

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*}, A. M. Donia^b, A. A. Atia^b, and E. Affi^a

^aNuclear Materials Authority, El Maadi, Cairo, Egypt.

doctor_daher@yahoo.com

^bDepartment of Chemistry, Faculty of Science, Menoufia University, Egypt.

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 Fe₃O₄ became completely coated with a film of the resin. 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 HNO₃ 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 [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.

Experimental

Chemicals

Glycidyl methacrylate (GMA), divinylbenzene (DVB, 55%), benzoyl peroxide

Bz₂O₂, zirconium oxychloride (ZrOCl₂.8H₂O), hafnium tetrachloride (HfCl₄), alizarin red S and xylenol orange were obtained from Aldrich, Germany. Bz₂O₂ 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 Bz₂O₂ (initiator) until complete dissolution of the Bz₂O₂. 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 Fe₃O₄ [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-PO₄H₂.

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

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..

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-PO₄H₂ 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.

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 HNO₃.

Results and discussions

Characterization of resin

The prepared magnetic resin (R-PO₄H₂) 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-PO₄H₂. Moreover, the characteristic peaks of phosphoric acid moiety; $\nu_{\text{P=O}}$, $\nu_{\text{P-O}}$ and $\nu_{\text{O-H}}$ appeared at 1120, 1054 and 3401 cm⁻¹, respectively, in the spectrum of R-PO₄H₂, Fig (1).

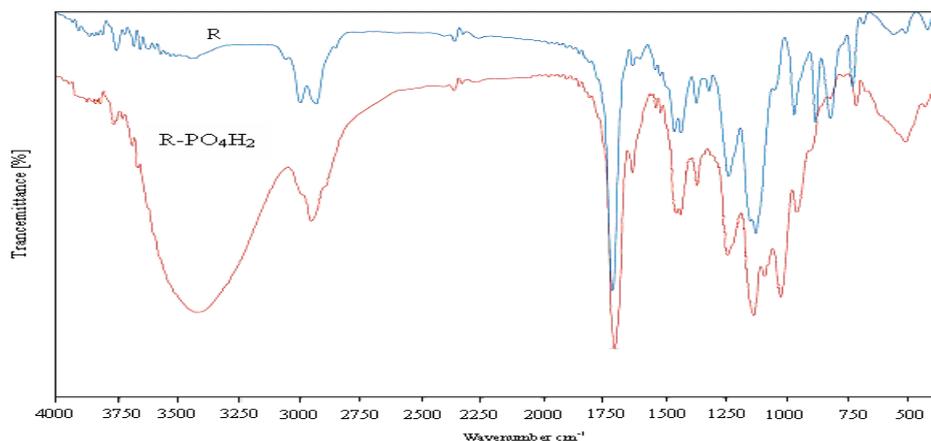


Fig. 1. IR spectra of GMA/DVB and R-PO₄H₂ resins.

This indicates the success of immobilization process. Figure (2) shows the XRD patterns of pure magnetite (Fe₃O₄) and R-PO₄H₂ resin. The most intense line of magnetite and studied resin appeared at $2\theta = 34.56$. This confirms the presence of magnetite inside the polymeric matrix. The resin was found to be stable in both mineral acids and alkalis

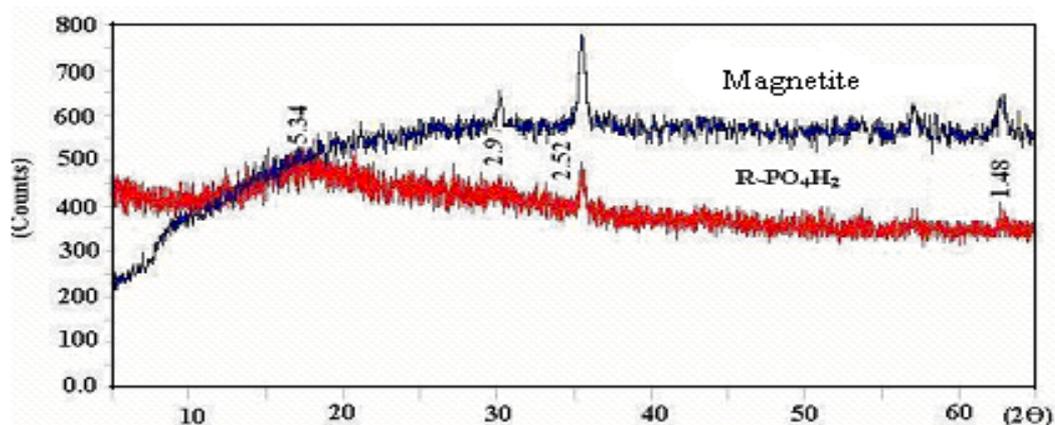


Fig. 2. X-ray diffraction patterns of resin R-PO₄H₂ and pure magnetic iron oxide.

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). It is noticed that breakthrough and exhaustion of the resin occur faster at higher flow rates. Also as the flow rate increases, the metal This behavior may be attributed to the insufficient residence time for the uptake of the metal concentration in the effluent increases rapidly resulting in much sharper breakthrough curves. 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]. 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). **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.

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

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)

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

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), v 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 v 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 critical bed height (Z_o) can be calculated by $t_s = 0$ in Eq (1) and rearranging to get equation [2]

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

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).

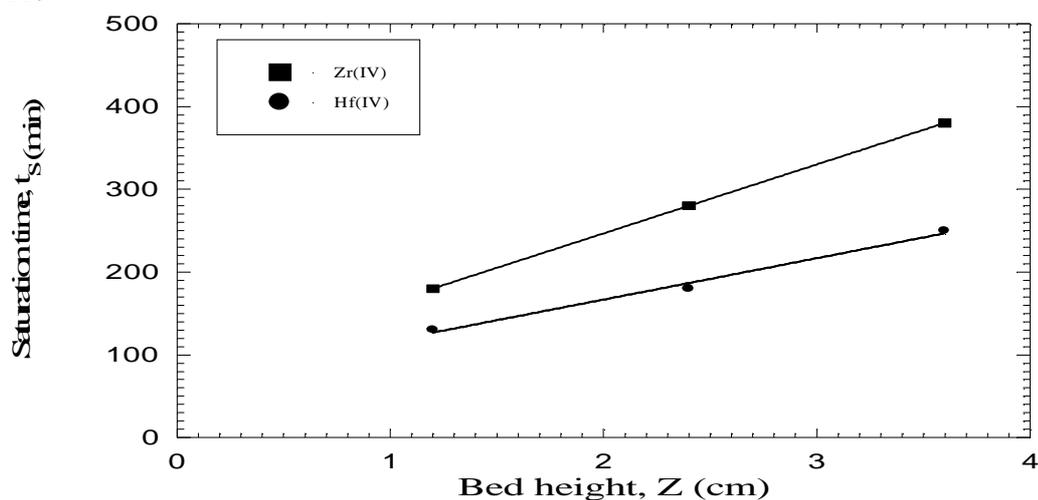


Fig. 3. Variation of saturation time as a function of bed height for uptake of Zr(IV) and Hf(IV)

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).

References

1. Yang, X.j., Fane, A.G., Pin, C., 2002a. Chem. Eng. J. 88, 37–44.
2. Purohit, R., Devi, S., 1997. Talanta. 44, 319 -326.
3. Ishida, K., 1991. Journal of Chromatography. 539, 169-175.
4. Yang, X.J, Pin, C., 2002b. Analytica Chimica Acta. 458, 375–386
5. Agrawal, Y.K., Sudhakar, S., 2002.. & Purif. Technol. 27, 111–119.
6. Donia, A.M., Atia, A.A., El-Boraey, H.A., Mabrouk, D., 2006a. 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. Eur. Polym. J. 39, 843-846.
8. Atia, A.A., Donia, A.M., Shahin, A.E., 2005a. Sep. Purif. Technol. 46, 208-213.
9. Atia, A.A., Donia, A.M., Yousif, A.M., 2005b. Appl. Polym. Sci. 97 (3), 806-816.
10. Donia, A.M., Atia, A.A., El-Boraey, H.A., Mabrouk, D., 2006b. Sep. Purif. Technol. 49, 64-70.
11. Vijayaaraghavan, K., Jegan, J., Palanivelu, K., Velan, M., 2005. Sep. & Purif. Technol. 44/1, 53-59.