding constant for U than Th (Table 2).

The calculated initial adsorption rate (H) and time required to adsorb half of the initial concentration ($t_{1/2}$) for both Th and U suggest a rapid adsorption process. There is agreement between the value of the equilibrium sorption capacity from the experimental data ($q_{E\ exp}$) and that from the modeling (q_{Emodel}), indicating that the adsorption process is concentration dependent [41].

The fitting of the experimental kinetic data by the intra-particle diffusion model results in a linear curve that does not intercept the origin point. This result indicates that the adsorption rate is affected by the intra-particle diffusion process [42]. However, the intra-particle diffusion coefficient (k_i) value denotes that the diffusion process is not a rate-limiting step. The larger intra-particle diffusion constant (I) for U signifies an improvement in the sorption rate and a better sorption mechanism because of the stronger bonding between the uranyl ion and the ligand site on the adsorbent surface [43], corresponding to its higher binding constant.

Effect of salinity and lanthanide concentration

To evaluate the capability of the HASi1 adsorbent to remove Th and U in a highly saline environment, batch studies were performed by equilibrating 10 mg of the adsorbent with 5 ml of 10 mg L^{-1} Th or U in a sodium chloride solution at a concentration from 0 to 1 mol L^{-1}. This evaluation is considered to be important because many Th and U occurrences in nature are associated with marine beach placer deposits and are susceptible to Th and U pollution. Figure 9a shows that salinity decreases the sorption capacity. In the case of Th, the sorption capacity decreases to 75 % (NaCl 0.75 M) of the initial sorption capacity (NaCl 0 M), while that of U is reduced to 70 % of the initial sorption capacity for the same sodium chloride concentration. The sorption capacity decrease due to the increasing salinity could be explained by the tendency of Th and U to form more stable anionic chloro complexes

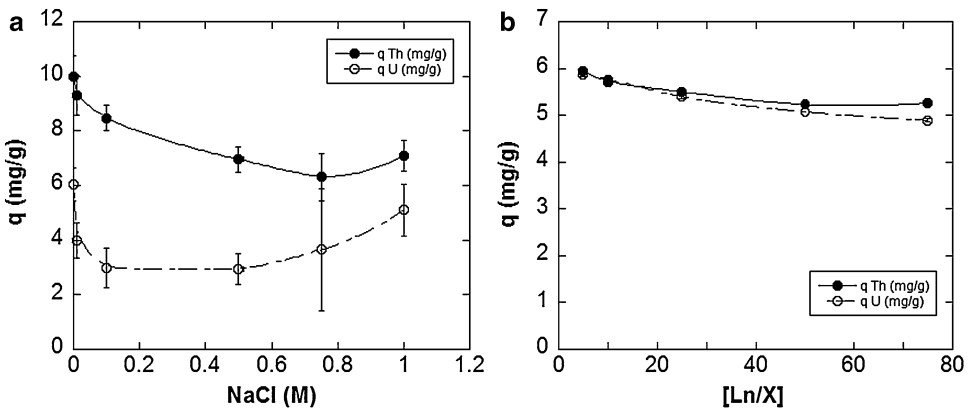

Fig. 9 Sorption capacities of the HASi1 adsorbent for Th and U as function of **a** salinity and **b** the ratio of their concentration to the total lanthanide concentration, [Ln/X]

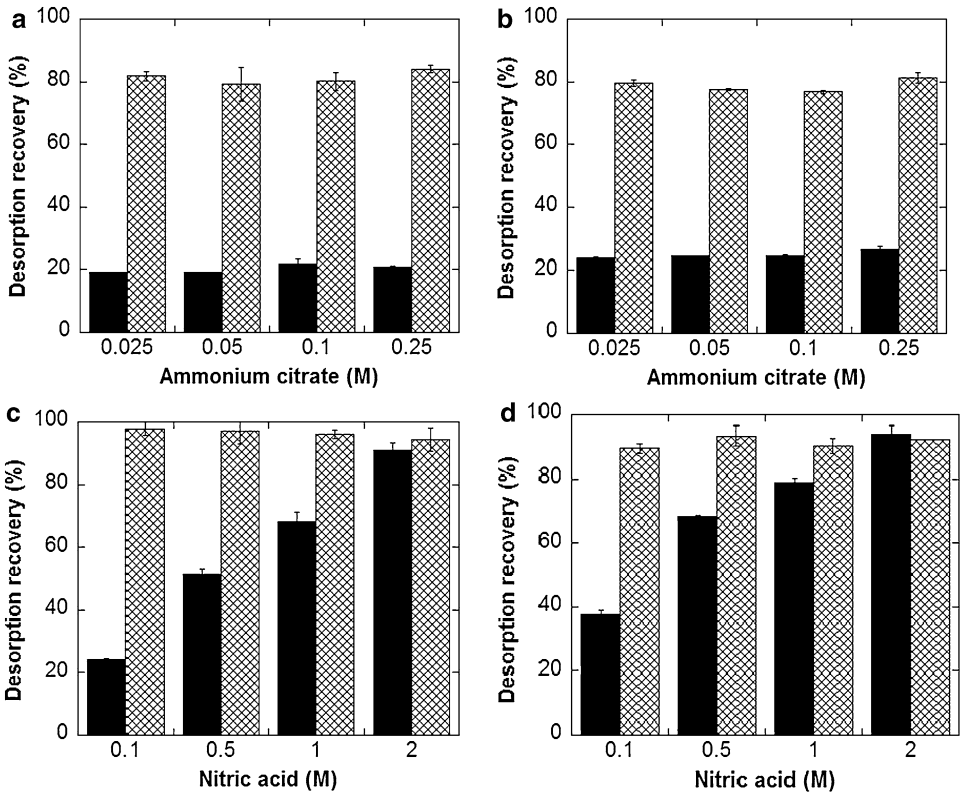

Fig. 10 Desorption of Th (*solid black column*) and U (*mesh column*) by ammonium citrate with a metal content in the HASi1 adsorbent of **a** 5 mg g^{-1} and **b** 12 mg g^{-1}. The desorption by nitric acid with a metal content of **c** 5 mg g^{-1} and **d** 12 mg g^{-1}

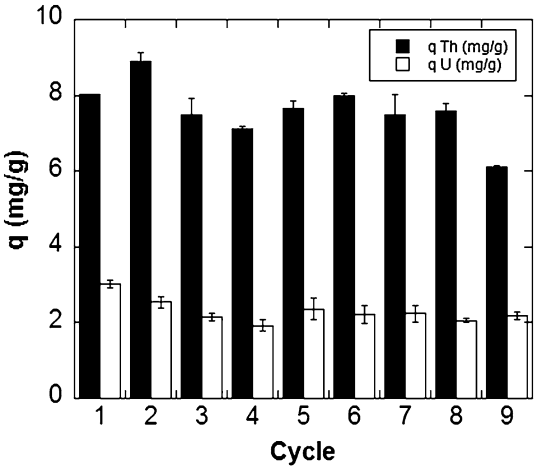

Fig. 11 Sorption capacity of the HASi1 adsorbent after nine cycles of Th and U removal and regenerated using 1 M nitric acid

[44]. Stronger affinities of Th and U to chloro ligands than to the ligand sites on the adsorbent surface would in turn decrease the sorption capacity value.

Figure 9b depicts the effect of the lanthanide concentration (Ln) on the HASi1 sorption capacity for Th and U removals. In batch studies, lanthanides were represented by La and Ce, which were used at the same amount to constitute the total lanthanide concentration, [Ln]. Typically, 10 mg of the HASi adsorbent was equilibrated with 5 ml of a Ln–Th or an Ln–U mixture solution, in which the Th or U ratio to the total lanthanides, [Ln/X], varied between 5 and 75. This study considers the close association between lanthanides and Th–U in nature, e.g., monazite sand. The results suggest that lanthanide concentration suppresses the Th and U removal capacities by up to 80 % when the Th/U—Ln ratio reaches 1:75. In addition, U is more affected by the Ln concentration, probably because of the small difference in ionic charged species (UO_2^{2+} to Ln^{3+}) compared with Th (Th^{4+} to Ln^{3+}).

Desorption and reusability studies

Desorption and reusability studies were carried out to determine the regeneration capability of the HASi1 adsorbent and the viability of recovering Th and U for further use. In the desorption experiment, 10 mg of the HASi1 adsorbent containing Th or U at a concentration of 5 or 12 mg g^{-1} was leached by 1 ml of nitric acid or 5 ml of ammonium citrate for 5 min. The results of the leaching experiment for different concentrations of nitric acid and ammonium citrate are presented in Fig. 10.

The concentration of ammonium citrate did not affect the recovery rate for either Th or U. In addition, U has a stronger affinity toward citrate, as demonstrated by the higher recovery leaching value (80 %). This result suggests that ammonium citrate is a suitable leaching reagent to

Table 4 Comparison of the Th and U sorption capabilities of the humic-acid-based adsorbents from previous reports and this study

Adsorbent material	pH	Q (mg g^{-1})		Equilib. time	Reusability (cycles)	Reference
		Th	U	(min)		
1. Humic acid immobilized on zirconium pillared clay	6		132.7	180	4	[7]
2. Humic acid-Amberlite XAD-4	4	35.0		60		[8]
3. Insolubilized humic acid	3	20.0	17.0	360		[28]
4. Humic acid modified silica gel (silylation)	3	28.0	31.3	180	4	Unpublished data
5. Humic acid–silica sol gel composite	3		33.2	180	9	This study
6. Humic acid-silica sol gel composite	2.5	32.3		180	9	This study

recover U from HASi1, including its regeneration and possible separation from Th. In the case of nitric acid, the concentration strongly affects the Th recovery. Th is quantitatively recovered by 2 M nitric acid, while quantitative U recovery is attained at a lower concentration. Based on a leaching experiment using different Th and U contents (5 or 12 mg g^{-1}) both with ammonium citrate and nitric acid, there is no significant difference regarding recovery, indicating the possibility of quantitatively recovering Th and U using a larger volume of leaching agent at a lower concentration.

The reusability studies included the sorption and desorption phases for each cycle. In these studies, 20 mg of the HASi adsorbent was equilibrated with 20 ml of a 10 mg L^{-1} Th or U solution (a solid–liquid ratio of 1 mg ml^{-1}). After Th and U were adsorbed, the supernatant solution was separated by centrifugation, and the HASi1 containing Th or U was then leached by 5 ml of 1 M nitric acid to recover Th and U (desorption). Following 5 min of agitation, the nitric acid containing Th or U was separated by centrifugation, and HASi1 was washed with Milli Q water, dried at 30 °C and used for the next sorption-desorption cycle.

The results in Fig. 11 show that the sorption capacity (q, mg g^{-1}) is relatively constant after nine regeneration cycles, demonstrating the stability of the HASi1 adsorbent and its suitability for repeated use. Table 4 compares the characteristics of several humic-acid-based adsorbents that have been reported to remove Th and U from an aqueous solution with respect to the optimum pH, maximum sorption capacity Q (mg g^{-1}), equilibrium time and reusability.

Conclusions

The results clearly demonstrate that the sol–gel method is a suitable method to attach humic acid as a functional group to silica gel. The success of humic acid mobilization in the silica gel matrix was confirmed by FTIR and SEM-EDS characterization. The performance of HASi1 for Th and U removal from an aqueous solution was best attained under acidic conditions (pH 2.5–3). The isotherm adsorption studies showed that the sorption process is concentration dependent because of the heterogeneous nature of the functional groups present. The maximum monolayer sorption capacity is found to be 32.3 and 33.2 mg g^{-1} for Th and U, respectively. Kinetics studies reveal that the pseudo-second-order model is best for describing the rapid adsorption process, of which 85 % removal could be attained within 5 min. Conversely, the intra-particle diffusion model suggests that the diffusion process affected the adsorption process. Based on the ion competition studies, HASi1 is suitable to remove Th and U from a high-saline environment and to separate them from lanthanides, as their closest associated elements in nature. HASi1 could be regenerated using nitric acid, and its performance is relatively stable after nine regeneration cycles. Furthermore, the results in terms of adsorbent performance for Th and U removal signify the viability of HASi as an inexpensive alternative adsorbent compared with the previously reported materials and highlight the importance of the sol–gel method as an underdeveloped yet versatile method to produce hybrid materials applicable to environmental remediation.

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