Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.989416

57 (2016) 3292–3297
February

Taylor & Francis
Taylor & Francis Group

Evaluation of mineral and organic acids on the selective separation of radioactive elements (U and Th) using modified carbon

S.M. Yakout[a,b]

[a]*Biochemistry Department, College of Science, King Saud University, P.O. Box, 2455, Riyadh 11451, Kingdom of Saudi Arabia, Tel. +966 558448693; Fax: +966 14675932; email: sobhy.yakout@gmail.com*
[b]*Hot Laboratories Centre, Atomic Energy Authority, Cairo 13759, Egypt*

Received 5 May 2014; Accepted 18 October 2014

ABSTRACT

Uranium (U) and thorium (Th) separation by batch adsorption onto rice straw-based activated carbon (RS carbon) was studied. The effect of pH, contact time adsorption, and desorption media on the selectivity and sensitivity of the removal process was investigated. Results show that the metal ion species rapidly move from liquid phase to carbon surface with 40–100 min equilibrium time for uranium and thorium, respectively. Uranium and thorium sorption reaches its maximum at pH 5.5 and 4, respectively. Thus, these radio nuclides can be separated by the careful adjustment of pH and contact time. Thorium can be highly selective separated from uranium at lower time and at pH 4. Lower concentration of acetic acid enhance uranium and thorium uptake when compared with other mineral and organic acids. Uranium can be selectively desorbed from RSK carbon using HCl leaving thorium onto the adsorbents. Thorium can be selectively eluted from RSK carbon by using HNO_3 or H_2SO_4 and from RSN carbon by $NaHCO_3$. These procedures may be successfully applied, in most cases, where a careful separation of two elements is required.

Keywords: Selectivity; Adsorption; Desorption; Uranium; Thorium; Activated carbon

1. Introduction

Uranium and thorium are the two most important elements for nuclear energy industries [1]. Taking into consideration wide usage of uranium and thorium for numerous industrial purposes and potential risks presented by radio nuclides for humans and the environment, reprocessing to purify and separate these radio nuclides is of great significance. Separation of uranium and thorium is relatively difficult since thorium does not have variable oxidation states. Thus, it should be used as the difference in the complexation behavior of thorium and uranium to obtain the desired separation [2].

Adsorption is by far the easiest way for removing radioactive ions from aqueous solutions. The process using adsorbents is thought to be the most effective method, due to its high selectivity, the ease of handling, and the environmental issues. Various types of materials have been used for thorium and uranium removal, for example activated carbon powder and zeolites [3], immobilized siloxane polymers [4], natural and modified clays [5], synthetic anion exchangers [6], pass cement dust [7], etc, Among many types of adsorbent materials, activated carbons which can be produced from any carbonaceous material, are the most widely used, because of their large adsorptive capacity and low cost [8,9]. Activated carbons adsorption technique has attracted particular interest in the pre-concentration and treatment of radioactive liquid wastes, because they have affinity for certain ions or groups of ions from both acidic and alkaline solutions [10]. Furthermore, their high stability toward chemicals, radiation, and heat, as well as their rigid porous structure and mechanical strength, give considerable advantages over other adsorbent materials [11]. Adsorption of uranium and thorium onto various solids is important from purification, environmental, and radioactive waste disposal points of view.

Separation and purification processes based on adsorption technique are also important in nuclear industry where activated carbon is often used for the separation of metal ions from solutions, due to its selective adsorption, high radiation stability, and high purity [11]. Uranium and thorium is the most important element for nuclear industry. Adsorption of uranium and thorium onto various solids is important from purification, environmental, and radioactive waste disposal points of view.

The efficiency of an adsorbent is not solely determined by sorption characteristics but also by desorption behavior. This desorption step allows the metal ion to be removed and recovered. Recovery of the adsorbed material as well as the regeneration of adsorbent is also an important aspect of wastewater treatment. Desorption studies help to elucidate the nature of adsorption and help to recover the precious metals from wastewater and the adsorbent

The objective of this study is to determine the optimized condition for separation of uranium and thorium by activated carbon prepared by single-step steam activation of locally available agricultural waste-rice straw either by adsorption or desorption.

2. Materials and methods

Rice straw-based activated carbon (RS carbon) was prepared using steam pyrolysis method according Hamed et al. [12]. Modified carbons were produced by oxidation of the prepared carbon using nitric acid (labeled as RSN carbon) and potassium hydroxide (labeled as RSK carbon) according to the procedures described earlier [13,14]. Oxidization of activated carbon by nitric acid and potassium hydroxide introduce oxygen-containing functional groups to carbon surface which result in more hydrophilic surface structure. These functional groups provide binding sites in the adsorption process.

Batch sorption experiments were done to get both rate and equilibrium data. Ten milligram of RSK and RSN carbon mixed and shook with 10 ml of 100 ppm uranium or thorium solution for different period of time (up to 300 min.). Next, the solution was filtered using a Whatman No. 42 filter paper and analyzed for the concentration of the metal ions continuing in the solution. Blank tests without activated carbon were included to check that no precipitation happened throughout experiments. The concentrations of uranium or thorium in the solutions were quantified by measuring absorbance at 665–655 nm with double-beam UV spectrophotometer (Shimadzu model 160A) using arsenazo (III) as coloring agent [15]. Sorption capacity of adsorbent was calculated by:

$$q\mathrm{e} = \frac{V(C_0 - C_\mathrm{e})}{M} \tag{1}$$

Sorption efficiency based on the percentage of metal removal was calculated by:

$$R\% = \frac{C_0 - C_\mathrm{e}}{C_0} \times 100 \tag{2}$$

where C_0 and C_e are the initial and equilibrium concentration (mg/l), respectively, M is the mass of dry carbon sample used (g), and V is the volume of solution (ml).

Desorption experiments were done after adsorption experiments using uranium-laden carbon by shaking for 24 h with 10 ml of desorping agent. The remaining procedure was the same as that in the sorption equilibrium experiments except that no pH adjustment was required. Desorbable amounts of metal ions expressed the amount to be desorbed (q_des) as follows:

$$q_\mathrm{des} = \frac{VC_\mathrm{des}}{m} \tag{3}$$

With C_des the desorbed metal concentration.

3. Results and discussion

Separation of radio nuclides may be of concern in nuclear technology. In this study, rice straw-based carbon was oxidized using potassium hydroxide RSK carbon and nitric acid RSN carbon. RSN was found to be superior for thorium removal while RSK carbon for uranium removal than non-oxidized carbon. Batch experiments were done to find optimum conditions of separation (time and pH).

The adsorptions of uranium and thorium metal ions were noticeably influenced by the pH of solution (Table 1). Even at lower pH, RSK and RSN carbon removes 60 and 50% of uranium and thorium,

Table 1
Fractional adsorption of U(VI) and Th(IV) as function of pH

pH	Uranium, *R*%	Thorium, *R*%
1.5	–	54.45
2.5	62.3	70
4	92.3	85
6	99.3	74
8.2	75	65.5
10	51.85	54.65

respectively. The adsorption percent removal *R*% increases as pH increase and then decreases with further increase in pH. Sorption reaches its maximum at pH 4 and 5.5 for thorium and uranium onto RSN and RSK carbons, respectively. These optimum pHs were used for the remaining tests. Above these pH values, sorption decreases as pH continues to rise.

Fig. 1 displays removal of uranium by RSK carbon and thorium by RSN carbon as a function adsorption reaction time. Uranium and thorium adsorption capacity increases as time increases and reach equilibrium at 40 min for uranium and 120 min for thorium. Short equilibrium adsorption time is one of the significant thoughts for economical wastewater treatment applications. According to these results, for the following batch adsorption experiments, one and two hours were selected as agitation time for uranium and thorium removal, respectively, to make sure whether the equilibrium is reached.

3.1. Adsorption selectivity

Uranium and thorium metal ions are chemically similar nuclear fuels. Comparative study of their selective adsorption on modified activated carbon is important from academic and practical view.

The adsorption selectivity (*S*) for a couple of metals, a and b, can be calculated by the ratio of $q_a(t)/q_b(t)$ as follows [16]:

$$S = \frac{q_a(t)}{q_b(t)} \tag{4}$$

where $q_a(t)$ and $q_b(t)$ denote to the amounts adsorbed of the species with a stronger and a weaker affinity toward an adsorbent at time *t*, respectively [16].

Fig. 2 shows the influence of reaction time on selective adsorption between uranium and thorium by RSK and RSN carbons at pH 5.5 and pH 4. The selectivity differences from one metal to another and from one system to another are related to pH and adsorbent type. The selectivity of U/Th-RSK system increases with the time and reaches its maximum at about 200 min for both pH 5.5 and 4. However, the selectivity at pH 4 ($S = 2.2$) is about two-fold greater that at pH 5.5 ($S = 1.3$). So that, uranium can be selectively separated from thorium at pH 5.5 or 4.0 after interaction time of 200 min with RSK carbon. In contrast, selectivity of Th/U-RSN system decreases with time by increasing pH at either 5.5 or 4.0. For all that, selectivity at pH 4 is about three-fold greater selectivity at pH 5.5. Thus, thorium can be highly selective separated from uranium at lower time and at pH 4 on RSN carbon. Consequently, thorium and uranium can

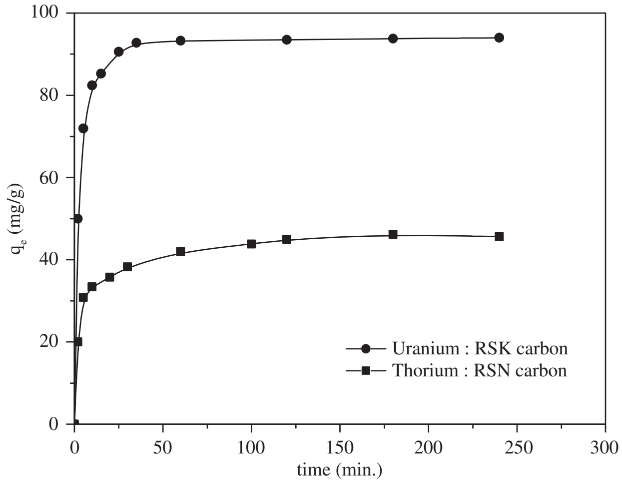

Fig. 1. Influence of agitation time on uranium and thorium adsorption.

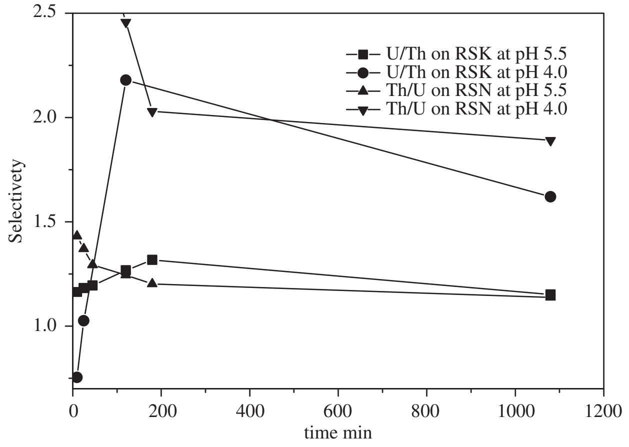

Fig. 2. Selectivity profiles of U/Th on RSK and Th/U on RSK and RSN carbons at pH 5.5 and 4.

be separated by the judicious adjustment of agitation time and pH.

Ground water frequently contains complexing ligands which play a significant role in determining the state and mobility of metal ions in aquatic systems and may compete with metal ions for adsorption. It is expected that these compounds will affect metal ions adsorption when they co-exist in solution.

Experiments were done to test the change in uranium and thorium adsorption behavior on RSK and RSN carbons as a function of using different complexing agents of organic and mineral acids that are significant in environmental and industrial processes.

Nitric acid was studied, as it forms the main component in nuclear spent fuels and hydrochloric acid was studied as the most of analytical techniques separation and pre-concentration of metal ion from environmental, geological, and biological samples are performed in this medium [17]. Oxalate can be formed in nuclear waste depositories by decomposition of organic compounds so that oxalic acid was used in this study [18]. Also acetic acid used because of acetate is one of the most common anion found in samples derived from subsurface locations containing interred waste uranium [19].

Table 2 displays the uranium and thorium sorption efficiency (%*R*) onto RSK and RSN carbon from different media (0.1 M). All organic and inorganic ligands influenced on the sorption of uranium and thorium by different degree. Both phosphoric and oxalic acids give negligible uranium and thorium adsorption on two carbons in U–Th binary solution except in case of thorium removal by RSN carbon in oxalic acid medium. On the contrary, acetic acid improves uranium and thorium removal when compared with mineral acids. These results agree with results obtained by Akhtar and Qadeer [20] and Yu et al. [21] for improved metal sorption using acetate medium.

Table 2
Sorption efficiency (%*R*) of uranium and thorium onto RSK and RSN carbon from different media (0.1 M)

	RSK		RSN	
Media	Uranium	Thorium	Uranium	Thorium
H_2O	32	41	32	28
HCl	25.2	12.5	21.2	21.0
HNO_3	23.2	19.2	19.3	1.6
H_2SO_4	1.5	17.7	0.77	1.2
H_3PO_4	1.3	2.9	1.2	6.5
Oxalic acid	0	5.1	0	38.6
Acetic acid	52.2	58.0	42.3	45.2

Presence of foreign ions in the solution may alter environment around the metal ion and consequently alter its solution chemistry and sorption characteristics. Foreign ions may reduce or enhance metal adsorption according to its ability to form complex with metal ion. If metal ion forms complex its adsorption increases. However, if not the foreign ions may compete with metal ion. There are three possible roles for foreign ions (ligands) in metal adsorption systems: (1) Ligands can hinder adsorption of metal ion by forming non-adsorbable complexes with it, or (2) by competition with the metal itself for available surface sites, and (3) Ligands can improve adsorption of metal by forming highly adsorbable complexes with the metal than free metal ions and result in the formation of metal–ligand surface complexes [22]. Otherwise, the activated carbon ability to sorb large organic molecules is well-known and widely used in wastewater treatment process [23].

The sorption of metal complex drop in the presence of oxalic and phosphoric acids may be because of stable complexes formation with these ions that have very low affinity toward the carbon sorbent. These complex may appear as precipitate for instance thorium oxalate precipitation in thorium-RSN system [24]. Strong ligand–metal complex means higher stability of complexes in aqueous solution and less adsorption of metal ions onto the surface of possible substrates [25]. Thus, oxalic and phosphoric ligands should be removed first from wastewater effluents, before processing for uranium and thorium removal.

Removal of uranium and thorium from acetate solution was high in comparison to their removal from chloride, nitrate, or sulfate solutions. Hydrogen ion concentration of solutions is one of the most important factors, effect on metal ion sorption. Generally, high hydrogen concentration (lower pH) inhibits metal ion adsorption. Strong acids like HCl, HNO_3, and H_2SO_4 almost completely dissociates and give high hydrogen ion activity, while weak acids like acetic acid is partially dissociated and give low hydrogen ion activity. As a result, acetic acid enhance uranium and thorium adsorption while HCl, HNO_3, and H_2SO_4 reduce their adsorption [26]. Other reason for this behavior is owing to the formation of uranium and thorium acetate complex which are more absorbable when compared with free species.

According to these results, adsorption behavior of uranium and thorium mixture on RSK carbon was measured in 0.01–1 M acetic acid solution (Fig. 3).With the increase in acid concentration, there is a significant decrease in the adsorption of both uranium and thorium. This can be described on the basis of a competitive reaction between positively charged uranium or

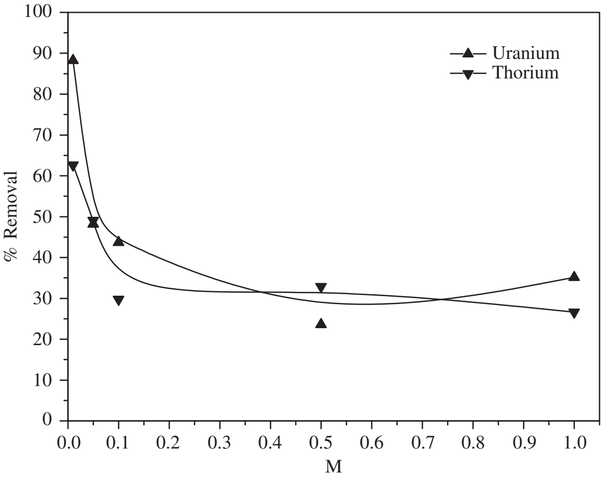

Fig. 3. Effect of acetic acid concentration on mixture of uranium and thorium adsorption onto RSK carbon.

thorium ions and hydrogen ions in the medium. At low acetic acid concentration the hydrolyzed species adsorbed on carbon surface, whereas increasing acid concentration inhibit the hydrolysis of uranium and thorium leading to lower adsorption percentage value. Hence, metal ions could be removed from high pH acetate solution.

3.2. Selective desorption of uranium and thorium adsorbed from acetic acid medium

Separation of uranium and thorium in desorption mode is obtained by selective elution of one ion over another. The elution may be carried out with a complexant that preferentially removes one or more ions, or by changing acidity or concentration of the eluent such that sorbed ions are eluted sequentially.

Taking into account of the overall adsorption behavior of the two elements, acetic acid medium (0.01 M) was chosen for adsorption. Several solutions, include HCl, HNO_3, H_2SO_4, and $NaHCO_3$, were tested in order to determine the best reagents for the separation of uranium and thorium by selective desorption.

By applying the selectivity Eq. (4) on desorption of uranium or thorium from RSK and RSN we obtain desorption selectively in Table 3. It is clear from that uranium can be selectively desorbed from both adsorbent by using HCl leaving thorium onto the adsorbents. Also Table 3 shows that thorium can be selectively eluted from RSK by using HNO_3 or H_2SO_4 and from RSN by $NaHCO_3$.

Nevertheless by comparing the selective desorption values in Table 3, it is clear that thorium recovery is the more difficult step owing to its great affinity toward the adsorbents. Both adsorption and desorption studies show that thorium was more chemisorbed than uranium.

Table 3
Selective desorption of uranium and thorium from RSK and RSN carbon by different media

	Uranium		Thorium	
Media	RSK	RSN	RSK	RSN
HCl	23.5	12.1	0.04	0.08
HNO_3	0.52	0.92	1.9	1.1
H_2SO_4	0.77	1.2	2.0	1.2
NaHCO3	0.5	0.9	0	2.4

4. Conclusion

This study tried to find the optimum experimental condition for uranium and thorium separation onto activated carbon. It was found that their separation affected by different factors include contact time, pH, sorption, and desorption medium. By the careful adjustment of pH and contact time, uranium and thorium can be separated. Lower concentration of acetic acid enhance uranium and thorium uptake when compared with other mineral acids. Uranium can be selectively desorbed from activated carbon using HCl leaving thorium onto the adsorbents. Thorium can be selectively eluted from RSK carbon by using HNO_3 or H_2SO_4 and from RSN carbon by $NaHCO_3$. These procedures may be successfully applied in most cases, where a careful separation of two elements is required.

Conflicts of interest

No competing financial interests exist.

Acknowledgment

The authors would like to extend their sincere appreciation to the Deanship of Scientific Research at King Saud University for its funding of this research through the Research Group Project No RGP-VPP-184.

References

[1] G. Seaborg, J.T. Katz, The Actinide Elements, McGraw-Hill, New York, NY, 1957.

[2] M.E. Nasab, Solvent extraction separation of uranium (VI) and thorium (IV) with neutral organophosphorus and amine ligands, Fuel 116 (2014) 595–600.

[3] C. Kutahyali, M. Eral, Sorption studies of uranium and thorium on activated carbon prepared from olive

stones: Kinetic and thermodynamic aspects, J. Nucl. Mater. 396 (2010) 251–256.
[4] E.O. Akperov, A.M. Maharramov, O.G. Akperov, Uranyl ion adsorption using novel cross-linked maleic anhydride–allyl propionate–styrene terpolymer, Hydrometallurgy 100 (2009) 76–81.
[5] D.L. Guerra, R.R. Viana, C. Airoldi, Adsorption of thorium cation on modified clays MTTZ derivative, J. Hazard. Mater. 168 (2009) 1504–1511.
[6] S. Korichi, A. Bensmaili, Sorption of uranium (VI) on homoionic sodium smectite experimental study and surface complexation modeling, J. Hazard. Mater. 169 (2009) 780–793.
[7] O.I. Ali, H.H. Osman, S.A. Sayed, M.E. Shalabi, The removal of some rare earth elements from their aqueous solutions on by-pass cement dust (BCD), J. Hazard. Mater. 195 (2011) 62–67.
[8] K. Othmer, Encyclopedia of Chemical Technology, Wiley-Interscience, New York, NY, 1997.
[9] H. Zhonghua, M.P. Srinisavan, N. Yaming, Novel activation process for preparing highly microporous and mesoporous activated carbons, Carbon 39 (2001) 877–886.
[10] H.M.H. Gad, Y.F. Lasheen, T.S. El-Zakla, Efficiency of locally prepared activated carbon in the preconcentration of barium-133 and radium-226 radionuclides in single and binary systems, Radiochemistry 55 (2013) 589–595.
[11] R. Qadeer, J. Hanif, M. Saleem, M. Afzal, Effect of alkali metals, alkaline earth metals and lanthanides on the adsorption of uranium on activated charcoal from aqueous solutions, J. Radioanal. Nucl. Chem. Lett. 165 (1992) 243–253.
[12] M.M. Hamed, S.M. Yakout, H.S. Hassan, Solid phase extraction of nitrate and nitrite anions using naturally and available sorbent, J. Radioanal. Nucl. Chem. 295 (2012) 697–708.
[13] A.W. Heinen, J.A. Peters, H. Bekkum, Competitive adsorption of water and toluene on modified activated carbon supports, Appl. Catal., A 194–195 (2000) 193–202.
[14] J.-W. Shim, S.-J. Park, S.-K. Ryu, Effect of modification with HNO_3 and NaOH on metal adsorption by pitch-based activated carbon fibers, Carbon 39 (2001) 1635–1642.
[15] Z. Marczenko, Spectrophotometric Determination of Elements, Wiley, New York, NY, 1986.
[16] L. Lv, M.P. Hor, F. Su, X.S. Zhao, Competitive adsorption of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions on microporous titanosilicate ETS-10, J. Colloid Interface Sci. 287 (2005) 178–184.
[17] S.R. Ch, M.S. Subramanian, DAPPA grafted polymer: An efficient solid phase extractant for U(VI), Th(IV) and La(III) from acidic waste streams and environmental samples, Talanta 67 (2005) 81–89.
[18] J. Havel, J. Soto-Guerrero, P. Lubal, Spectrophotometric study of uranyl/oxalate complexation in solution, Polyhedron 21 (2002) 1411–1420.
[19] W. Chien, V. Anbalagan, M. Zandler, M.V. Stipdonk, D. Hanna, G. Gresham, G. Groenewold, Intrinsic hydration of monopositive uranyl hydroxide, nitrate, and acetate cations, J. Am. Soc. Mass. Spectrom. 15 (2004) 777–783.
[20] S. Akhtar, R. Qadeer, Activated carbon as an adsorbent for lead ions, Adsorpt. Sci. Technol. 15 (1997) 815–825.
[21] B. Yu, Y. Zhang, A. Shukla, S.S. Shukla, K.L. Dorris, The removal of heavy metals from aqueous solutions by sawdust adsorption—Removal of lead and comparison of its adsorption with copper, J. Hazard. Mater. 84 (2001) 83–94.
[22] A.P. Davis, V. Bhatnagar, Adsorption of cadmium and humic acid onto hematite, Chemosphere 30 (1995) 243–256.
[23] A. Paajanen, J. Letho, T. Santapakka, J.P. Morneau, Sorption of cobalt on activated carbons from aqueous solutions, Sep. Sci. Technol. 32 (1997) 813–826.
[24] V.M.T. Ganzerli, L. Maggi, C.V. Caramella, Thorium adsorption behaviour on mixed ammonium lanthanum oxalate, LAOX, Appl. Radiat. Isot. 51 (1999) 21–26.
[25] D.S. Kim, Adsorption characteristics of Fe(III) and Fe (III)-NTA complex on granular activated carbon, J. Hazard. Mater. 106 (2004) 45–54.
[26] A. Shukla, Y.H. Zhang, P. Dubey, J.L. Margrave, S.S. Shukla, The role of sawdust in the removal of unwanted materials from water, J. Hazard. Mater. 95 (2002) 137–152.