

Solid Phase Extractive Preconcentration of Some Actinide Elements Using Impregnated Carbon

H. H. Sameda and R. R. Sheha*

Nuclear Chemistry Department, Hot Laboratories Center, Atomic Energy Authority, P.O. 13759, Cairo, Egypt.

Received: April 12, 2006; In Final Form: November 17, 2006

Apricot stone shells were carbonized under certain chemical and thermal conditions. The produced sorbent had been impregnated with different concentrations of oxalic and succinic acids. They were physically characterized and used for preconcentration of U(VI) and Th(IV) from acidified aqueous solutions. Batch equilibrium studies revealed that a quantitative preconcentration could be achieved at pH ~2 for U(VI) and ~1.3 for Th(IV). The equilibrium time was extended up to 24 h for U(VI) and 40 min for Th(IV). The modified sorbent showed a superior extractability for U(VI) and Th(IV) with distribution coefficient mean values of 2084 and 7808 mL g⁻¹, respectively. The sorption capacity values are 2.39 and 8.47 mg g⁻¹ for U(VI) and Th(IV) sorption onto apricot stone anchored with oxalic acid and 2.3 and 9.18 mg g⁻¹ for sorbent anchored with succinic acid. Desorption of loaded uranium ions was effectively achieved using 1 M HNO₃ while only 0.5 M HNO₃ was recommended to release retained thorium ions.

1. Introduction

Trace analysis of metal ions poses unique problems to analysts, as it involves rigorous requirements of versatility, specificity, sensitivity, and accuracy during chemical analysis. These factors are crucial mainly in separation of ultra trace amounts of inorganic species, decontamination of toxic metals and nuclear spent fuel reprocessing processes. In such cases, metal quantification at trace and macro quantities is of immense value. To face these problems, one needs to look for methods that are both efficient and economical for such separation processes. Solvent extraction technique using organo phosphorous extractants was considered for this purpose.¹⁻³ But owing to their tendency to undergo faster radiolytic degradation, formation of large secondary waste volumes, a better alternative to these extractants was explored. Recently, solid phase extraction (SPE) has been increasingly used for preconcentration/separation of trace and ultra trace amounts of inorganic and organic species from complex matrices.⁴⁻⁷ Various researchers have highlighted the advantages of SPE over other preconcentration techniques and in particular over liquid-liquid extraction.⁶⁻⁸ Chelating resins have been frequently used SPE's as they provide good stability, high sorption capacity for metal ions, and good flexibility in working conditions. Iminodiacetate resins^{9, 10} and others including Amberlite XAD series are widely used for this purpose.¹¹⁻¹³ One of the new developments in recent years is the usage of polymer fibers to extract some actinide elements and remove heavy metal ions from aqueous solutions.¹⁴⁻¹⁶ Also various natural compounds as clay minerals,¹⁷⁻¹⁸ zeolites,¹⁹ and meal wood²⁰ were successfully used for preconcentration of some metal ions. In particular, carbonized apricot stone (CAS) is reported to be one of the promising natural and cheap materials used in preconcentration and decontamination processes.²¹ It has high surface area and porosity, good thermal and radiolytic stability, and high retention ability for metal ions.²² To improve the sorption selectivity of this new sorbent toward some actinides elements, which is an important task in nuclear reprocessing and decontamination processes, it was the thought to couple it with some carboxylic acids. The applied acids are oxalic and succinic acids, ligands widely used in liquid-liquid extraction for sepa-

ration of inorganic species.²³

The current paper focuses on applying a new solid phase extraction method using CAS anchored with oxalic or succinic acids for the extractive preconcentration of uranium and thorium elements from slightly acidic media. The extractive preconcentration behavior of the two actinide elements on the applied solid supported matrix was studied under varying experimental conditions using batch operation mode.

2. Experimental

2.1. Reagents. All chemicals and reagents used in this work were of analytical grade purity and used without further purification. Apricot was obtained, as a natural fruit, from El-Amaar region, Banha city. This region locates in Kalubia governorate and is about 50 km from Cairo. The individual stock solutions of uranium (VI) and thorium (IV) were prepared by dissolving appropriate amounts of UO₂(NO₃)₂·6H₂O and Th(NO₃)₄·5H₂O, (Aldrich, USA) in bi-distilled water. Five mL of conc. HNO₃ was added to each 100 mL of stock solution to suppress hydrolysis. Arsenazo-III (Aldrich, USA) solution was prepared by dissolving 0.1 g of the reagent in 100 mL of bi-distilled water.

2.2. Instrumentation. A Pore Size Micrometric-9320, USA equipment and a FT BOMEN-Michelson IR Spectrometer were employed for structural characterization of the anchored sorbent. The determination of metal ion concentrations was performed using UV-Vis spectrophotometer UV-2401 (Shimadzu, Japan). MA-235 digital pH meter (Mettler Toledo, UK) was used for pH measurements. A SBS-30 thermostated water bath shaker (Stuart Scientific, UK) was used for batch equilibration experiments.

2.3. Sorbent preparation. The apricot stone shells were crushed to a fine form. The powdered shells were immersed with H₃PO₄ and then carbonized at 250 °C. The produced carbon was washed with bi-distilled water, dried and sieved into various particle size ranges. Impregnation with oxalic or succinic acids was carried out by conducting, in series, 10 g of CAS particles with 100 mL oxalic or succinic acids aqueous solutions in tightly sealed glass bottles. The initial concentration of the impregnants solutions are 10⁻¹, 5×10⁻², 10⁻², and 10⁻³ M. The samples were shaken for a sufficient time to reach equilibrium. The progress of impregnation, after equilibrium, was verified by taking certain volumes of both adsorbate solutions and subjecting to spectrophotometric analysis at λ = 285

*Corresponding author. E-mail: rsheha68@yahoo.com.

nm to determine oxalic acid concentration while succinic acid concentration was determined by titration against NaOH in presence of phenolphthalein. Then the impregnated carbon was dried at 35 °C for 24 h and kept in a desiccator, to prevent water vapour sorption, for further usage.

2.4. Recommended procedure. The experiments performed in this study were carried out in duplicates in most cases and triplicates whenever needed. The extractive preconcentration was carried out by equilibrating 0.1 g of apricot stone impregnated with oxalic or succinic acids with 10 mL metal ion solution of 10^{-5} M U(VI) or 2.5×10^{-5} M Th(IV) initial concentrations in sealed glass bottles. The samples were shaken with 200 rpm shaking rate at 26 °C. Samples were taken at appropriate time intervals as necessary and centrifuged, and metal ion concentration was determined spectrophotometrically using Arsenazo-III reagent. The solution pH value was adjusted at ~ 2-3 for U(VI) complexation while 3 M HCl medium was applied for Th(IV)-Arsenazo complexation. The absorbance of Arsenazo-III complexes was measured at 656 nm. The sorbed amount (%) of each metal ion and the distribution coefficient (K_d) were calculated using the relationships:

$$\text{Sorbed amount (\%)} = \frac{C_i - C_f}{C_i} \times 100, \quad (1)$$

$$K_d = \frac{C_i - C_f}{C_f} \times \frac{V}{m}, \quad (2)$$

where C_i and C_f are the initial and final concentrations of metal ion in aqueous solution and V/m is the ratio of aqueous volume to the sorbent weight. The metal capacity of the sorbents was determined as follows: One g of impregnated CAS is added to a vessel containing 100 mL volume of U(VI) or Th(IV) solutions of known initial concentrations and shook till equilibrium under optimum conditions. The aqueous phase was separated and analyzed periodically with time for cation concentrations and then replaced with a fresh solution of the same cation. These procedures were repeated until no further uptake is observed. The sorption capacity was calculated as:

$$\text{Sorption capacity} = \frac{\text{Sorbed amount (\%)}}{100} C_i Z \frac{V}{m}, \quad (3)$$

where Z represents the ion valency.

Similar batch studies were performed by conducting the sorbents, loaded with metal ions, with fresh solutions of different HNO_3 concentrations or bi-distilled water. The mixtures were shaken for different time intervals and centrifuged, and the concentrations of metal ions desorbed in solution were analysed. The desorbed amount was calculated using the relation:

$$\text{Desorbed amount (\%)} = \frac{C_d - xC_f}{C_i - C_f} \times 100, \quad (4)$$

where C_d is the total desorbed concentrations of metal ion after time t , and x is the volume fraction of aqueous solution left initially with sorbent (mL).

3. Result and Discussions

3.1. Characterization studies. The surface characteristics of carbonized apricot stone (CAS) is given in Table 1. The data reveal a high surface area and provide porous surface structure. The IR spectra of free and impregnated CAS are given in Figure 1. The spectra show broad band at 3433 cm^{-1} that may be attributed to OH stretching vibration. The bands at 2856 and 2928 cm^{-1} could be assigned to C=C vibration while bands at 1702 and 1614 cm^{-1} can be ascribed to C=O and/or COO⁻ stretching frequency. The bands imposed at 1171 and 991 cm^{-1} are indicative to the presence of oxygenated inorganic constituents (M-O vibration interactions). After impregnation with oxalic acid the bands at 2856 and 1614 cm^{-1} disappeared while

TABLE 1: The physical characteristics of carbonized apricot stone (CAS)

Property	Value
- BET surface area	$85.8 \text{ m}^2 \text{ g}^{-1}$
- Median pore volume	$5.24 \text{ } \mu\text{m}^3$
- Average pore diameter	$0.089 \text{ } \mu\text{m}$
- Apparent density	0.858 g cm^{-3}
- Solid density	0.636 g cm^{-3}
- Porosity	25.85%
- Grain size	0.125-0.09 mm

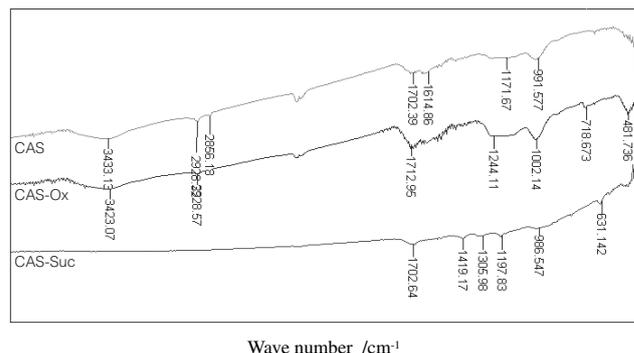


Figure 1. FT-IR spectra for carbonized apricot stone (CAS) impregnated with oxalic and succinic acids.

1702 cm^{-1} band was shifted to 1712 cm^{-1} and new bands at 1244 , 718 , and 481 cm^{-1} were obtained. Also, impregnation with succinic acid caused the peaks at 3433 , 2928 , and 2856 cm^{-1} to disappear and two new peaks appeared at 1419 and 1305 cm^{-1} . This indicates that the molecules of oxalic and succinic acids were attached to apricot stone surface through chemical interactions. These interactions result in certain chemical bonds caused a change in the vibrational frequencies of the chemical groups in apricot stone surface. On the light of this investigation, it can be assumed that the applied impregnants are trapped to CAS surface through crosslinking interactions between the carbonyl sites on the sorbent surface and the oxygenated groups of the impregnant structure.

3.2. Impregnation tolerance limits. Different concentrations of oxalic and succinic acids ranged from 10^{-3} – 10^{-1} M were applied individually to impregnate our new sorbent (CAS). The obtained data show that both oxalic and succinic acids were completely sorbed on CAS surface with 100% uptake. This behavior is coincident with the sorption of other organic acids on CAS.²² The release of these impregnants from loaded CAS using dilute solutions of HNO_3 have pH range 1.5–5 does not exceed 1.9% and 2.6% for oxalic and succinic acids, while bi-distilled water was found to have no effect. This negligible release illustrates the stability of the impregnated sorbents under the applied experimental conditions. The sorption of U(VI) and Th(IV) from nitric acid solution using the prepared impregnated sorbents is clarified in Figures 2 and 3. It is evident from Figure 2 that, CAS impregnated with 10^{-3} M oxalic acid records a U(VI) sorbed amount of 42% decreased to 31% by increasing oxalic acid concentration up to 10^{-1} M. The sorption extent on free CAS was 34% and this value is very similar to that obtained by Starvin et al²⁴ on studying the sorption of U(VI) by activated carbon. This means that impregnation with 10^{-3} M oxalic acid enhances the sorption process but higher concentrations of this impregnant have no effect. Impregnation of CAS with succinic acid increases the sorbed amount of U(VI) and the sorption extent enhances regularly with increasing the impregnant concentration.

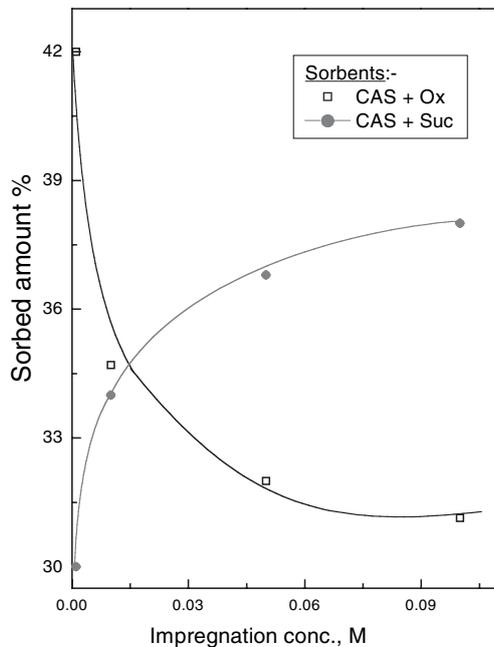


Figure 2. Sorption of UO_2^{2+} from HNO_3 aqueous solution on CAS impregnated with different concentrations of oxalic and succinic acids ($V/m=100$, $\text{pH}=-2$, $\text{time}=48$ h, $\text{temp.}=26\pm 2$ °C).

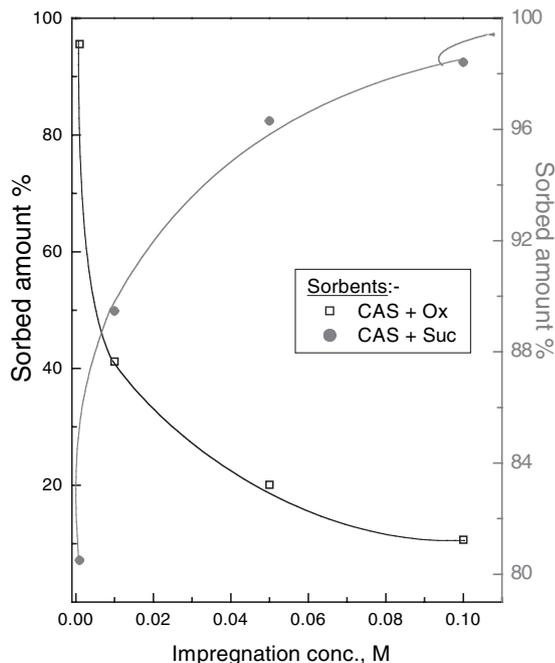


Figure 3. Sorption of Th^{4+} from HNO_3 aqueous solution on CAS impregnated with different concentrations of oxalic and succinic acids ($V/m=100$, $\text{pH}\sim 1.5$, $\text{time}=2$ h, $\text{temp.}=26\pm 2$ °C).

Figure 3 shows the sorption of Th(IV) onto CAS anchored with different concentrations of oxalic and succinic acids. The plots imply that the sorbed amount of Th(IV) decreased from 95% to 11% by increasing the concentration of oxalic acid, as an impregnant, from 10^{-3} to 10^{-1} M. This sorption reduction clarifies that increasing the impregnant concentration decreases the sorption ability of CAS towards thorium species. This behavior can be referred to the formation of thorium-oxalate complex species having the composition $\text{Th}(\text{C}_2\text{O}_4)_4^{-4}$.^{25, 26} These highly anionic species increase the solubility of thorium ions in aqueous phase and consequently decrease their retention on carbonized apricot stone surface. On other hand, impregnation with 10^{-3} M succinic acid slightly increases the sorbed amount percent of thorium ions on CAS and this enhancement was improved by increasing succinic acid concentrations up to 10^{-1} M. Therefore, CAS impregnated with

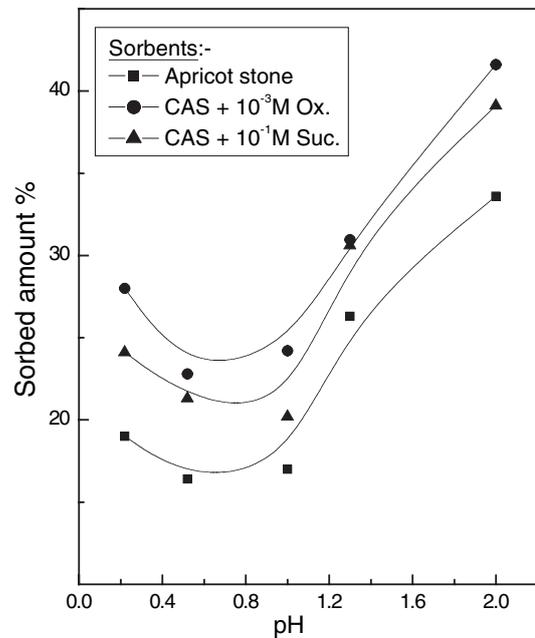


Figure 4. Effect of pH on sorption of UO_2^{2+} from HNO_3 aqueous solution on different apricot stone sorbents ($V/m=100$, $\text{time}=48$ h, $\text{temp.}=26\pm 2$ °C).

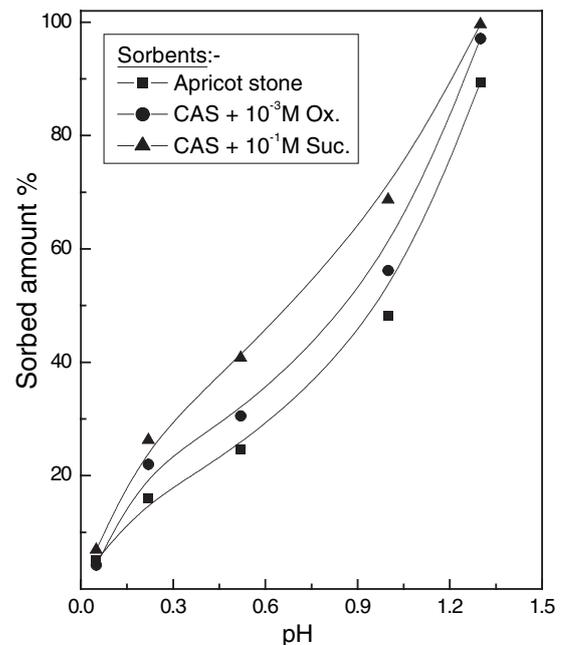


Figure 5. Effect of pH on sorption of Th^{4+} from HNO_3 aqueous solution on different apricot stone sorbents ($V/m=100$, $\text{time}=2$ h, $\text{temp.}=26\pm 2$ °C).

10^{-3} M oxalic acid and 10^{-1} M succinic acid was subjected into the further investigations.

3.3. Sorption studies

3.3.1. pH effect. Sorption of U(VI) and Th(IV) from aqueous solution as a function of solution pH was studied using the previously described anchored sorbents and the revealed data are illustrated in Figures 4 and 5. The results clarify that the sorption of both analytes generally increases with increasing the pH value. The average sorbed amount was increased from 19–24% to 33.6–41.6% as pH value increased from 0.2 up to 2 for U(VI) and increased from 5–6.9% to 94–99.6% by rising pH value from 0.05 up to 1.3 for Th(IV). This behavior can be discussed on the light of the exchangeable properties of hydrogen ions and their effect on the solubility equilibria. At low pH value, hydrogen ions compete for the available active sites on sorbent surface protonating their function groups and this neg-

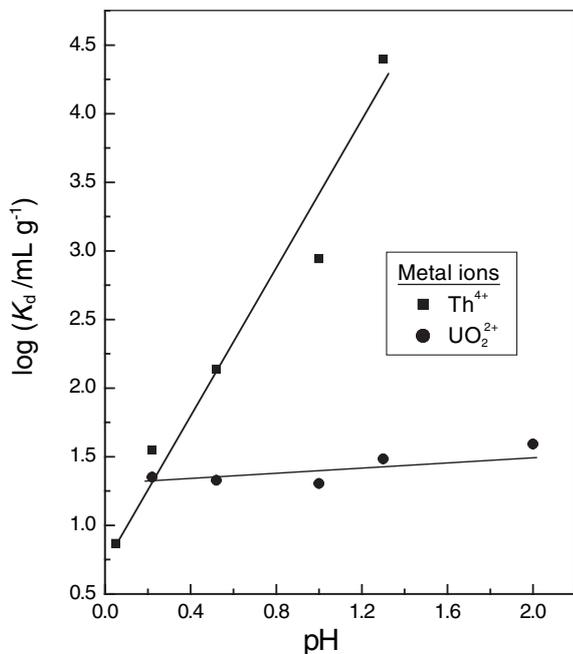
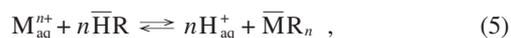


Figure 6. Variation of $\log K_d$ versus pH for sorption of UO_2^{2+} and Th^{4+} from aqueous solution on CAS impregnated with succinic acid.

atively affects the sorption of both U(VI) and Th(IV) where the electrostatic interactions would be electrically unfavorable. Also, acidification with HNO_3 forms the neutral nitrate salts $\text{UO}_2(\text{NO}_3)_2$ and $\text{Th}(\text{NO}_3)_4$ that expected to be the likely predominating species in this acidic range. The absence of electrical charge at the surface of these neutral species and hence the surface inactivity may be a reasonable proof for the observed decrease in sorption extent at low pH range. The loose contact of both analytes on the sorbent surface was probably an acceptable reason for the effective regeneration of these analytes using acidic eluents. As pH increase, hydrolysis was occurred and different proportions of several hydrolyzed species are formed changing the net charge at the interface between the working solution and the applied sorbents surfaces. It was identified that the hydrolyzed ionic species of U(VI) have the forms $\text{UO}_2(\text{OH})^+$, $[(\text{UO}_2)_2(\text{OH})_2]^{2+}$, and $[(\text{UO}_2)_3(\text{OH})_5]^{3+}$.²⁷ The species $[\text{Th}(\text{OH})]^{3+}$, $[\text{Th}(\text{OH})_2]^{2+}$, $[\text{Th}_2(\text{OH})_2]^{6+}$, $[\text{Th}_4(\text{OH})_8]^{8+}$, and finally $[\text{Th}_6(\text{OH})_{15}]^{9+}$ were reported as hydrolyzed thorium species.²⁸ These hydrolyzed species exhibit an overall positive charge, therefore their surface interactions with CAS would be electrically attractive. This may explain the gradual increase in sorption of these cationic species with increasing pH up to 2 and 1.3 for U(VI) and Th(IV), respectively.

The interaction of the hydrolyzed species of uranyl and thorium ions with CAS sorbent is more complex where the different species interact with the sorbent surface through different mechanisms and are substantially different in their affinities. The mechanism considered to predominate the sorption behavior of the studied metal ions can be explained on the light of ion exchange process between metal ion and the weakly acidic functional groups in the sorbent surface. It is likely that carboxylic groups are largely responsible for such ion exchange interactions. Therefore, the cation exchange process between a metal ion M^{n+} and a proton in a dilute aqueous solution, activity coefficient ~ 1 , could be described by the following equilibrium reaction:



where $\text{M}_{\text{aq}}^{n+}$ is the cation exchanged in solution and the superscript bar denotes the exchanger phase. The equilibrium constant for such reactions is given by the following equation:

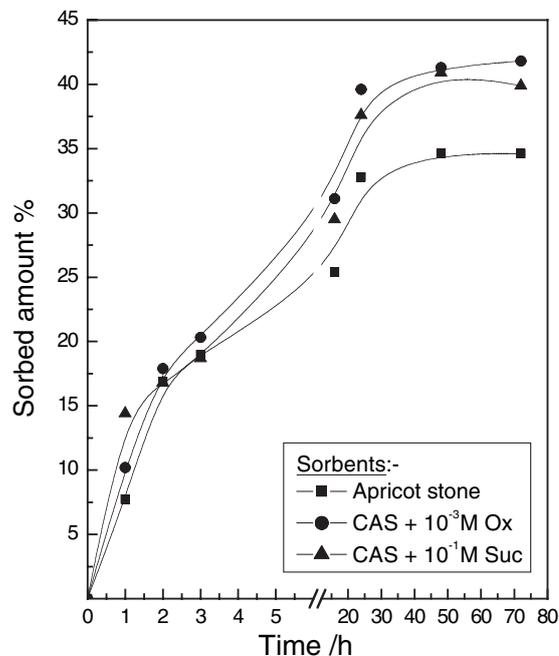


Figure 7. Effect of contact time on sorption of UO_2^{2+} from HNO_3 solution on different apricot stone sorbents ($V/m=100$, $\text{pH}=-2$, $\text{temp.}=26 \pm 2^\circ\text{C}$).

$$K_{\text{H}}^{\text{M}} = \frac{[\text{H}_{\text{aq}}^+]^n [\overline{\text{MR}}_n]}{[\overline{\text{HR}}]^n [\text{M}_{\text{aq}}^{n+}]}, \quad (6)$$

where $[\overline{\text{MR}}_n]$ and $[\overline{\text{HR}}]^n$ are the concentration of M^{n+} and H^+ ions in sorbent surface, $[\text{H}_{\text{aq}}^+]^n$ and $[\text{M}_{\text{aq}}^{n+}]$ are their concentrations in aqueous solution. At equilibrium, the distribution coefficient (K_d) is given by the equation:

$$\log K_d = C + n\text{pH}. \quad (7)$$

Plotting $\log K_d$ values of $n+$ valent metal ion against pH values of aqueous solution should give a straight line of slope (n) which equals to the charge on the metal ion, if the sorption is a pure ion exchange process. The variation of $\log K_d$ values for UO_2^{2+} and Th^{4+} ions against pH of the aqueous solution is clarified in Figure 6. The plots show linear relations with slopes equal to 0.14 and 2.36 for sorption of U(VI) and Th(IV) on CAS anchored with succinic acid. The slope values 0.13 and 2.12 were obtained for sorption of U(VI) and Th(IV) on CAS anchored with oxalic acid, respectively. This behavior represents a deviation from ideal sorption and thus the mechanism is not pure ion exchange. The non-ideality may be due to the presence of other mechanisms besides the ion exchange mechanism such as specific complexation and/or coulombic interactions. This is due to the complexity of systems involving sorption onto natural sorbents where there is a possibility of sharing of more than one mechanism in the sorption process.

3.3.2. Contact time effect. The changes in sorption of U(VI) and Th(IV) onto free and impregnated CAS as a function of time at a solution pH about 2 and 1.3 for U(VI) and Th(IV) are represented in Figures 7 and 8. The figures show that the sorption percentage generally increases with elapsed time till reaching equilibrium where the sorbed amount of U(VI) attains values ranged from 34% up to 42% after elapsing 24 h while the sorption equilibrium was reached very fast for Th(IV) and took only about 40 min to achieve values of the range 92–100%. On the light of these data, the sorbed amount of tetravalent thorium is greatly high comparing to that of uranyl ions, and this can be explained on the basis of increasing the electrostatic interactions between the analyte species and impregnant groups with increasing the cationic charge of the analyte.²⁹ In addition, the steric hindrance of the oxygenated U(VI) ions has a negative contribution to their sorption extent.

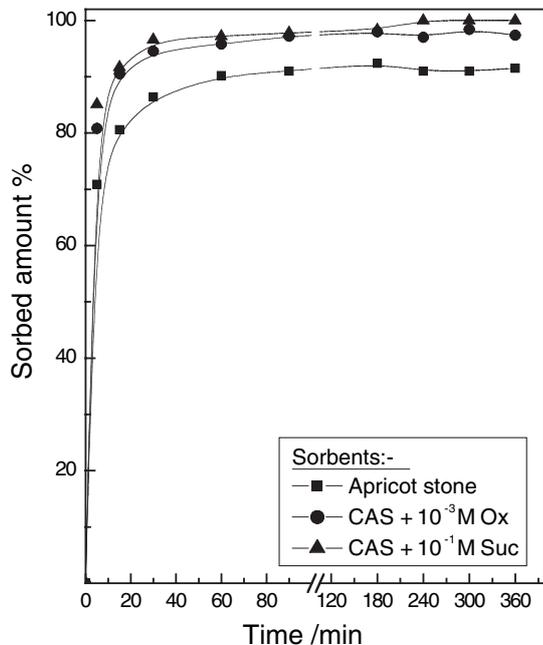


Figure 8. Effect of contact time on sorption of Th^{4+} from HNO_3 aqueous solution on different apricot stone sorbents ($V/m=100$, $\text{pH} \approx 1.3$, $\text{temp.} = 26 \pm 2^\circ\text{C}$).

3.3.3. Reproducibility. The distribution coefficient (K_d) for sorption of $\text{Th}(\text{IV})$ on CAS, oxalic anchored CAS, and succinic anchored CAS achieves the values 1927, 3550, and 12066 mL g^{-1} , respectively while $\text{U}(\text{VI})$ ions attain the values 1007, 2718, and 1450 mL g^{-1} for their sorption onto the same sorbents. The reproducibility of the distribution of $\text{U}(\text{VI})$ and $\text{Th}(\text{IV})$ onto CAS anchored with oxalic and succinic acids was clarified by performing four parallel series of batch experiments. The standard deviation for a single distribution coefficient determination (ΔK_d) was calculated using the following relation.³⁰

$$\Delta K_d = \sqrt{\frac{\sum(K_{di} - K_d)^2}{n-1}}, \quad (8)$$

where K_{di} is the distribution coefficient for an experiment, K_d is the mean value of distribution coefficients for all experiments.

$$K_d = \frac{K_{d1} + K_{d2} + K_{d3} + \dots}{n}, \quad (9)$$

where n is the number of experiments carried out under the same experimental conditions.

The sorption of $\text{U}(\text{VI})$ and $\text{Th}(\text{IV})$ onto CAS impregnated with oxalic and succinic acids was classified into four categories of experiments. Each set was performed four times and one of the data revealed is represented in Table 2. The standard deviation for a single distribution coefficient determination (ΔK_d) for sorption of $\text{U}(\text{VI})$ on CAS anchored with oxalic and succinic acids are 0.56 and 3.7% while that for sorption of $\text{Th}(\text{IV})$ are 1.98 and 0.85%, respectively. The obtained data show that ΔK_d does not exceed 3.7% for any working system of the studied

TABLE 2: The standard deviation for a single distribution coefficient determination (ΔK_d) for sorption of $\text{U}(\text{VI})$ on CAS anchored with oxalic acid

Experiment No.	K_{di}	$K_d - K_{di}$	$(K_d - K_{di})^2$	ΔK_d
1	2733	-15	225	15.25 $\pm 0.56\%$
2	2698	20	400	
3	2715	3	9	
4	2726	-8	64	

$K_d = 2718$

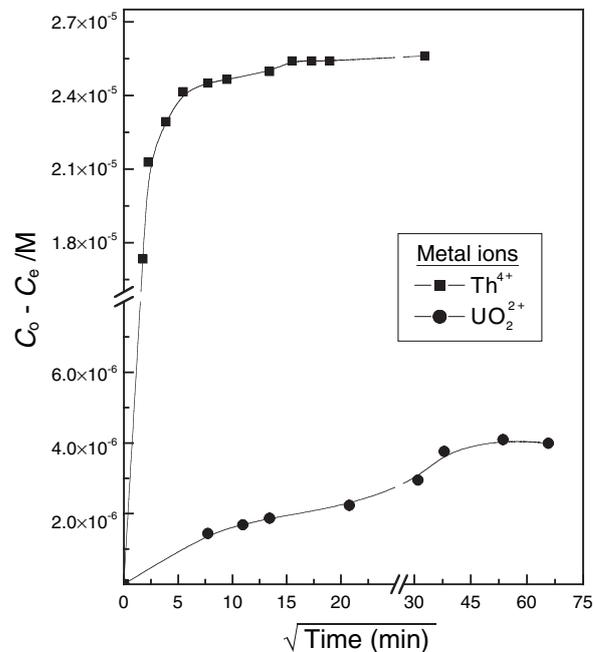


Figure 9. The rate of UO_2^{2+} and Th^{4+} ions sorption from solution on CAS impregnated with succinic acid.

ones and the values of deviation between the repeated experiments, under the same conditions, confirm the reproducibility of the revealed results. Hence, the change in behavior of the different impregnated CAS could not be attributed to the intrinsic irreproducibility of these raw materials but may be implied to the role played with the applied impregnants.

3.4. Sorption kinetics. The process of mass transfer associated with sorption of metal ions from aqueous solution by porous sorbents occurs via three consecutive steps of bulk, film, and intraparticle transport and the predominant rate of sorption is determined by one of these steps. To determine which of these processes is the rate controlling step, the sorption data were plotted as a function of the square root of contact time, Figure 9. The plots clarify that the initial sorption step is relatively high for $\text{Th}(\text{IV})$ ions where more than 85% are already sorbed within 10 min, while the rate of $\text{U}(\text{VI})$ sorption is relatively low. Also, the figure implies two distinguishable sorption stages. The first one may be related to the sorption of metal ions, at phase boundaries, to sorbent surface while that remaining in bulk solution are directed to sorbent-liquid interface under the influence of concentration gradient forces.³¹ At the second stage, the sorbed molecules diffuse into the pores of sorbent surface.

From a diffusion point of view, these multistage sorption processes reflect that the rate of sorption of both ions is not purely controlled by a certain one diffusion mechanism where external mass transfer and intraparticle diffusions are sharing in the rate controlling step. The relative sorption rate constant (K_{rel} , $\text{mg g}^{-1} \text{min}^{-0.5}$), that is characteristic to the rate of sorption under the working conditions, was graphically determined from the plots given in Figure 9 and found to have the values 8.03×10^{-6} and $4.67 \times 10^{-8} \text{ mg g}^{-1} \text{min}^{-0.5}$ for $\text{Th}(\text{IV})$ and $\text{U}(\text{VI})$, respectively. This significant difference in the rate values indicates that different interaction mechanisms are taking place between the two ions and the sorbent surface during sorption process. The rapid rate of sorption of $\text{Th}(\text{IV})$ may be ascribed to that the anchored sorbents have high retainability to $\text{Th}(\text{IV})$ ions that easily sorbed and quickly diffused into the pores of sorbent, and thus sorption of $\text{Th}(\text{IV})$ is suggested to be controlled by their transport from bulk solution to sorbent surface. On other hand, the low rate of $\text{U}(\text{VI})$ sorption can be considered as an indication that intraparticle diffusion, i.e. transport

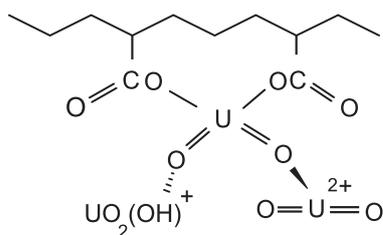
TABLE 3: Sorption capacities of impregnated CAS sorbents for U(VI) and Th (IV)

Metal ion	Sorption capacity /mg g ⁻¹	
	Oxalic acid impregnated CAS	Succinic acid impregnated CAS
U(VI)	2.39	2.30
Th (IV)	8.47	9.18

of metal ions from the exterior surface of sorbent to the interior sites is possibly the sorption rate controlling step.

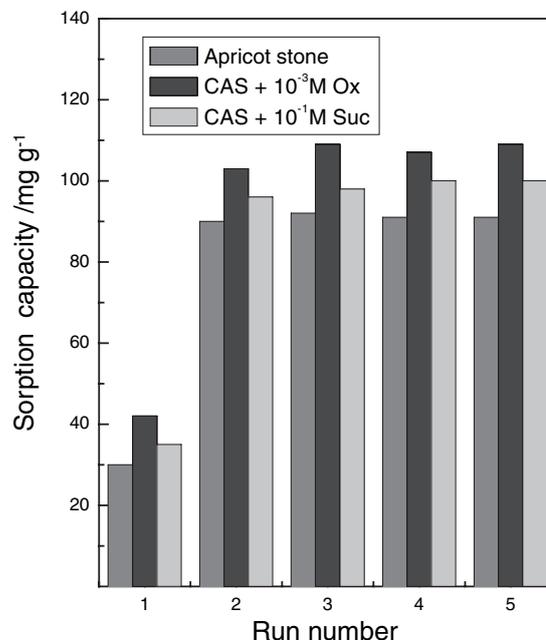
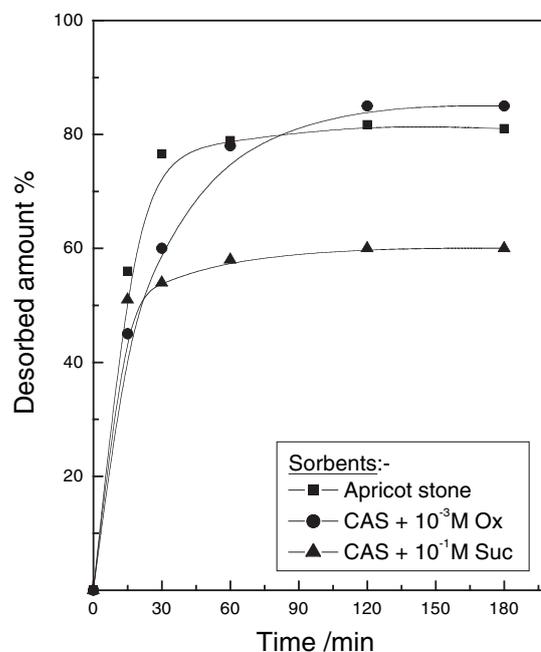
3.5. Sorption capacity. The metal sorption capacity of anchored CAS sorbent for the analytes of interest was individually determined via batch operation mode and data are given in Table 3. The data clarifies that impregnated CAS exhibited a higher sorption affinity to Th(IV) rather than for U(VI). Comparing with other reported data, the capacity of carboxylic acids impregnated CAS is higher than that of 5,7-dichloroquinoline-8-ol supported on naphthalene (1.88 mg g⁻¹)³² and similar to that of benzophenone supported on poly acrylonitrile (2.34 mg g⁻¹).³³ Other compounds as diarylazobisphenol modified activated carbon²⁴ and Amberlite XAD4 functionalized with succinic acid¹² were reported to have higher sorption capacity values. The high sorption capacities of such compounds for U(VI) may be referred to the technique applied to impregnate the solid support with the chelate.

One of the promising findings noticed in the successive sorption of uranyl ions on the applied anchored sorbents is the great enhancement in sorption extent during reloading processes. It was found out that, uranyl ions were weakly sorbed in the first run where their sorbed amount reached only about 39%. By subjection in consecutive runs, the sorbed amount was highly promoted to 96% and the sorbent retainability still constant up to five runs, Figure 10. This promotion, in sorption extent, may be referred to that the firstly sorbed uranyl ions may serve as a surface moderator for the further sorption runs. This modification can be highlighted through the following proposed sorption scheme.



Uranyl ions seem to behave as rather like divalent and accordingly they readily form complexes with O-donor ligands. Due to the presence of empty f-orbitals, the O=U=O groups are linear in all cases and coordination of a further 4, 5, and 6 ligands is possible in equatorial plane.³⁴ These ligands laying the plane may be neutral molecules or bidentate anions. Since there are empty f-orbitals and lone pairs of electrons in oxygen atoms of uranyl molecules, these pairs can be donated to form a shared bond between the sorbed uranyl ions and other free species in bulk solution. Hence, this type of surface complexation or chelation interactions probable plays an important role in increasing the sorbed amount in the consecutive runs. Also considering the former scheme, one can expect a formation of hydrogen bonding, between H-atom in the hydrolyzed species and O-atom in uranyl molecules, would occur and this increase the contribution of hydrogen bonding in enhancing the sorption extent.

3.6. Desorption studies. The recovery of U(VI) and Th(IV) from loaded sorbents was checked using distilled water and different concentrations of nitric acid as eluants and data obtained are given in Figures 11, 12, and 13. The desorption of

**Figure 10.** Comparison of sorption capacity of different apricot stone sorbents for UO₂²⁺ ions.**Figure 11.** Desorption of Th⁴⁺ from different loaded apricot stone sorbents using 0.5 M HNO₃.

loaded thorium ions from CAS was very fast with using 0.5 M HNO₃ as an eluant and it took only about 1 h to reach equilibrium, Figure 11. In contrast, H₂O slightly eluted Th(IV) ions from the applied solid matrix, Figure 12. The description of desorption behavior of U(VI) ions is depicted in Figure 13. The plots show that U(VI) is highly eluted with using 1 M nitric acid and equilibrium was achieved after 24 h of contact. These performances reflect the potential recovery of the studied analytes using acidic eluants and verify the reusability of the proposed CAS sorbent.

4. Conclusion

Carbonized apricot stone (CAS) anchored with oxalic and succinic acids is effectively used as a sorbent for preconcentration of U(VI) and Th(IV) from slightly acidic aqueous solutions. The analytical data confirm that the sorption of both analytes increases with rising pH value of the aqueous solution

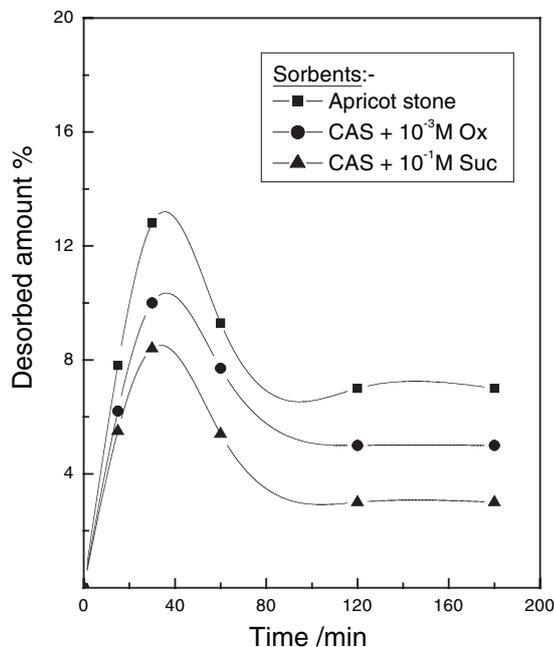


Figure 12. Desorption of Th^{4+} from different loaded apricot stone sorbents using H_2O .

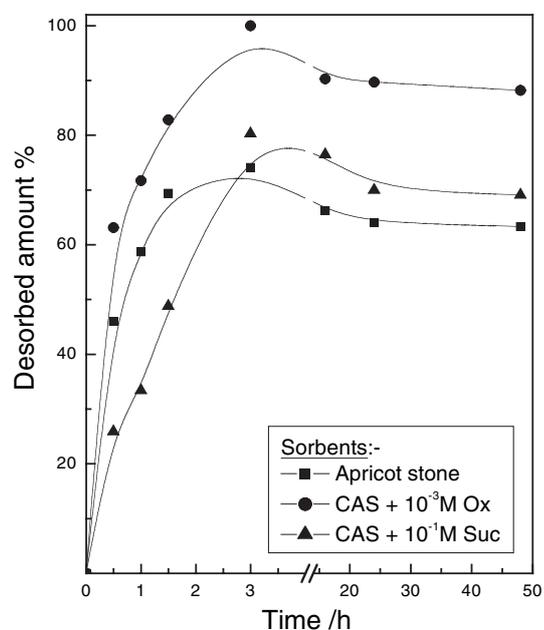


Figure 13. Desorption of UO_2^{2+} from different loaded apricot stone sorbents using 1 M HNO_3 .

and a quantitative preconcentration achieved at $\text{pH} \sim 2$ for U(VI) and ~ 1.3 for Th(IV) . The values of deviation between the repeated experiments under same conditions confirm the reproducibility of the obtained results and the change in behavior of the different impregnated CAS could not be attributed to the intrinsic irreproducibility of these row materials. The sorption of Th(IV) is probably controlled by their transport from bulk solution to sorbent surface while intraparticle diffusion could be considered as the rate controlling step in U(VI) sorption. The produced CAS sorbent has better metal sorption capacity and exhibits a new dimension for actinides separation from acidic waste solutions. It provides a novel and economical solid matrix appears promising for a number of industrial applications. The sorption performance highlights better reliability and reproducibility of the sorbent matrix even up five cycles of consecutive usage. Desorption of loaded uranium ions was effectively achieved using 1 M HNO_3 while only 0.5 M HNO_3 was recommended to release retained thorium ions.

References

- (1) W. W. Schulz and D. J. Navratil, *Sep. Sci. Tech.* **19**, 927 (1984).
- (2) R. J. Ferraro, A. W. Herlinga, and R. Chiariza, *Sol. Extr. Ion Exch.* **16**, 775 (1998).
- (3) R. Chiarizia, E. R. Barrans, R.J. Ferraro, and R. D. McAlister, *Sep. Sci. Tech.* **36**, 687 (2001).
- (4) T. Prasada Rao and J. M. Gladis, *Rev. Anal. Chem.* **20**, 145 (2001).
- (5) T. Prasada Rao and C. R. Preetha, *Sep. Purif. Rev.* **32**, 1 (2003).
- (6) V. Camel, *Spectrochim. Acta Part B* **58**, 1177 (2003).
- (7) N. Masque, R. M. Marce, and F. Borull, *Trends. Anal. Chem.* **17**, 384 (1998).
- (8) C. R. Preetha, J. M. Gladis, and T. Prasada Rao, *Talanta* **58**, 701 (2002).
- (9) C. Kantipuly, S. Katragadda, A. Chow, and H. D. Gesser, *Talanta* **37**, 491 (1990).
- (10) A. Agarwal, K. K. Sahu, and J. P. Rawat, *Solvent Extr. Ion Exch.* **21**, 763 (2003).
- (11) J. Mary Gladis and T. Prasada Rao, *Anal. Bioanal. Chem.* **373**, 867 (2002).
- (12) P. Metilda, K. Sanghamitra, J. M. Gladis, G. R. K. Naidu, and T. Prasada Rao, *Talanta* **65**, 192 (2005).
- (13) M. Pesavento, R. Biesuz, and G. Alberti, *Anal. Bioanal. Chem.* **376**, 1023 (2003).
- (14) S. Katragadda, H.D. Gesser, and A. Chow, *Talanta* **44**, 1865 (1997).
- (15) D. Prabhakaran and M. S. Subramanian, *Talanta* **65**, 179 (2005).
- (16) S. Deng and R. Bai, *Water Res.* **38**, 2423 (2004).
- (17) N. L. Dias Filho, W. L. Polito, and Y. Gushikem, *Talanta* **42**, 1031 (1995).
- (18) Z. Hongxia, X. Yongxin, and T. Zuyi, *Collids Surf. A* **252**, 1 (2005).
- (19) S. Kesraoul-Ouke, C. Cheeseman, and R. Perry, *Environ. Sci. Technol.* **27**, 1108 (1993).
- (20) N. Belacy and H. H. Sameda, *J. Radional. Nucl. Chem.* **219**, 55 (1997).
- (21) H. H. Sameda, M. R. Ezz El-Din, R. R. Sheha, and H. A. El-Naggar, *J. Radioanal. Nucl. Chem.* **254**, 373 (2002).
- (22) R. R. Sheha, Ph. D Thesis, Faculty of Science, Ain Shams University, Egypt (2001).
- (23) M. C. Hennion, *J. Chromatogr. A* **856**, 3 (1999).
- (24) A. M. Starvin and T. Prasada Rao, *Talanta* **63**, 225 (2004).
- (25) K. B. Yatsimirskii and Yu. A. Zhuukov, *Zh. Neorg. Khim.* **7**, 818, 1463 (1962).
- (26) A. I. Moskvina and L. N. Essen, *Zh. Neorg. Khim.* **12**, 359 (1967).
- (27) *Gmelin Handbook of Inorganic Chemistry*, U Supplement, Vol. DI, Springer-Verlag, Berlin (1984).
- (28) C. F. Baes Jr, N. J. Meyer, and C. E. Roberts, *Inorg. Chem.* **4**, 518 (1965).
- (29) A. Clearfield, *Inorganic Ion Exchange Materials*, CRC Press, Boca Raton, FL (1982).
- (30) K. Eckschlager, *Errors, Measurements and results in chemical analysis*, Van Nostrand Reinhold Company, London (1969).
- (31) G. McKay, *J. Chem. Tech. Biotechnol.* **33(A)**, 196 (1984).
- (32) J. Mary Gladis and T. Prasada Rao, *Anal.* **35**, 501 (2002).
- (33) C. R. Preetha and T. Prasada Rao, *Radio. Chim. Acta* **91**, 247 (2003).
- (34) N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, 2nd Edition, Pergamon Press PLC (1997).