Extraction and Separation of Zr(Iv) and Hf(Iv) from Chloride Media Using Glycidyl Methacrylate Magnetic Resin with Phosphoric Acid Functionality

A. M. Daher[a*], E. Afifi[a] A. M. Donia[b] and A. A. Atia[b.]
[a]Nuclear Materials Authority, El Maadi, Cairo, Egypt.
[b]Department of Chemistry, Faculty of Science, Menoufia University, Egypt.
*Corresponding author: doctor_daher@yahoo.com

Summery: Glycidyl methacrylate/divinylbenzene (GMA/DVB) resin modified by embedded magnetite was prepared. The resin was immobilized with phosphoric acid functionality and used to recover Zr(IV) and Hf(IV) from aqueous solutions using column technique. The resin obtained was investigated by means of IR and XRD. The measurements showed that the particles of Fe_3O_4 became completely coated with a film of the resin. The resin containing magnetite particles displayed a higher uptake capacity compared to the magnetite-free one. Uptake values of 0.94 and 0.24 mmol/g were recorded for Zr(IV) and Hf(IV). The loaded resin with metal ions was regenerated using 1 M HNO_3 with efficiency of 93.3% and 98.4% for Zr(IV) and Hf(IV), respectively.

Introduction

Zirconium and hafnium are two of the most important nuclear materials. The use of zircaloy in the construction of fuel elements as well as other structural components in reactor cores meets many physical and technological requirements [1]. One advantage of Zr in nuclear applications is its low thermal neutron capture cross-section, whereas Hf has 640 times higher neutron absorption [2]. Therefore, the amount of Hf present in Zr has a direct effect on the efficiency of the reactor core and thus on the cost of producing nuclear power. Moreover, the total amount of Hf in the reactor core affects the reactor shutdown margin [3]. The chemical similarity between Zr and Hf in both metallic and compound states is greater than that obtained between any other elements in the periodic table.. Therefore, the problem of Zr/Hf separation has acquired significant importance [3,4,5]. Magnetic resins represent an important class of those materials because they are easily trapped from the medium using a magnetic field (6,7).

The present study was directed for the preparation and characterization of magnetic glycidyl methacrylate resin bearing phosphoric acid moiety. The uptake

behavior as well as the selectivity of the resin towards Zr(IV) and Hf(IV) was investigated. The adsorption data obtained were treated according to the Langmuir adsorption isotherm. Kinetic and thermodynamic parameters of adsorption reaction were calculated.

Experimental

Chemicals

Glycidyl methacrylate (GMA), divinylbenzene (DVB, 55%), benzoyl peroxide Bz_2O_2, zirconium oxychloride ($ZrOCl_2.8H_2O$), hafnium tetrachloride ($HfCl_4$), alizarin red S and xylenol orange were obtained from Aldrich, Germany. Bz_2O_2 was purified through crystallization from ethanol/methanol mixture to give pure needles. All other chemicals were ADWIC products, Egypt.

Preparation of GMA/DVB-magnetic resin

The resin was prepared through the polymerization of GMA in the presence of DVB as a cross-linking agent at weight ratio 9.5:0.5 following the previously reported method [8,9]: The requisite volumes of GMA and DVB were mixed well with 0.1 g Bz_2O_2 (initiator) until complete dissolution of the Bz_2O_2. One mL isopropyl alcohol and 12.6 mL cyclohexane were mixed then added to the former solution. The contents were poured into a flask containing 73 mL of 1% polyvinyl alcohol and 0.5 g of the dried Fe_3O_4 [10]. The mixture was refluxed on a water bath at 75-80°C with continuous stirring for 3 h. A gray precipitate was formed, filtered off, subsequently washed with distilled water and methanol to remove the unreacted materials and then dried in air.

Preparation of GMA/DVB- magnetic resin immobilized with phosphoric acid moiety

One gram of resin obtained in pervious step was added to 4 mL of (0.5 M) O-phosphoric acid and 12 mL DMF. The reaction mixture was refluxed at 75-80°C in an oil bath with stirring for 72 h. The product obtained was filtered off, washed with distilled water then methanol and dried in air. The resin obtained is referred as R-PO_4H_2.

Characterization of the resin

IR spectra of the synthesized resins were performed using FT-IR Nexeus-Nicolite- Model 640-MSA. FT-IR, Thermo Electronics Co., USA.X-ray powder diffraction (XRD) measurements were carried out with a Philips X-ray generator model PW 3710/31 a diffractometer with automatic sample changer model PW1775 (scintillation counter, Cu-target tube and Ni-filter at 40 KV and 30 mA).

Uptake experiments

Effect of flow rate

A column with internal diameter of 0.4 cm and 5 cm in length was packed with 0.6 g of resin (bed height 3.6 cm). Metal ion solution at initial concentration of 2×10^{-3} M for Zr(IV) or 1×10^{-3} M for Hf(IV) at pH = 2.5 was allowed to flow downward gradually through the column under the force of gravity and at different flow rates of 1, 2 or 3 mL/min. Samples were collected from the outlet of the column at different time intervals and analysed for metal ion concentration. The operation of the column was stopped when the initial and final metal ion concentrations of metal ions became equal.

Effect of bed height

The effect of bed height of the resin on the uptake was carried out by packing the column with 0.2, 0.4 and 0.6 g of resin $R-PO_4H_2$ to give bed heights of 1.2, 2.4 and 3.6 cm, respectively. Metal ion solution was allowed to flow downward gradually through the column under the force of gravity and a flow rate of 1 mL/min. Ten milliliters of the underflow solution were removed at different time intervals where the residual concentration of metal ion was determined.

Regeneration

Regeneration experiments were performed by placing 0.1 g of the resin in the column and then loaded with metal ions up to the maximum capacity at a flow rate of 1 mL/min. Afterwards the column was washed thoroughly with distilled water and then subjected to elution of Zr(IV) or Hf(IV) from the resin using 1 M HNO_3. The resin packed in the column was washed repeatedly with distilled water then reloaded with metal ions and the uptake capacity was estimated. The regeneration efficiency

was calculated by taking the ratio of the uptake in the 2nd and 1st runs.

Results and discussions

Characterization of resin

The prepared magnetic resin (R-PO$_4$H$_2$) was investigated using different spectral techniques. IR spectra showed that the peak of epoxy group at 1260 cm^{-1} in the spectrum of GMA/DVB resin (R) was disappeared in that of R-PO$_4$H$_2$. Moreover, the characteristic peaks of phosphoric acid moiety; $\nu_{P=O}$, ν_{P-O} and ν_{O-H} appeared at 1120, 1054 and 3401 cm^{-1}, respectively, in the spectrum of R-PO$_4$H$_2$, Fig (1).
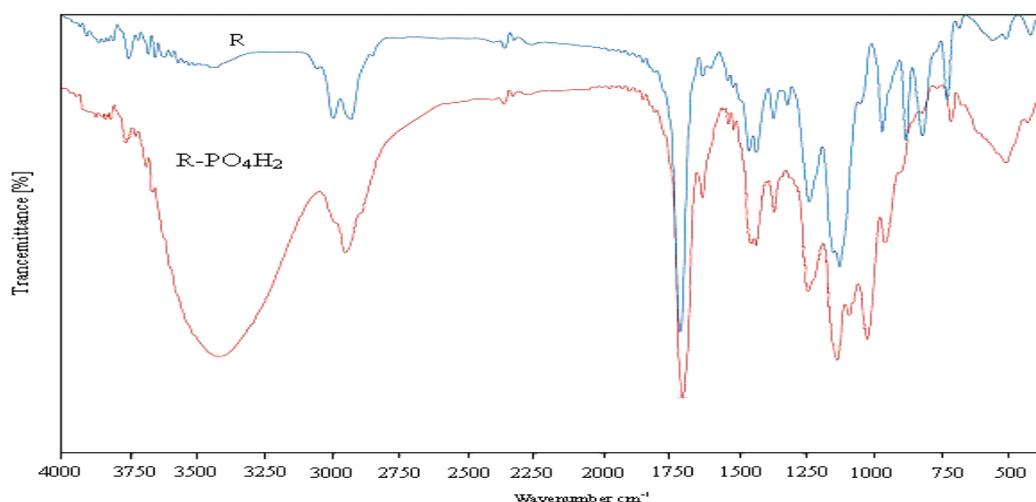

**Fig. 1**. IR spectra of GMA/DVB and R-PO$_4$H$_2$ resins.

This indicates the success of immobilization process. Figure (2) shows the XRD patterns of pure magnetite (Fe$_3$O$_4$) and R-PO$_4$H$_2$ resin. The most intense line of magnetite and studied resin appeared at 2θ = 34.56. This confirms the presence of magnetite inside the polymeric matrix. The spectrum displays two strong lines correspond to iron and phosphorous elements.
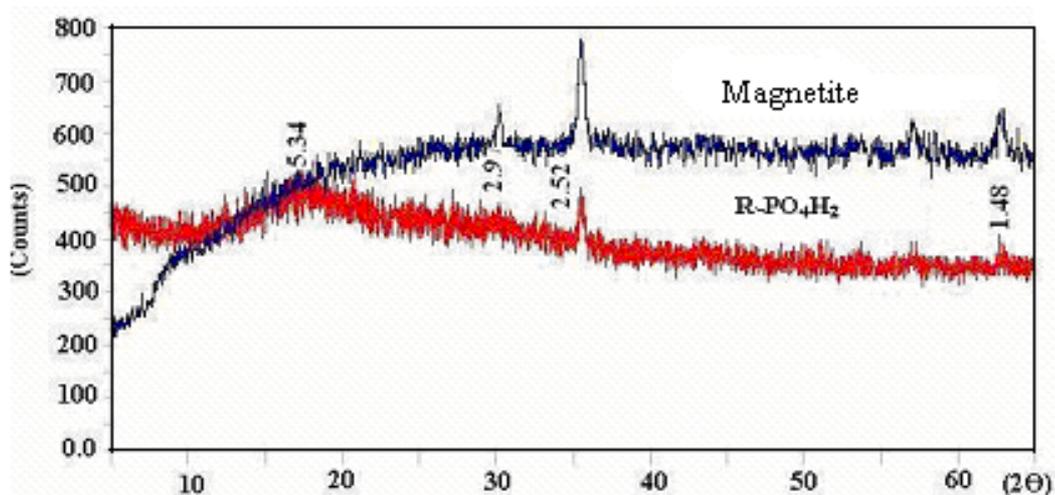
Metal Ion	Flow rate, ml/min	Bed Height,cm	t_b, min	t_s, min	K_a, l/mol.min	N_o, Mmol/g	Z_o, cm

Fig. 2. X-ray diffraction patterns of resin R-PO$_4$H$_2$ and pure magnetic iron oxide.

The resin was found to be stable in both mineral acids and alkalis. The chemical structure of the resin may be represented as
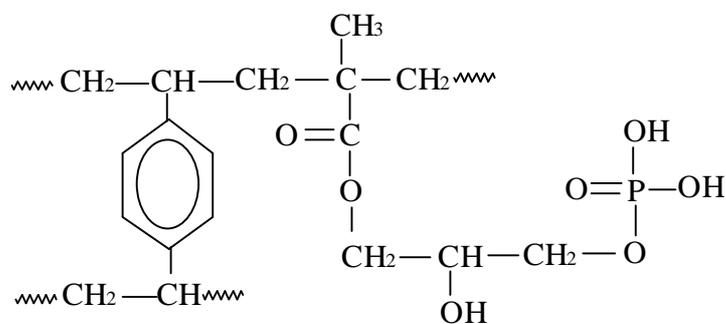
Column method
Effect of flow rate

The breakthrough curves of the studied resin towards adsorption of Zr(IV) or Hf(IV) at flow rates of 1, 2 and 3 mL/min and a fixed bed height of 2.4 cm as shown in Table (1).

Zr(IV)	1	3.6	130	380			
	2	3.6	35	120			
	3	3.6	13	67	57.5	1.15	0.24
	1	2.4	80	280			
	1	1.2	30	180			
Hf(IV)	1	3.6	50	250			
	2	3.6	10	85			
	3	3.6	3.4	43.4	69.0	0.30	1.33
	1	2.4	30	180			
	1	1.2	0.0	130			

Table 1:Column data of studies for the uptake of Zr(IV) and Hf(IV) on the resin at different bed heights and flow rate.

It is noticed that breakthrough and exhaustion of the resin occur faster at higher flow rates. Also as the flow rate increases, the metal concentration in the effluent increases rapidly resulting in much sharper breakthrough curves. This behavior may be attributed to the insufficient residence time for the uptake of the metal ions by the resin. This negatively affects the interaction process as well as the diffusion of metal ions through the pores of the resin [11]. At the same bed height and a flow rate of 1 mL/min, the breakthrough points for Zr(IV) and Hf(IV) were 70 and 40 min, respectively. The longer breakthrough time in the case of Zr(IV) refer to its higher affinity as well as strong binding with the resin's active sites compared to Hf(IV).

Effect of bed height

The effect of bed height on the removal efficiency was studied at 1.2, 2.4 or 3.6 cm while the flow rate was held constant at 1 mL/min as shown in table (1).The influence of bed height on the removal efficiency was well tested in terms of breakthrough time (t_b) and saturation time (t_s). The removal efficiency of the resin was found to be directly proportional with bed height. Bed depth service time model (BDST) is a simple model, which states that bed height (Z) and saturation time (t_s) of the column gives a linear relationship, as given in the following equation [1]

$$t_s = \frac{N_o Z}{C_o n} - \frac{1}{K_a C_o} \ln\left(\frac{C_o}{C_t} - 1\right) \tag{1}$$

where C_t is the concentration of the metal ion at the saturation time just prior to equal the initial concentration C_o (i.e. $C_o/C_t = 100/99$), N_o is the total adsorption capacity

(mmol of solute/L of sorbent bed), υ the linear velocity (cm/min) and K_a is the rate constant of transfer of the metal ion to the resin surface (L/mmol.min). The values of N_o and K_a were calculated from the slope and intercept of the BDST plots, Fig. (3). The values of both C_o and υ should be kept constant during the column operation. The calculated values of N_o for Zr(IV) and Hf(IV) were found to be 1.15 and 0.3 mmol/g, respectively. If K_a is large, even a short resin's bed depth will avoid the breakthrough limit. In case of small values of K_a a progressively longer bed would be required to extend the breakthrough point. The values of K_a for Zr(IV) and Hf(IV) are 172 and 138 (L/mmol.min). This indicates the higher efficiency of the resin toward Zr(IV) relative to Hf(IV). The critical bed height (Z_o) can be calculated by $t_s = 0$ in Eq (1) and rearranging to get equation [2]

$$Z_o = \frac{n}{K_o N_o} \ln\left(\frac{C_o}{C_b} - 1\right) \qquad (2)$$

where C_b is the breakthrough metal ion concentration (mmol/L). The above equation implies that Z_o depends on the kinetics of the sorption process, the residence time of the solute and the adsorption capacity of the resin [11]. The critical bed height of the resin for Zr(IV) and Hf(IV) were found to be 0.24 and 1.33 cm, respectively. This indicates that the studied resin displays a great removal efficiency towards Zr(IV) relative to Hf(IV).
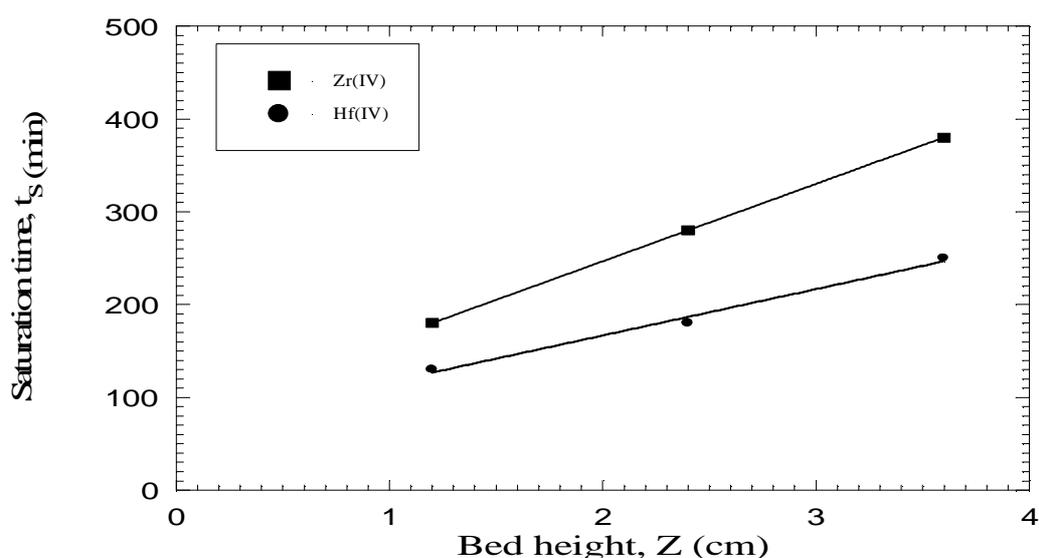

Fig. 3. Variation of saturation time as a function of bed height for uptake of Zr(IV) and Hf(IV) by resin R-PO$_4$H$_2$

Regeneration

Eight adsorption/desorption cycles were carried out on a column charged with the resin. The column was loaded with Zr(IV) or Hf(IV) followed by regeneration using 1 M HNO₃. Regeneration efficiency was calculated using the following equation

$$\text{Regeneration efficiency } (\%) = \frac{Total\ adsorption\ capacity\ in\ the\ \sec ond\ run}{Total\ adsorption\ capacity\ in\ the\ first\ run} \times 100\% \quad (3)$$

Regeneration efficiencies were found to be 93.3 and 98.4% for Zr(IV) and Hf(IV). Finally, the adsorption and selectivity characteristics obtained for the studied resin make it promising for extraction as well as separation Zr(IV) and Hf(IV).

Conclusions: Phosphoric acid containing GMA/DVB-magnetic resin was prepared and characterized by means of IR and XRD. The phosphoric acid content was also estimated. The uptake behaviour of the resin obtained towards Zr(IV) and Hf(IV) at pH = 2.5 was investigated. The investigated resin showed A higher affinity towards Zr(IV) relative to Hf(IV). The adsorption reaction was found to be endothermic with pseudo second order kinetics. Both thermodynamic and kinetic parameters of the adsorption reaction were calculated.

<div align="center">

References

</div>

1- Yang, X.j., Fane, A.G., Pin, C., 2002a. Separation of zirconium and hafnium using hollow fibers. Chem. Eng. J. 88, 37–44.

2- Purohit, R., Devi, S., 1997. Determination of nanogram levels of zirconium by chelating ion exchange and on-line preconcentration in flow injection UV-visible spectrophotometry. Talanta. 44, 319 -326.

3- Ishida, K., 1991. Thin-layer chromatographic behaviour and separation of zirconium(IV) and hafnium(IV) on silica gel in mineral acid hydrogen peroxide media. Journal of Chromatography. 539, 169-175.

4- Yang, X.J, Pin, C., 2002b. Determination of niobium, tantalum, zirconium and

hafnium in geological materials by extraction chromatography and inductively coupled plasma mass spectrometry. Analytica Chimica Acta. 458, 375–386

5- Agrawal, Y.K., Sudhakar, S., 2002. Extraction, separation and preconcentration of zirconium. Sep. & Purif. Technol. 27, 111–119.

6- Donia, A.M., Atia, A.A., El-Boraey, H.A., Mabrouk, D., 2006a. Adsorption of Ag(I) on glycidyl methacrylate/N,N'-methylenebis-acrylamide chelating resins with embedded iron oxide. Sep. Purif. Technol. 48, 281-287.

7- De SantaMaria, L.C., Leite, M.C.A.M., Costa, M.A.S., Ribeiro, M.S., Senna, L.F., Silva, M.R., 2003. Preparation of composite materials containing iron in across-linked resin host based on styrene and divinylbenzene. Eur. Polym. J. 39, 843-846.

8- Atia, A.A., Donia, A.M., Shahin, A.E., 2005a. Studies on the uptake behavior of a magnetic Co_3O_4-containing resin for Ni(II), Cu(II) and Hg(II) from their aqueous solutions. Sep. Purif. Technol. 46, 208-213.

9- Atia, A.A., Donia, A.M., Yousif, A.M., 2005b. Comparative study on the recovery of silver(I) from aqueous solutions using different chelating resins derived from glycidyl methacrylate. Appl. Polym. Sci. 97 (3), 806-816.

10- Donia, A.M., Atia, A.A., El-Boraey, H.A., Mabrouk, D., 2006b. Uptake studies of copper(II) on glycidyl methacrylate chelating resin containing Fe_2O_3 particles. Sep. Purif. Technol. 49, 64-70.

11- Vijayaaraghavan, K., Jegan, J., Palanivelu, K., Velan, M., 2005. Biosorption of cobalt(II) and nickel(II) by seaweeds: batch and column studies. Sep. & Purif. Technol. 44/1, 53-59.