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Abstract

To separate Zr(IV) and Hf(IV) in acidic solution, several silica-based macroporous adsorbents were synthesized. Their adsorption selectivity for Zr(IV) and Hf(IV) in HCl solution was investigated, and the TODGA adsorbent exhibited the largest adsorption difference for the two elements. Batch experiments were conducted to study the effects of acid type, HCl concentration, and temperature on the adsorption behavior of Zr(IV) and Hf(IV) onto the TODGA adsorbent. It was found that H+ exerted a quite strong influence on the adsorption capacity of Zr(IV) and Hf(IV). Isotherm fitting showed that the Langmuir model agrees well with the experimental data. The thermodynamic parameters indicate that the adsorption processes for both elements are endothermic reactions. The TODGA adsorbent demonstrated higher adsorption selectivity for Zr(IV) over Hf(IV) and shows promise for their mutual separation.

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Preamble

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Adsorption behavior of Zr(IV) and Hf(IV) on a silica-based macroporous TODGA adsorbent

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Abstract: In order to separate Zr(IV) and Hf(IV) in acidic solution, several kinds of silica-based macroporous adsorbents were synthesized. Their adsorption selectivity for Zr(IV) and Hf(IV) in HCl solution was investigated, and the

TODGA adsorbent for the two elements had the largest adsorption difference. The effects of acid type, HCl concentration, and temperature on the adsorption behavior of Zr(IV) and Hf(IV) onto the TODGA adsorbent were conducted by batch experiments. It was found that H+ exhibited a quite strong influence on adsorption capacity of Zr(IV) and Hf(IV). Isotherm fitting showed that the Langmuir model agrees well with the experimental data. The thermodynamic parameters indicate that the adsorption processes for both elements are endothermic reactions. The TODGA adsorbent had the higher adsorption selectivity for Zr(IV) over Hf(IV) and could be promising for their mutual separation.

Key words: Zirconium, Hafnium, TODGA/SiO2-P, Adsorption characteristics, Selective separation

Introduction

Zirconium and hafnium, a pair of co-existing elements, are commonly used as engineering materials in nuclear industry for their specific nuclear properties. Zircaloy is generally used as structural components in reactor cores for its low thermal neutron capture cross-section, whereas hafnium alloy has been employed as controlling materials because of its 640 times higher neutron adsorption cross-section. The hafnium ratio in zirconium has a direct effect on the safety and efficiency of the reactor cores. Therefore, the nuclear grade zirconium sponge requires to contain hafnium of less than 100 ppm[1,2]. However, as brother symbiosis of the same subgroup, their chemical similarity is greater than that of any other two elements in the periodic table (atomic radius: Zr=0.145 nm, Hf=0.144 nm; ionic radius: Zr(IV)=0.074 nm, Hf(IV)=0.075 nm)[3]. The mutual separation of Zr and Hf is recently of intriguing interest in the area of nuclear industry.

Numerous processes for separating zirconium and hafnium have been conducted, and there are only three established technologies in industrial scale, i.e., the multiple crystallization of potassium zirconium fluoride, the solvent extraction using methyl isobutyl ketone (MIBK) or tributyl phosphate (TBP) or tri-n-octylamine (TOA) and the extractive distillation of the chlorides[4–6]. There are still many problems inherent inextricable in these processes, such as emulsification, flooding and loading limits, sophisticated technologies, phase disengagement, and large solvent consumption[7]. Recently, increasing environmental concern and energy consumption lead to the search for a new effective separation process.

One of the most efficient methods is the adsorption and separation based on solid phase, for example, the organic (synthetic/natural) or inorganic adsorbents can be treated as extraction chromatography[8]. In extraction chromatography, an inert support either alone or in combination with a suitable diluent is impregnated with an organic extractant, producing a solid sorbent capable of selectively removing certain metal ions. In brief, the extraction chromatography combines solvent extraction process with the simplicity and the selectivity of multistage character of the column chromatographic system, so it has some attractive advantages such as minimal organic solvent utilization, less waste accumulation, compact equipment, simple operation and simultaneous separation of multi-components. Hence, as an alternative separation method, the extraction chromatography used for separation of zirconium and hafnium is desirable[9,10].

An ideal extractant in separation process should consist only of C, H, O, and N atoms rather than S or P atoms to make them combustible to gaseous products after utilization. In recent years, a chelating agent, N, N, N , N -tetraoctyl-3-oxapentane-1,5-diamide (TODGA) containing no S or P atoms is attracting extensive attentions as a promising extractant to separate high-valence metal ions. There have been many reports on its systematic adsorption ability to various elements[11–16]. A. Sh. Saleh et al. investigated the extraction behaviors of zirconium and hafnium by TODGA, the effective extraction from HNO3 $\geq$ 3 mol/L[17]. Also, several other extractants abbreviated as BTP, Calix[4]arene-R14 and HDEHP were extensively used to separate Zr and Hf[18–20]. The present work mainly deals with preparing a silica-based macroporous TODGA adsorbent, exploring the optimum adsorption condition and mechanism of Zr(IV) and Hf(IV) from HCl solution.

2.1 Materials

A neutral chelating agent, TODGA (more than 96.5% purity), was used without further purification, along with BTP, Calix-arene-R14, and HDEHP (Kanto Chemical Co. Inc.). The silica-based polymer support (SiO2-P) was synthesized as described previously[21]. The symbol (P) contained in the SiO2-P particles refers to copolymer prepared by means of a polymerization reaction inside the macroporous SiO2 substrate. The Zr(IV) and Hf(IV) standard solutions (1000 $\mathrm{mg \cdot L^{-1}}$) were from Alfa Aesar. Zirconium oxychloride ($ZrOCl_2 \cdot H_2O$, 99.8%) and hafnium tetrachloride ($HfCl_4$, 99.9%) were from J&K Scientific Ltd. Dichloromethane, dodecyl-benzenesulfonic acid, methanol, HCl, and NaOH (SDB) standard solutions and other chemicals were all analytical reagent (Sinopharm Chemical Reagent Co. Ltd.). The distilled water was further purified using a Milli-Q (Millipore) system (18-MΩ resistance) and used throughout the experiments.

2.2 Preparation of Adsorbents

In order to improve affinity between SiO2-P particles and extractant, the SiO2-P particles were activated by methanol as follows. The SiO2-P particles were mechanically mixed with methanol in a conical flask for about 1 h at 20 r/min, and separated using a sintering glass filter of 0.45 m pore. The similar operation was repeated three times. The activated SiO2-P particles were dried in a vacuum oven at around 313 K for 12 h.

The TODGA/SiO2-P adsorbent was synthesized as follows. The weighted quantity of extractant was dissolved completely in dichloromethane (200 mL) and double the amount of activated SiO2-P particles were weighed accurately, mixed into a conical flask (300 mL), and stirred mechanically for 120 min at room temperature. For Calix[4]arene-R14 adsorbent, proportional dodecyl benzene sulphonic acid was simultaneously added as a molecule modifier. Then the mixture was moved subsequently into a silicon-oil bath and further stirred at about 313 K for 120 min to impregnate and immobilize TODGA molecules into the pores of the SiO2-P particles. The operation temperature in the synthesis process was kept using an EYELA OHB-2000 Model temperature controller (Tokyo Rikakikai Co. Ltd., Japan). The impregnation process was continued until almost all organic solvent (i.e., dichloromethane) was evaporated. Following drying in a vacuum drying oven at around 313 K overnight, light yellow macroporous silica-based polymeric composite was obtained.

Thermal stability of the adsorbent was evaluated by a thermal gravimetry analyzer (Shimadzu T-60) at temperature range from 30–600°C with a heating rate of $2°\mathrm{C} \cdot \mathrm{min}^{-1}$ under oxygen atmosphere.

2.3 Batch Adsorption Experiments

The adsorption evaluation of the adsorbent was conducted using a thermostatic water bath shaker in a wide range of acidity, metallic ion concentration, and temperature. All solutions used for adsorption were freshly prepared because both Zr(IV) and Hf(IV) metal ions are apt to hydrolyze and polymerize. The concentration of mineral acids in aqueous phase was investigated in the range of 0.1–8.0 mol/L and the operation temperature was controlled in the range of 298 K–323 K. The phase ratio was 0.05 g of adsorbent to 5 cm^3 of solution. A weighed quantity of adsorbent was put into a 10 cm^3 glass flask with 5 cm^3 solution described above, then the mixture was shaken at 120 r/min for determined contact time under given temperature. After phase separation through a membrane filter with a mean pore of 0.45 µm, the concentrations of Zr(IV) and Hf(IV) metal ions before and after adsorption in aqueous phase were determined utilizing an ICP-AES instrument (Shimadzu ICP-7510). The equilibrium adsorption capacity (Qe, mmol/g), distribution coefficient (Kd, cm^3/g), and separation factor (SF) were calculated as follows:

$$K_d = \frac{(C_0 - C_e) \cdot V}{C_e \cdot m}$$

$$SF = \frac{K_d^{Zr}}{K_d^{Hf}}$$

where C_0 and C_e denote the initial and equilibrium concentrations in aqueous phase (mg/L); M means the molar mass of Zr and Hf; m represents the mass of adsorbent (g); V (cm^3) is the volume of the aqueous phase used in the experiment.

3.1 Screening of Adsorbents

In order to choose the optimum adsorbent to separate Zr(IV) and Hf(IV), adsorption selectivity with different adsorbents was firstly investigated in batch experiments under the same metal ion concentration in HCl solution. Fig. 1 shows the variation in distribution coefficient and separation factor of Zr(IV) and Hf(IV) with different adsorbents. The results indicated that the TODGA adsorbent had the largest SF between Zr(IV) and Hf(IV), though the HDEHP adsorbent had the maximal adsorption capacity. As a result, the TODGA adsorbent was chosen as the candidate adsorbent in the next experiments for its excellent separation performance and environmental friendliness.

[Figure 1: see original paper] Kd and SF of Zr(IV) and Hf(IV) in HCl solution with different adsorbents. V/m: 100 cm^3/g; [Metal]: 2.5 mmol/L; [HCl]: 1 mol/L; 303 K; Speed: 120 r/min; Contact time: 12 h.

3.2 Characterization of Adsorbents

The microscopic images are shown in Fig. 2. Scanning electron microscopy (SEM) images revealed the porous structure of the SiO2-P support and the TODGA/SiO2-P adsorbent, with the upper panel showing the interior of SiO2-P and the lower panel showing the TODGA/SiO2-P composite.

[Figure 2: see original paper] SEM images of porous SiO2-P support and TODGA/SiO2-P adsorbent (upper: SiO2 inner, lower: TODGA/SiO2-P).

The TG–DTA curves for TODGA/SiO2-P indicated obvious weight losses at about 300°C due to thermal decomposition of the styrene-divinylbenzene (SDB) copolymer, which corresponds to the letter 'P' in SiO2-P. The overall weight loss of SiO2-P was estimated to be 16.9%, indicating that 16.9 wt% SDB had been polymerized inside the SiO2 substrate. For TODGA/SiO2-P, the TG curve showed two weight loss peaks at around 200°C and 300°C, indicating that TODGA mainly decomposed at about 200°C. Based on the TG-DTA analysis, the composition of TODGA/SiO2-P adsorbent was determined as: TODGA 33.1 wt%, SDB 11.3 wt%, and SiO2 55.6 wt%. Generally, the adsorption capacity of adsorbents increases with the TODGA content inside SiO2-P particles. However, it was observed that when the impregnated content of TODGA exceeded 33.3%, redundant TODGA molecules could not enter the pores of the SiO2-P particles and only adhered to the particle surface[22], as shown in Fig. 3. The physical and chemical parameters of SiO2-P and TODGA/SiO2-P are listed in Table 1.

[Figure 3: see original paper] TG/DTA curves of SiO2-P (A) and TODGA/SiO2-P (B) under oxygen atmosphere.

The physical and chemical parameters of TODGA/SiO2-P adsorbent

Physical parameters of SiO2-P	
Mean pore size	50 nm
Bead diameter	40–60 µm
Specific surface area	80 m^2/g
Pore volume	1.0 cm^3/g
SDB inside SiO2-P support	16.9 wt%

Chemical component of TODGA/SiO2-P	
SiO2	55.6 wt%
SDB	11.3 wt%
TODGA	33.1 wt%

3.3 Effects of Acid Variety and Concentration on Kd

Generally, the extraction mechanism of TODGA as a neutral chelating agent for metallic ions is direct and uncomplicated. According to Hecke and Goethals' report, the diglycolamide (DGA) moiety in the TODGA chelating agent contains three oxygen atoms that vigorously capture metallic ions, acting as a tridentate ligand[23]. While various species such as M^{4+}, MO^{2+}, $[M(OH)]^{3+}$, $[M(OH)_2]^{2+}$, $[M(OH)_3]^{+}$, $[M(OH)_4]$, and $[M(OH)_5]^{-}$ may be formed since Zr(IV) and Hf(IV) are both hydrolysable and prone to polymerization in hydrochloric acid solutions (where M represents Zr or Hf)[24,25]. The aqueous chemistry of zirconium and hafnium has been the subject of much controversy, with several papers reporting on their aqueous solution chemistry and hydrolytic polymerization[26–29]. In order to estimate the optimum conditions for separation between Zr(IV) and Hf(IV), uptake experiments were carried out with three kinds of inorganic acids in the concentration range from 0.1 mol/L to 8 mol/L. Higher pH values were not examined due to precipitation of Zr(IV) and Hf(IV) at $pH > 2$[30].

The distribution coefficients of zirconium and hafnium as a function of acid concentration are shown in Fig. 4. The results demonstrate that the adsorption behavior is complex. The TODGA/SiO2-P adsorbent exhibited a larger separation factor in the chloride system than in the other two acid systems. This phenomenon may be explained by stronger complexation of zirconium and hafnium metallic ions with chloride ions at low acidities. Therefore, adsorption behaviors of the adsorbent in batch experiments were evaluated in hydrochloric acid solution.

[Figure 4: see original paper] Kd of Zr(IV) and Hf(IV) in different acid solutions with TODGA/SiO2-P adsorbent. V/m: 100 cm^3/g; [Metal]: 2.5 mmol/L; 298 K; Speed: 120 r/min; 24 h.

Combining X-ray absorption spectroscopy (XAFS) and nano-electrospray mass spectrometry (ESI-MS), Walther et al. investigated polynuclear species of zirconium in acidic aqueous solution at $0 < pH < 3$ for $[Zr] = 1.5$–10 mmol/L. While the monomer remained predominant, the formation of tetramers, pentamers, octamers, and larger polymers was observed with increasing pH[26]. Johnson et al. studied hydrolytic behaviors of ca. 0.05 mol/L Zr(IV) and Hf(IV) at acidities of 0.5–5 mol/L HCl[27]. As a conclusion, Hf(IV) was probably present as either a trimer or tetramer with relatively low degree of polymerization in the range of 0.5–2 mol/L HCl. While at acidities of 0.2 mol/L or lower, Hf(IV) was more highly polymerized and polydisperse. In the range of 0–2 mol/L HCl, polymerization of Zr(IV) was similar. The principal difference is that Zr(IV) was more highly aggregated than Hf(IV) at lower acidity.

As shown in Fig. 5, the adsorption of Zr(IV) and Hf(IV) onto TODGA/SiO2-P adsorbent showed similar trends, with the Kd value changing greatly in a parabolic manner with increasing HCl concentration from 0.1 to 6 mol/L. The maximum Kd value was obtained at about 0.8 mol/L and 0.5 mol/L HCl for Zr(IV) and Hf(IV), respectively. These results indicate that TODGA had relatively greater extracting ability for the trimer or tetramer species of Zr(IV) and Hf(IV) in HCl solution. At the same acidity, Zr(IV) had a higher Kd than Hf(IV), probably because Zr(IV) was more highly aggregated than Hf(IV) at lower acidities as mentioned above. Under higher pH conditions, increased polymerization and formation of tetramers, pentamers, octamers, and larger polymers decreased the extraction of hydrolyzed Zr(IV) and Hf(IV) species[26,27]. The drop in Kd for both elements at higher HCl concentration may be due to a higher degree of protonation of the extractant. On the other hand, it is also possible that high HCl concentration restricted hydrolysis, promoting polymerization of Zr(IV) and Hf(IV) metallic ions to form trimers or tetramers. The findings indicate that the TODGA/SiO2-P adsorbent has stronger adsorption and higher selectivity for Zr(IV) over Hf(IV), with maximum separation achieved at 0.8–1.5 mol/L HCl.

[Figure 5: see original paper] Effect of HCl concentration on SF. V/m: 100 cm^3/g; [Metal]: 2.5 mmol/L; 298 K; Speed: 120 r/min; 24 h.

3.4 Adsorption Isotherms

Adsorption isotherms were obtained within a wide range of initial total concentrations at two different temperatures, as shown in Fig. 6. The results demonstrate that the adsorbent had a larger adsorption capacity for Hf(IV) than Zr(IV) in single-component solutions, and that adsorption capacity for both ions increased with rising temperature.

[Figure 6: see original paper] Adsorption isotherms of Zr(IV) and Hf(IV) with TODGA/SiO2-P adsorbent. [HCl]: 1 mol/L; V/m: 100 cm^3/g; 24 h; Speed: 120 r/min.

To explore the adsorption mechanism and calculate the maximum capacity of the adsorbent after achieving adsorption saturation, theoretical isotherm models of Freundlich and Langmuir equations were adopted. The Langmuir equation assumes that the adsorption process is monolayer adsorption on a homogeneous surface, while the Freundlich equation is an empirical equation applied to monolayer adsorption on heterogeneous surfaces[31,32]. They are expressed as follows:

Langmuir equation:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{max}} + \frac{1}{K_L Q_{max}} \quad (7)$$

Freundlich equation:

$$Q_e = K_f C_e^{1/n} \quad (8)$$

where C_e ($\mathrm{mmol \cdot dm^{-3}}$) denotes the equilibrium concentrations of Zr and Hf in aqueous phase; Q_e ($\mathrm{mmol \cdot g^{-1}}$) and Q_{max} ($\mathrm{mmol \cdot g^{-1}}$) denote the adsorption amounts at equilibrium and at maximum adsorption capacity, respectively; K_L ($\mathrm{dm^3 \cdot mmol^{-1}}$) is the Langmuir constant related to the energy of adsorption; $1/n$ is the Freundlich exponent constant related to adsorption intensity; and K_f ($\mathrm{mmol \cdot g^{-1}}$) is the Freundlich constant.

Figs. 7A and 7B show the linearized Langmuir and Freundlich adsorption isotherms, respectively. The fitting parameters and correlation coefficients (R^2) are presented in Table 2. The better correlation coefficient (0.99) obtained from the Langmuir isotherm suggests that adsorption of Zr and Hf was monolayer adsorption controlled by homogeneous active sites on the adsorbent. Since K_L reflects the affinity between active sites and metallic ions, the gradual increase of K_L value in the Langmuir isotherm with temperature indicates positive activation energy. Meanwhile, we can conclude that Zr(IV) had stronger affinity than Hf(IV) to the TODGA/SiO2-P adsorbent.

[Figure 7: see original paper] Isotherm fitting for Zr and Hf adsorptions by (a) Langmuir model and (b) Freundlich model. V/m: 100 $\mathrm{cm^3/g}$; [HCl]: 1 mol/L; Speed: 120 r/min; 24 h.

Fitting parameters of isotherm for Zr and Hf adsorptions onto the TODGA/SiO2-P adsorbent

Metal	T (K)	Langmuir isotherm			Freundlich isotherm	
		Qmax (mmol/g)	kL (L/mmol)	R^2	Kf (mmol/g)	1/n
Zr	298	-	-	-	-	-
Zr	313	-	-	-	-	-
Hf	298	-	-	-	-	-
Hf	313	-	-	-	-	-

3.5 Adsorption Thermodynamics

The values of standard ΔH° and ΔS° for Zr and Hf in adsorption reactions were calculated from the slopes and intercepts of the linear van't Hoff equation, as shown in Fig. 8. The Gibbs free energy of adsorption, ΔG°, was calculated from:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (6)$$

[Figure 8: see original paper] Linear least square plots for obtaining thermodynamic parameters. V/m: 100 cm^3/g; [Metal]: 2.5 mmol/L; [HCl]: 1 mol/L; Speed: 120 r/min; 24 h.

The thermodynamic parameters are summarized in Table 3. Negative ΔG° values indicate that the adsorption processes occurred spontaneously. The positive enthalpy change values for both metallic ions indicate that adsorption of zirconium and hafnium are endothermic processes. This is notable because adsorption processes for some trivalent rare earths using this type of adsorbent are typically exothermic[29]. The system is complex, but one reasonable interpretation may be that raising temperature facilitates metal ion hydrolysis. Additionally, the data $|\Delta H^\circ| < |-T\Delta S^\circ|$ in Table 3 show that the adsorption processes were dominated by entropic changes rather than enthalpy changes. By comparing the enthalpy change values, it is obvious that temperature has a greater influence on the adsorption of Hf(IV) than on Zr(IV), which could be controlled to increase the adsorption difference for better separation.

Thermodynamic parameters of Zr and Hf adsorptions onto the TODGA/SiO2-P adsorbent

Parameter	Zr(IV)	Hf(IV)
ΔH° ($kJ \cdot mol^{-1}$)	-	-
ΔS° ($J \cdot mol^{-1} \cdot K^{-1}$)	-	-
ΔG° ($kJ \cdot mol^{-1}$)	-	-
TΔS° ($kJ \cdot mol^{-1}$)	-	-

4 Conclusion

Several kinds of macroporous silica-based adsorbents were synthesized, and the TODGA/SiO2-P adsorbent was found to have higher adsorption selectivity for Zr(IV) over Hf(IV). The adsorbent was characterized by means of SEM and TG-DTA. The uptake behaviors in three kinds of inorganic acid solutions were investigated, and the adsorption mechanism was attempted to be explained. By fitting different isotherm models and calculating thermodynamic parameters, the adsorption processes for both metals were found to be endothermic with monolayer adsorption on a homogeneous surface. The TODGA adsorbent could be promising for separation between Zr(IV) and Hf(IV) due to its good adsorptive selectivity in preliminary experiments.

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