Separation of Zirconium and Hafnium
from Chloride Solution Using Strongly Basic Anion Resins

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ABSTRACT: *The ion exchange process was employed to separate zirconium from hafnium in solution. To this end, four effective parameters, involving resin type, HCl concentration, Time, and initial zirconium concentration, were selected as the main variables. The sorption of zirconium and hafnium in the presence of six commercial macroporous anion exchangers of Dowex and Amberlite series and different HCl concentrations of 8-12 M were investigated. Furthermore, the distribution ratio, as a function of time in the range of 0.5-3 h and initial zirconium concentration of 500-3000 mg/L, were studied. The highest separation factor of 10.29 was obtained under equilibrium conditions in the presence of Amberlit CG-400II Ion Exchange Resin (IER) at a concentration of 9.5 M hydrochloric acid. Equilibrium isotherms of the system under optimized conditions were analyzed by Langmuir, Freundlich adsorption models. The experimental data are well-described by the Langmuir equation for both zirconium and hafnium.*

KEYWORDS: *Zirconium; Hafnium; Ion exchange; Strong Basic Anion Resin; Amberlite.*

INTRODUCTION

The primary source of zirconium mineral in nature is zircon (ZrSiO4), which is also the most abundant of this element [1]. zirconium (Zr) minerals naturally contain around 5% of hafnium (Hf), which makes it necessary to separate these elements [2, 3]. Furthermore, today the separation of zirconium and hafnium isotopes from the early actinides and rare earth elements, including yttrium and Neodymium, is of interest for isotope production [4, 5].

Hf and Zr are two of the most significant nuclear materials [6]. Zr is used in the nuclear industry owing to its excellent corrosion resistance and shallow neutron-capture cross-section (0.18 barns)[7]. Versus, Hf has a high neutron absorption cross-section (115.2 barns) and is used as a control material in water-cooled nuclear reactors [8].

Therefore, the quantity of Hf present in Zr has a direct effect on the efficiency of the reactor core. Moreover, the total content of Hf in the reactor core affects the reactor shutdown margin, a significant safety concern [9].

The chemical similarity of Zr and Hf, both in their metallic and compound states, is greater than that between any other homologous elements in the periodic table (the atomic and ionic radii of Zr and Hf are virtually identical;

atomic radius: Zr = 1 .45 Å, Hf = 1 .44 Å; ionic radius: Zr^{4+} = 0 .74 Å, Hf^{4+} = 0 .75 Å) [9-12]. Therefore, the Zr/Hf separation has acquired great importance.

Several ways such as ion exchange/sorption,[13-15] solvent extraction,-[16-18], reversed-phase liquid chromatography[19, 20], and biosorption [21] have been introduced to separate Zr from Hf present in different aqueous solutions.

The use of ion exchange in the separation process offers some advantages since it allows the recovery of ions from highly dilute solutions, where precipitation or solvent extraction would be unfavorable. It also has the capacity for treating large volumes of solutions [22]. Both cation and anion exchange resins have been used for the zirconium/hafnium separation.

The most often used are strong-base anion exchange resins, where zirconium is adsorbed in preference to hafnium from concentrated hydrochloric acid or dilute sulfuric acid solutions [23], and cation exchange resins where hafnium is preferentially adsorbed from diluted sulfuric acid solution [24, 25].

Lister has described the development of a cation-exchange process in which they effect the separation by taking advantage of the different complex-forming tendencies of the Hf and Zr ions with sulfuric acid. However, the overall throughput rate was too slow for industrial application[26].

Smolik et al. examined the sorption and separation behavior of Zr and Hf from sulfate solutions. Also they reported that it was possible to separate Zr and Hf using Diphonix ion-exchange resin containing diphosphonic, sulfonic, and carboxylic acid groups[12]. Mu. Naushad et al. studied the adsorption characteristic of modified Amberlite IRA-120 resin for removal of Co, and they were found that modified resin was found to be an excellent adsorbent for the removal of Co^{2+} ion from aqueous medium[27].

Chelex 100, a chelating resin, was found to be effective for the concentration of several γ-emitting fission-product radionuclides from seawater, as reported by Lai and Goya. The sorption behavior of Zr^{4+}, Nb^{5+}, Mo^{6+}, Tc^{7+}, Te^{4+}, and U^{6+} from acids solutions (HCl and H_2SO_4) on Chelex-100 has also been studied[28].

Research has shown that there is no systematic process to investigate the effect of main effective parameters on the separation of zirconium from hafnium. In addition,

type of resins, especially anionic resins have received less attention.

Therefore, in the present work, the effect of the HCl concentration and the initial Zr/Hf molar ratio on zirconium/hafnium separation in presence of different types of Dowex and Amberlite IERs, have been studied. We also examined the kinetics and adsorption equilibrium of metal with the best separator IER.

EXPERIMENTAL SECTION
Chemicals Preparation.

$ZrCl_4/HfCl_4$ mixtures with 98% Zr/(Zr + Hf) molar ratio supplied by Alfa Aesar, United states, used for solution making. Standard solutions of zirconium/hafnium (IV) were prepared by dissolving the $ZrCl_4/HfCl_4$ mixtures at different ratios of 8, 9, 10, and 12 molars of HCl solution. Analytical-grade HCl from Merck Co used for solution making. NaOH standard solution was also obtained from Merck. Deionized water was used throughout all experiments.

Ion-Exchange Resins Preparation

In this study, three samples of Amberlite resins including, IRA900, IRA910, CG400II, and three samples of Dowex resins including, 1X2, 1X4, and 1X8 with an average particle size of 100 mesh were used.

The choice of these resins is based on the fact that amine-based resins can be used to separate Zr and Hf at high concentrations of hydrochloride acid (more than 7 M) [1, 8]. The resins listed in Table 1 show changes in amine function [29]. All IERs selected from the Amberlit, and Dowex series are strong basic anionic resins with styrene matrices and different functional groups. They are also all in the form of chloride. In addition, selected Dowex resins (1X2, 1X4, and 1X8) are fine resins containing 2, 4, and 8% divinylbenzene (DVB), respectively.

All resins were washed successively in columns (1 L/100 mL of resin) with deionized water, methanol, deionized water, and 1.0 N NaOH. Resins were then washed with deionized water until the pH of the eluents was neutral. The 1.0 N HCl solutions (1 L/100 mL of resin) were passed through the columns, and the resins were washed by deionized water until the pH of the eluents was neutral. The resins were then partially dried by filtration through a Buchner funnel. Finally, all resins were heated in an oven at 105 ° C for 12 hours, and after drying, they were prepared for use.

Table 1: Characteristics of the resins used.

Name	Functional group	TAEC[(1)] eq/L (Cl⁻ form)
Dowex 1X2	Trimethyl benzyl ammonium	0.6
Dowex 1X4	Trimethyl benzyl ammonium	1
Dowex 1X8	Trimethyl benzyl ammonium	1.2
Amberlite IRA900 Cl	Trimethyl ammonium	≥ 1
Amberlite IRA910 Cl	Dimethyl ethanol ammonium	≥ 1
Amberlite CG400II	-	≥ 1

(1) Toatl exchange capacity

Batch-equilibrium sorption studies

In this study, the effect of 4 effective parameters, including resin type, HCl concentration, time, and zirconium concentration, on zirconium/hafnium optimized separation, has been investigated. The conditions of experiments performing in the order of execution are as follows:

Effect of resin type

For all batch-equilibrium Sorption studies, the testing used a quantity of 1gram oven-dried resin according to the reported conditions. The resin samples were accurately weighed into six glass bottles (150-mL) and first pre-equilibrated with 9M HCl solution. The pre-equilibrations were performed to ensure that the Zr and Hf uptake was measured in an environment where the resins were already at equilibrium. At the end of the 1-h treatment, the resins were filtered through the Buchner funnel and placed back into glass bottles. Then, 20 mL of the Zr/Hf solution produced by dissolution of 2.5 gram $ZrCl_4/HfCl_4$ mixtures with 98% Zr purity in 1000 ml of 9 M HCl was added separately to each of 6 bottles containing 1gram introduced resins and shaken mechanically with a shaker for 3 h. The concentration of zirconium and hafnium in the aqueous phase was then determined by inductively coupled plasma-atomic emission spectroscopy (ICP, VARIAN OES). The extraction efficiency (E (%)), distribution ratio (D (ml/g)), and separation factor (SF) were calculated using equations 1, 2, and 3, respectively.

$$D = \frac{C_i - C_f}{C_f} \times \frac{v}{m} \tag{1}$$

$$E = \frac{C_i - C_f}{C_f} \times 100 \tag{2}$$

$$SF = \frac{D_{zr}}{D_{Hf}} \tag{3}$$

In this equations, C refers to the metal concentration in the aqueous phase (mg/L), V refers to the volume of the aqueous phase (ml), m represents the mass of the resin (g). The subscripts "i" and "f" refer to the initial and final conditions, respectively.

Effect of HCl concentration

In this investigation, three resins with the highest separation factor from previous experiments were selected for new experiments to determine the optimal concentration of HCl in the separation of Zr from Hf. In these experiments, each of the three chosen resin from the previous step was subjected to an ion-exchange process at concentrations of 8, 10, and 12 M HCl, respectively, under the same conditions as the earlier experiments. The values of distribution coefficient (D) and adsorption percentage (E), and separation factor (SF) were calculated as before and finally compared with the results of the previous experiment at a concentration of 9 M HCl.

The significant effect of hydrochloric acid concentration on the separation of Zr from Hf led to new experiments were designed in the presence of two selected IERs with the maximum separation factor from previous stage experiments at concentrations of 9, 9.5 and, 10 M HCl. Thus, the type of resin and the optimal concentration of HCl were determined to achieve the maximum separation factor.

The effect of time

The zirconium and hafnium ion adsorption kinetics were carried out by stirring (150 r/min) 100.0 mg of Amberlite CG400II IER in 100.0 ml Zr/Hf solution of

Table 2: The extraction efficiency (E) for Zr and Hf, distribution coefficient (D) and separation factor (SF) for the resins.

Ion Exchanger	E_{Zr} (%)	E_{Hf} (%)	D_{Zr} (ml/g)	D_{Hf} (ml/g)	SF
Amberlit CG- 400II	74.14	33.33	57.33	10	5.73
Amberlit IRA-900	79.31	42.86	76.67	15	5.11
Amberlit IRA-910	72.85	35.71	53.65	11.11	4.83
DOWEX 1X2	40.52	28.57	13.62	8	1.70
DOWEX 1X4	59.05	29.19	28.84	7.10	4.06
DOWEX 1X8	59.05	30.95	28.84	8.97	3.22

9.5M HCl with uniform initial Zr^{4+}/Hf^{4+} concentration of 869.5/19.98 mg/L at 293 K, and the Zr^{4+}/Hf^{4+} concentrations of supernatant solution were determined by ICP at different reaction time until the attainment of equilibrium. The amount of Zr^{4+} and Hf^{4+} adsorbed per gram of Amberlite IERs (q (mg/g) or (mmol/g)) were also calculated according to equation (4).

$$q = (C_i - C_f) \times \frac{V}{m} \qquad (4)$$

Effect of initial zirconium concentration

These experiments were performed to plot and identify the adsorption isotherms. In this work, two isotherm equations of Langmuir and Freundlich, have been used to provide the equilibrium data. The quality of the isotherm fit to the experimental data is assessed on the magnitude of the correlation coefficient for the regression. So, these experiments were performed in the optimal conditions of previous experiments in the presence of 1 g of Amberlite CG400II IER floating in 20 ml of 9.5 M HCl solution with different zirconium concentrations of 500, 700, 1000, 2000, and 3000 mg/L in 3 hours. The analyses have been made from the R^2 values, based on the actual deviation between the experimental points and the theoretically predicted data points.

RESULTS AND DISCUSSION
Effect of resin type

Table 2 shows the extraction efficiency for zirconium and hafnium (E. in %), as well as the distribution coefficient (D) and separation factor (SF) of the IERs used.

In general, Amberlite IERs presented the highest values of SF for Zr separation from Hf in 9M HCl. As follow from literature [30], ion-exchangers of amino-acid type at low pH may behave like weakly basic anion-

exchangers. The differences in the reaction of these ion-exchangers may be caused by slower complexing kinetics, degree of cross-linking, and matrix structure. Therefore, the selectivity of IERs is influenced by a reciprocal position of functional groups, their spatial configuration, steric effects, and sometimes, the distance of functional groups from matrix and kind of matrix. Due to the better performance of Amberlite series resins, the continuation of studies was done in their presence.
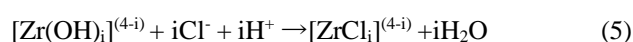
Effect of HCl concentration

The sorption of zirconium and hafnium on Amberlite IERs (IRA-900, IRA-910, and IRA-CG400II) were investigated as a function of the HCl concentration (Tables 3 and 4).

No sorption on Amberlite resins was seen at HCl concentrations of <7 M. As awaited, the sorption of zirconium on anion exchange resins improved incredibly as the HCl concentration increased. The Hf adsorption also increased with HCl concentration, but the adsorption happened at higher HCl concentrations. For both metals, the nature of the species existing in an aqueous solution is strongly influenced by polymerization and hydrolysis reactions. The chemistry of zirconium in aqueous media is controlled by the complexation of Zr^{4+} with OH^-, and where the chloride figures outer-sphere complexes, i.e., $[Zr(OH)_i]^{(4-i)+}$ (4 - i)Cl^- (for i = 1 -5) [31].

Indeed, an extension in HCl concentration (up to 7 M) increases depolymerization and thus, develops the extraction of Zr or Hf by neutral extractants [32].

At high HCl concentrations, OH^- ions joined to Zr are replaced by Cl^- ions to form inner-sphere complexes. This reaction can be expressed by eq 5:

$$[Zr(OH)_i]^{(4-i)} + iCl^- + iH^+ \rightarrow [ZrCl_i]^{(4-i)} + iH_2O \qquad (5)$$
where i = 4 [32], 5 [33] or 6 [34].

Table 3: The extraction efficiency (E) for Zr and Hf, distribution coefficient (D) and separation factor (SF) for the resins

Ion Exchanger	HCl Concentration(M)	E_{Zr} (%)	E_{Hf} (%)	D_{Zr} (ml/g)	D_{Hf} (ml/g)	SF
Amberlit CG- 400II	8	19.32	4.52	4.79	0.95	5.06
Amberlit IRA-900	8	17.05	6.45	4.11	1.38	2.98
Amberlit IRA-910	8	31.82	9.68	9.33	2.14	4.36
Amberlit CG- 400II	10	77.56	27.69	69.14	7.66	9.03
Amberlit IRA-900	10	78.40	30.77	72.58	8.89	8.17
Amberlit IRA-910	10	78.85	30.77	74.55	8.89	8.39
Amberlit CG- 400II	12	98.42	96.43	1241.50	540	2.30
Amberlit IRA-900	12	98.79	96.43	1636.60	540	3.03
Amberlit IRA-910	12	99.09	96.43	2166.70	540	4.01

Table 4: The extraction efficiency (E) for Zr and Hf, distribution coefficient (D) and separation factor (SF) for the resins.

Ion Exchanger	HCl Concentration (M)	E_{Zr} (%)	E_{Hf} (%)	D_{Zr} (ml/g)	D_{Hf} (ml/g)	SF
Amberlit CG- 400	9	74.14	33.33	57.33	10	5.73
Amberlit CG- 400	9.5	54.02	10.25	23.50	2.28	10.29
Amberlit CG- 400	10	88.54	46.27	154.47	17.22	8.97
Amberlit IRA-910	9	72.85	35.71	53.65	11.11	4.83
Amberlit IRA-910	9.5	54.28	12.36	23.74	2.82	8.42
Amberlit IRA-910	10	82.38	37.09	93.48	11.79	7.93

The increase in the extraction of Zr and Hf at high HCl concentrations could be described by the formation of the Zr and Hf chlorocomplexes that, according to eq 6, could be adsorbed on the IERs.

$$R^+\text{-}Cl^- + [ZrCl_i]^{(4-i)} + (i\text{-}4)H^+ \rightarrow R^+H_{i\text{-}4}\,ZrCl_{i+1} \qquad (6)$$
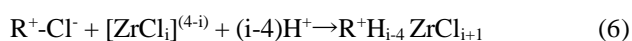
It is also apparent that Hf has a lower tendency to create anionic complexes than Zr. Therefore, at 8 M HCl, the extraction of Hf by Amberlit IERs is <10%, whereas the extraction of Zr is ~20%. At high HCl concentrations (12 M), both Zr and Hf are formed anionic complexes which are extracted by Amberlit IERs, and a low selectivity toward Zr is achieved.

It was also recognized that the resins exhibited the highest Zr selectivity toward Hf ions between 9.0 M and 10.0 M HCl (Table 4). A separation factor of SF > 10 was obtained using 9.5 M HCl with Amberlite CG- 400II IER. Therefore, the concentration of HCl was fixed at 9.5 M for the equilibrium studies.

Effect of initial zirconium concentration

Figs. 1 and 2 show the zirconium/hafnium adsorption isotherms of the Amberlite CG400II IER. These results indicate that an increase in the Zr concentration led to a rise in the number of ions adsorbed. The experimental isotherm data were correlated using Langmuir and Freundlich adsorption isotherm models. The parameters listed in Table 5 were obtained through the linear least-squares fitting of the data. The states of the isotherm fit the experimental data. In all cases, the Langmuir equation illustrates a better fit of the experimental data than the Freundlich equation. It is apparent that the zirconium exchange process is well accorded with the Langmuir isotherm. This is confirmed by the more values of R^2, which are a measure of the goodness of fit.

Kinetics of metal extraction

The impact of contact time on Zr and Hf removal was studied in 9.5 M HCl, using a Zr concentration of 869.5 mg/L

Table 5: Langmuir and Freundlich Isotherms Constants for Single-Component zirconium and hafnium.

Hafnium	Zirconium	Constants	Isothermic Model
0.340	42.194	q_{max} (mg/g)	Langmuir
0.152	0.010	K_L(L/mg)	
0.993	0.968	R^2	
0.103	6.73	K_f	Freundlich
3.443	4.214	n	
0.944	0.809	R^2	
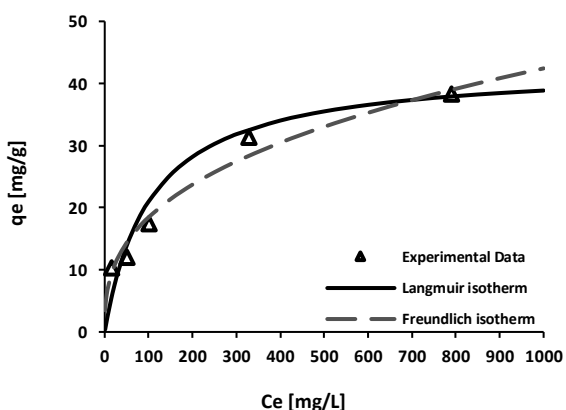
Fig. 1: Comparison of experimental data and Langmuir, Freundlich isotherms for a zirconium system in presence of Amberlite CG400II. Conditions: [HCl]: 9.5 M at 25 °C for 3 h.
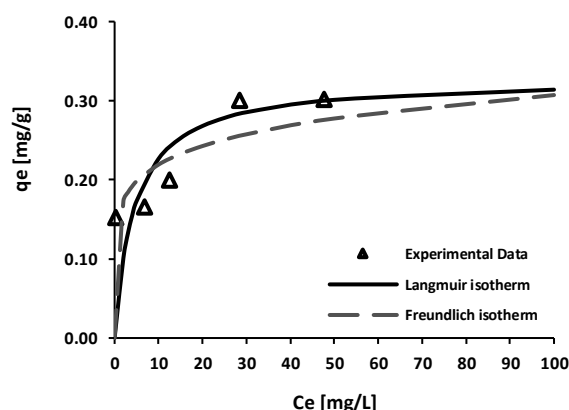

Fig. 2: Comparison of experimental data and Langmuir, Freundlich isotherms for a hafnium system in presence 0f Amberlite CG400II. Conditions: [HCl]: 9.5 M at 25 °C for 3 h.

and 19.98 mg/L of Hf, respectively. Results take up to a period of 3 h are shown in Figs. 3 and 4. For a solution, the amount of adsorbed Zr/Hf ions becomes asymptotic to the time axis after 150 min, which is almost at a state of equilibrium. After 180 min, the extraction percentage remained constant.

According to these data, adsorption of Zr and Hf from a solution results in the same two phases: (I) a linear phase, in which fast uptake occurs, and (II) a quasi-stationary state. This event could be associated with the immediate utilization of the most actively available ion-exchange sites on the adsorbent surface. Phase II may be attributed to a meager diffusion rate of the metal ion through the adsorbent micropores. Figs. 3 and 4 also show the zirconium and hafnium adsorption kinetics of Amberlite CG400II IER. They show that the adsorption rate can be well described by first-order kinetics Lagergren equation ($\ln(Q_e-Q_t)=\ln Q_e-k_{ads}\cdot t$)[35], which Q_e and Q_t are

amounts of metal ion adsorbed per gram adsorbent at equilibrium and time *(* mmol/g) respectively. The value of the zirconium adsorption rate constant (k_{ads}) is calculated to be 4.16×10^{-7} s^{-1}, indicating a relatively slow adsorption rate.

CONCLUSIONS

The ion exchange process of Zr and Hf in HCl solution, using six different commercial ion exchange resins (IERs), has been investigated in the batch. The best adsorption performance of IERs was attributed to Amberlite CG400II IER. The distribution coefficient of Zr and Hf raised dramatically as the HCl concentration increased. The zirconium sorption is happened due to the formation of anionic chloro-complexes in concentrated HCl. A separation factor of >10 was obtained using 9.5 M HCl. The validity of the adsorption isotherm model in predicting the Zr and Hf metal adsorption was evaluated on Amberlite
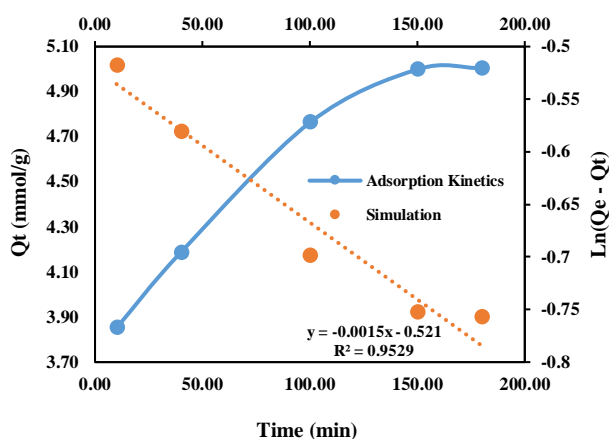
Fig. 3: Zirconium adsorption kinetics of the Amberlite CG400II ion exchange resin and simulation according to Lagergren equation.
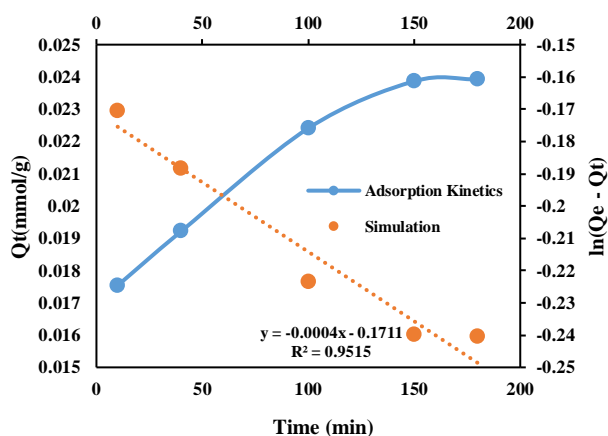

Fig. 4: Hafnium adsorption kinetics of the Amberlite CG400II ion exchange resin and simulation according to Lagergren equation.

CG400II-Cl using 9.5 M HCl. The essential parameters for each isotherm have been prepared for the system using a linear least-square regression algorithm. The correlation coefficients between experimental and simulated data have been calculated. All presented models show a good fit with the Langmuir equation on the Zr and Hf isotherms.

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