1. Introduction

Several approaches have been used for the separation of metals from aqueous solutions such as, chemical precipitation, liquid–liquid extraction, ion-exchange, adsorption, filtration, reverse osmosis and membrane technologies (Mukherji, 1970). Ion exchange and solvent extraction are the two principal methods currently being used for the separation of metals from solutions. These processes require bulky equipment and large chemical inventories which are in some cases expensive.

Nanotechnology, is considered as one of the most important advancements in science and technology of the past decade. It is related to the manipulation of materials and systems at the nanometer scale. At this scale, materials exhibit new properties suitable for novel applications (Khodabakhshi et al., 2011; Uheida et al., 2006). Nanostructuring of magnetic materials, on the other hand, is a widespread phenomenon in the field of nanoscience and nanotechnology. Magnetite (Fe₃O₄) is a particular magnetic material which has received special attention due to its potential applications (Fajaroh et al., 2012; Harraz, 2013). The magnetically assisted chemical separation (MACS) process has the advantages of (1) using less complex tools (compared to solvent extraction and ion exchange) (2) simplicity of operation that would facilitate scale-up (3) production of lesser amount of secondary waste (4) providing a cost-effective way for separation of metal ions (Nunez et al., 1995).

In the MACS process, metal ions are separated from aqueous solutions using a magnetic nanoparticle core which is coated with a selective organic material. The surface of magnetic carriers is modified with a material (an extractant) that has attraction for the targeted metals. The modified nanoparticles are added to the solution containing the metal ions, mixed thoroughly, and recovered efficiently with a magnet. Shaibu et al. (2006) have used Cyanex 923-coated magnetic particles for uptake of Th (IV), U(VI), Am(III) and Eu(III) from simulated nuclear waste solutions. They showed that MACS process has more efficiency over traditional solvent extraction and generates only a small secondary waste stream. Furthermore, reusability of the coated magnetic particles and reliability of the coating procedure make the MACS process an interesting alternative for separation of lanthanides and actinides from nuclear waste streams. Nunez et al. (1995) examined extractant coated magnetic carriers for efficient separation of radionuclides such as plutonium, americium and uranium from acidic solutions. Ngomsik et al. (2005) investigated the ability of magnetic alginate beads containing Cyanex 272 for the removal of Co(II) ions from aqueous solutions. They showed that pH is an important factor affecting the removal of cations from aqueous solutions and suggested a pseudo-second order equation to describe the adsorption kinetics. Kaminski and Nunez (1999) examined the MACS process for recovering cobalt and nickel from acidic solution. The magnetic particles coated with Cyanex 272 and D2EHPA displayed excellent separation of Co(II) and Ni(II) from...
acidic solution but did not display pronounced selective recovery of Co (II). Khajeh and Khajeh (2009) used morin-modified magnetic nanoparticles for selective extraction and pre-concentration of Zinc (II) ions from aqueous and biological solutions. They evaluated the influence of different parameters such as the presence of extractant, amount of extractant loaded on the nanoparticles, pH, adsorption time, type and the minimum amount of eluent for stripping of zinc from magnetic nanoparticles, breakthrough volume, and limit of detection. Ashtari et al. (2009) used the MACS method for extraction of beryllium from aqueous solutions. They investigated the influence of different parameters such as type and amount of extractant, pH, equilibrium time and ionic strength. They found that the best results were achieved under the following conditions: pH 7.4, extraction time 10 min and 0.5 M nitric acid concentration. Faraji et al. (2010) used sodium dodecyl sulfate-coated magnetite nanoparticles (SDS-coated Fe3O4 NPs), for extraction of Hg (II) from aqueous solutions. The results imply that pH = 3, extractant amount = 50 mg, nanoparticles mass = 100 mg and extraction time = 1 min give the best results. Banerjee et al. (2010) used CMPO-coated magnetite nanoparticles for U-extraction from aqueous solutions. A magnetic field around the solution was created and nanoparticles were collected and stripped after the process. Ambashta et al. (2010) used the MACS process to extract Cu, Co and Cd from waste solutions. They used a high gradient magnetic field for the separation of nanoparticles from the solution. Ambashta et al. (2005) compared physical and chemical properties and extraction behavior of nanoscale magnetite-based solvent extractant for extraction of potassium and strontium from waste solutions. They used a magnetic field for the separation of nanoparticles from the solution and showed that the extractant loaded magnetic beads possess bulk super paramagnetic property and surface decontamination behavior.

As shown above, there are several reports of MACS separation processes for various ions but separation of hafnium from zirconium by MACS process has not yet been reported. In this study, tributylphosphate (TBP) modified ferromagnetic nanoparticles with a particle size of 10 nm were evaluated for the extraction and separation of hafnium and zirconium. In the present study, tributylphosphate (TBP) was used because this extractant is more effective, less expensive and more easily available compared to other extractants such as cyanex-301, cyanex-302 and triphenyl phosphine oxide (TPPO).

2. Material and methods

2.1. Synthesis of super paramagnetic iron oxide nanoparticles (SPIONs) coated by polyethylene glycol (PEG)

In the first step, solutions were prepared using de-ionized (DI) water after 30 min of bubbling with argon for de-oxygenation. Next, iron salts were dissolved in DI water containing 1 M HCl, where the mole fraction of Fe3+ to Fe2+ was adjusted to 2:1 for all samples. The co-precipitation was performed by drop-wise addition of NaOH to iron containing solution under an argon atmosphere. To control mass transfer (which may allow particles to combine and build larger polycrystalline particles) turbulent flow was created by placing the reaction flask in an ultrasonic bath and changing the homogenization rates during the first 2 min of the reaction. The molarity of the NaOH solution was 1.2. After 30 min, the solution was centrifuged at 10,000 g for 7 min and re-dispersed in DI water several times. Next, the PEG solution was diluted with DI water and added gradually with a syringe (100 μL per drop) and stirring at 1000 rpm was continued for 1 h in order to coat the nanoparticles. It is worthy to note that the PEG/iron mass ratio was 2. The particles were collected by centrifugation at 10,000 g for 7 min and re-dispersed in DI water. Typical TEM micrographs for SPIONs coated by PEG are shown in Fig. 1. It is clear that SPIONs coated by PEG had a mean diameter of 10 nm. Fig. 2 shows the XRD peaks for the naked SPIONs which reveal that the resultant SPIONs were composed of magnetite and maghemite-C.

Fig. 1. TEM image of the SPIONs coated by PEG (scale 20 nm).

2.2. Preparation of TBP-modified nanoparticles

The following steps have been performed for modifying the surface of nanoparticles:

- Washing nanoparticles (three times) with de-ionized water, twice with 0.02 μm filtered de-ionized water, and twice with 0.02 μm filtered ethanol to remove the preservatives,
- Drying overnight in a fume hood,
- Grinding the dried particles using a mortar and pestle,
- Adding 2 mL of 0.02 μm filtered ethanol to 0.1 g of nanoparticles in a Teflon container, stirring the mixture until the nanoparticles are dispersed in the ethanol,
- Adding 0.25 mL of 1.2 M TBP/ethanol solution to the nanoparticles,
- Sonication for 10 min, with constant stirring,
- Heating in a water bath at 60 °C until the ethanol is evaporated, with constant stirring of the mixture,
- Drying the nanoparticles in an oven at 120 °C for 17 h.

2.3. Preparation of solutions

Partitioning experiments were carried out with suspensions of nanoparticles in nitric and hydrochloric acids and simulating solutions containing Zr and Hf. The partition coefficients for different concentrations of nitric and hydrochloric acids were monitored using Zr and Hf tracers. Measurements were made in 1-, 4- and 8 M HNO3 and HCl with 1.2 M TBP. The suspensions were held in a sonic cleaning bath to enhance the dispersion and agitation with a stirrer to disperse the solid suspension further. Next, the mixture was placed in a magnet rack to separate the nanoparticles.

2.4. Measurements of partitioning coefficients and separation factor (SF)

Extraction partition coefficient was calculated using the following equation:

$$K_d = \frac{C_{en} - C_{en}}{C_{en}} \times \frac{V}{m}$$  \hspace{1cm} (1)

where Cen and Cf are the metal ion concentrations in the aqueous phase before and after extraction, V is the volume of the aqueous phase (in mL) and m is the weight of the modified magnetic nanoparticles (in g). Strip partition coefficient was calculated using the following equation:

$$K_{strip} = \left( \frac{g_{strip}}{V} \right) \frac{k_{strip}^{final} - k_{strip}^{final}}{C_{strip}^{final}}$$  \hspace{1cm} (2)
where \( g_p = \text{mass of the nanoparticles (g)} \), \( V = \text{volume of waste solution (mL)} \), \( C_{\text{strip final}} = \text{final concentration after stripping} \), \( C_{\text{ext final}} = \text{final concentration after extraction} \), and \( K_{d_{\text{ext}}} = \text{extraction partition coefficient} \).

The separation factor (SF) was calculated using the following equation:

\[
\text{SF} = \frac{K_{d_A}}{K_{d_B}}
\]

where \( K_{d_A} \) and \( K_{d_B} \) are partitioning coefficients of A and B ions.

### 3. Results and discussion

#### 3.1. Effect of HNO\(_3\) and HCl concentrations on the separation factor

The separation factors of hafnium and zirconium (SF = \( K_{d_{\text{Hf}}} / K_{d_{\text{Zr}}} \)) at 1-, 4- and 8 M solutions of nitric and hydrochloric acids for extraction and stripping stages are shown in Tables 1 and 2. The initial concentrations of Hf and Zr ions and concentrations of TBP and nanoparticles were 10 ppm, 1.2 M, and 2.5 g/L, respectively. It is clear from the results that the SF values are higher for hydrochloric acid when compared with nitric acid. Maximum SF (1.4) was achieved at 4 M hydrochloric acid concentration. Next, this concentration was selected for the following experiments. In the stripping stage, the maximum separation factor was achieved with sample no. 2, i.e., when hydrochloric acid concentration was equal to 4 M. This is a good result because the maximum SF in extraction and stripping stages occurs in 4 M hydrochloric acid.

#### 3.2. Effect of Zr and Hf concentrations on the separation factor

Figs. 3 and 4 show the effect of Zr and Hf concentrations on the separation factor in extraction and stripping stages, respectively. This experiment was performed in 1.2 M, 4 M and 2.5 g/L concentrations of TBP, HCl and nanoparticles, respectively. According to the tables and the results, it was concluded that by fixing the Hf concentration and increasing the Zr concentration, SF value decreases. In other words, SF value in experiments with 7.5 ppm Hf and 10 ppm Zr is higher than other concentrations in both stages.

### 4. Conclusions

In this study, the MACS process was used successfully to separate hafnium from zirconium. Results showed that the type and amount of acid and concentration of the metals are the three important parameters affecting the separation factors in the extraction and stripping stages. Optimun condition achieved were 4 M for hydrochloric acid concentration, 10 ppm for Zr concentration and 7.5 ppm for Hf concentration. Under these conditions, SF values obtained in the extraction and stripping stages were 1.4 and 1.5, respectively. It seems that this method can separate these metals successfully, but several parameters such as concentration of extractant and nanoparticles in solution, and synergic effects of metals present in the solution have influential effects on the efficiency of extraction and separation stages which will be published in the next paper.

### Acknowledgments

We are grateful to Dr. Abbas Fazeli and Mr. Abbas Abdolmaleki for the facilities, and scientific and technical assistance. We also wish to thank our honorable partners on the project for their contributions to the work reported in this paper.
References


Fig. 3. Effect of Zr and Hf concentrations on the separation factor in extraction stage.

Fig. 4. Effect of Zr and Hf concentrations on the separation factor in stripping stage.