

Use of Coated Magnetic Nanoparticles with Cyanex272 for Heavy Metal Removal Extraction from Wastewater

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Abstract—In the Magnetically Assisted Chemical Separation (MACS) process, tiny ferromagnetic particles coated with solvent extractant are used to selectively separate radionuclides and hazardous metals from aqueous waste streams. The contaminant-loaded particles are then recovered from the waste solutions using a magnetic field. In the present study, Cyanex272 or C272 (bis (2,4,4-trimethylpentyl) phosphinic acid) coated magnetic particles are being evaluated for the possible application in the extraction of Thorium (IV) from nuclear waste streams. The uptake behaviour of Th(IV) from nitric acid solutions was investigated by batch studies.

Adsorption of Thorium (IV) from aqueous solution onto adsorbent was investigated in a batch system. Adsorption isotherm and adsorption kinetic studies of Thorium (IV) onto nanoparticles coated Cyanex272 were carried out in a batch system. The factors influencing Thorium (IV) adsorption were investigated and described in detail, as a function of the parameters such as initial pH value, contact time, adsorbent mass, and initial Thorium (IV) concentration. Magnetically Assisted Chemical Separation (MACS) process adsorbent showed best results for the fast adsorption of Th (IV) from aqueous solution at aqueous phase acidity value of 0.5 molar. In addition, more than 80% of Th (IV) was removed within the first 2 hours, and the time required to achieve the adsorption equilibrium was only 140 minutes. Langmuir and Freundlich adsorption models were used for the mathematical description of the adsorption equilibrium. Equilibrium data agreed very well with the Langmuir model, with a maximum adsorption capacity of 48 mg.g⁻¹. Adsorption kinetics data were tested using pseudo-first-order, pseudo-second-order and intra-particle diffusion models. Kinetic studies showed that the adsorption followed a pseudo-second-order kinetic model, indicating that the chemical adsorption was the rate-limiting step.

Keywords— Thorium (IV) adsorption, MACS process, magnetic nanoparticles, Cyanex272.

I. INTRODUCTION

ION exchange and solvent extraction are two primary technologies currently being employed for the separation of transuranics and hazardous metal ions from waste solutions. These are complex processes that in some cases require expensive, bulky equipment and large chemical inventories.

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Further, they generate significant amounts of secondary waste. On the other hand, the Magnetically Assisted Chemical Separation (MACS) process provides a cost-effective way of removing transuranics from nuclear wastes [1,2].

The MACS process was developed at Argonne National Laboratory as a compact, simple process for selectively separating transuranics and fission product radionuclides from radioactive liquid waste streams. It employs small ferromagnetic composite particles coated with a selective solvent extractant or ion exchange material. The coated particles are mixed with the waste solution in situ or in a reactor vessel. The hazardous metals are selectively extracted onto the particle surface because of the chelating or exchange properties of the particle coating. The particles are removed by magnetic filtration or simply recovered with a magnet. The clean water can be reused by the facility or sent to sewerage. The target metals can be concentrated into a small volume by stripping the metals of the surface using an appropriate stripping agent. The concentrated product can be disposed properly, reused by the facility, or sent for resale and the MACS particles can be reused. There is an ongoing effort to evaluate the MACS process for the recovery of hazardous metals from industrial wastes for waste minimization and recycling efforts.

The most used methods for separation and preconcentration of Thorium and Uranium include precipitation, coprecipitation, solvent extraction, membrane dialysis, chromatographic extraction, ion exchange, flotation and adsorption [3–11]. Most of these methods suffer from technical, economic and health problems related to selectivity, long time of extraction and large quantity of hazardous materials used.

New stringent regulations have prompted the development of various technologies for Thorium removal from wastewater produced from nuclear industries and mining activities. Adsorption using magnetic nanoparticles coated with a polymer is an important area of research. Grafting of new functional groups and chemical coating increases its adsorption capacity and selectivity towards metal ions in solution through the formation of different chelates (Anirudhan and Radhakrishnan, 2009). The metal uptake by magnetic nanoparticles coated with Cyanex272 is primarily attributed to the phosphor and hydroxyl groups present in the polymer chain, which can interact with various metallic species through ion exchange and/or chelation mechanism.

Mechanisms responsible for Cyanex, although understood to a limited extent, may be one or combination of ion exchange, complexation, coordination, adsorption, electrostatic interaction, chelation and microprecipitation (Vijayaraghavan and Yun, 2008). However, nanoparticles have several drawbacks. Nanoparticles are basically small particles, with low density, poor mechanical strength and little rigidity (Vijayaraghavan and Yun 2008).

Magnetic nanoparticles are currently being widely studied and application of magnetic nanoparticle technology for remediating environmental problems has received attention in recent years (Oliveira et al., 2002; Castro et al., 2009; Chang and Chen, 2005; Chang et al., 2006; Ngarmkam et al., 2010). It is believed that magnetic nanoparticles (Fe₃O₄) show the finite-size effect and high ratio of surface-to-volume, resulting in a higher adsorption capacity (Shen et al., 2009). Magnetic nano-carriers can be easily manipulated by an external magnetic field and hence should be suitable as the support of adsorbents. The super paramagnetic Fe₃O₄ nanoparticles coated with polymers are usually composed of the magnetic cores to ensure a strong magnetic response and a polymeric shell to provide favourable functional groups and features. A composite of Cyanex272 with magnetic Fe₃O₄ nanoparticles would result in an adsorbent with high binding capacity of metals (Saifuddin and Dinara, 2011).

In this work has combined magnetic nanoparticles into Cyanex272. The sorption process was studied with regard to the effects of aqueous phase acidity, initial Thorium concentration, contact time, and dose of adsorbent. Equilibrium isotherms will be determined using Langmuir and Freundlich equations. The kinetics of the adsorption process will be analysed using pseudo-first-order, pseudo second-order and intra-particle diffusion models.

II. MATERIAL AND METHODS

A. Materials

Cyanex272, Iron (III) chloride hexahydrate (FeCl₃•6H₂O), iron (II) chloride tetrahydrate (FeCl₂•4H₂O), sodium hydroxide (NaOH), hydrochloric acid (HCl, 35wt.%), nitric acid (HNO₃, 63wt.%), polyethylene glycol-6000 (PEG-6000) were purchased from Merck, Germany. pH of the working solutions was regulated by addition of HNO₃ or NaOH solution. All the reagents used were of analytical-reagent grade and used as received. Ultrapure deionized water was obtained using the ELGA LabWater (UK) water purification system in our laboratory and was used to prepare all the solutions.

B. Reagent

Cyanex272 was kindly supplied by Cytec, Holland. The active component is bis (2,4,4-trimethylpentyl) phosphinic acid (M.W 290; density 0.95g.cm⁻³) having the following structure (Cyanex 272- Technical Brochure, 1989).

III. RESULTS AND DISCUSSIONS

3.1. Physicochemical characterization

3.1.1. X-ray power diffraction

Fig. 1.shows the XRD pattern of the sample, which is quite identical to pure magnetite and matched well with that of it, indicating that the sample has a cubic crystal system. Also, we can see that no characteristic peaks of impurities were observed. The mean particle diameters were also calculated from the XRD pattern according to the line width of the plane refraction peak using Scherrer Eq. (2):

$$D_c = K\lambda / (b \cdot \cos^2 \theta) \quad (2)$$

The equation uses the reference peak width at angle θ , where λ is the X-ray wave length, b is the width of the XRD peak at half height and K is a shape factor, about 0.89 for magnetite. The crystal structures of as-synthesized MNPs and MNPs-PEG were characterized by XRD and the results are presented in Fig. 1. and 2. The XRD patterns show the characteristic peaks for Fe₃O₄ at 30.1 (220), 35.5 (311), 43.1 (400), 53.4 (422), 57.0 (511) and 62.6 (440), which are in agreement with the database in JCPDS file (PCPDFWIN v.2.02, PDF No. 85-1436). The diffraction peaks reveal that the MNPs are pure Fe₃O₄ with a spinel structure (Fig. 1). Also Fig. 2.shows XRD result of MNPs-PEG and that their size is 19 nm.

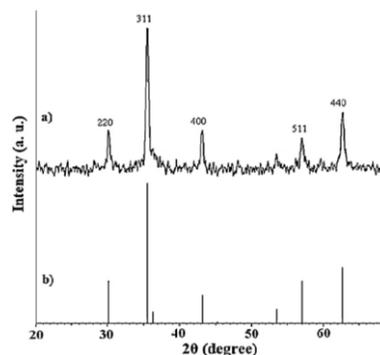


Fig. 1 the XRD pattern of pure nanoparticles (b) and pure synthesized magnetic nano particles

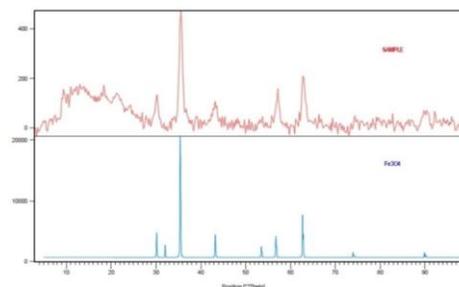


Fig. 2.the XRD pattern of nanoparticles with coated PEG (below) and coated PEG synthesized magnetic nanoparticles

3.1.2. FT-TR spectra of Fe₃O₄ nanoparticles with PEG

The presence of PEG layer on nanoparticle surface was more characterized by FT-IR spectroscopy as shown in Fig. 3. FT-IR spectra of PEG-6000 and unmodified nanoparticles are demonstrated in Fig. 3a and c for comparison. The -C-O-C-

ether stretch band and the vibration band (antisymmetric stretch) are appeared in PEG spectrum at 1101.1 cm⁻¹ and 1349.4 cm⁻¹, respectively (Gupta and Wells, 2004). Besides, the absorption bands of 1281.3 cm⁻¹ and 1468.8 cm⁻¹ attribute to the vibration of -CH₂ (Hu et al., 2008) and that around 953.2 cm⁻¹ corresponds to -CH out-of-plane bending vibration. The transmittance band at 578.1 cm⁻¹ of Fig. 3c is the stretching mode of Fe-O in Fe₃O₄ (Ahmadi et al., 2011). The broad peak near 3450 cm⁻¹ in both spectra of PEG and iron oxide belongs to attached hydroxyl groups (Gupta and Wells, 2004). The PEG modified nanoparticle spectrum in Fig. 3b comprises the main absorbance of ether stretch band at the 1104.6 cm⁻¹ and -CH₂ vibrational band at 1260.8 cm⁻¹ and 1411.5 cm⁻¹. This spectrum verifies that PEG can be found on the surface of synthesized nanoparticles. However, the characteristic absorbance peaks show a small shift to lower frequencies due to changing the environment of PEG added layer (Gupta and Wells, 2004). Effective chemical bonding likely leads to such a phenomenon (Basti et al., 2010). Similarly, shift of Fe-O vibration of coated nanoparticles to 598.2 cm⁻¹ suggests the new band formation between iron oxide surface and PEG coating (Kim et al., 2010).

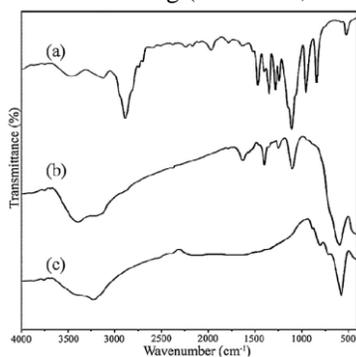


Fig. 3. FTIR spectrum of (a) PEG-10000, (b) PEG-coated and (c) bare iron oxide nanoparticles.

3.1.3. FT-TR spectra of Fe₃O₄ nanoparticles coated Cyanex272

The FT-IR spectra of Cyanex 272 and its sodium salt synthesized in laboratory were analysed and compared (Fig. 4 and 5). The FT-IR spectra of Cyanex 272 show bands corresponding to vibrations of phosphinic moiety: the P=O stretching bands at 1170 cm⁻¹ and the P-OH band at 1048 cm⁻¹. The O-H moiety gives the broad bands at 3351, 2699 and 2294 cm⁻¹ corresponding to the bonded O-H vibrations and the broad band at 1695 cm⁻¹ representing O-H deformation vibrations. The spectrum also shows a strong band at 960 cm⁻¹ which is assigned to the P-O-H group.

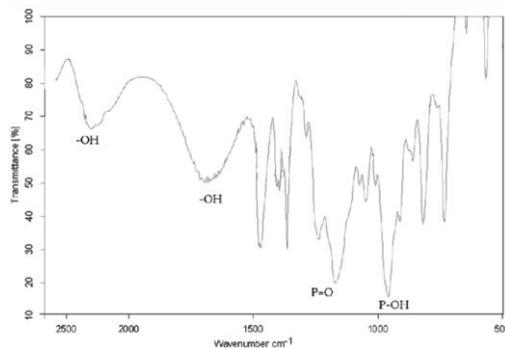


Fig. 4. FT-IR spectra of the organic phase of Cyanex 272.

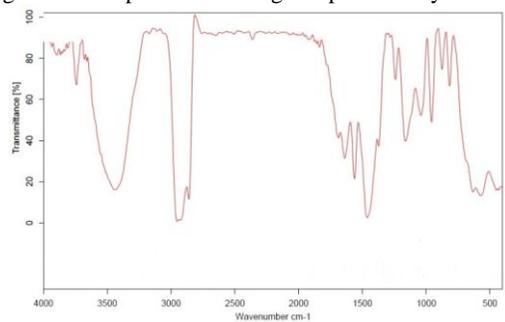


Fig.5. FT-IR spectra of the nanoparticles coated

3.2. Effect of HNO₃ concentration Variation on the uptake of Th (IV) with Cyanex272-coated magnetic particles

The HNO₃ concentration variations effect on the adsorption of Thorium (IV) onto Cyanex272 coated magnetic nanoparticles was investigated using 50 mg.L⁻¹ of Thorium (IV) concentration for an aqueous phase acidity range of 0.1 to 5 molar at 25°C for 180 min. The results are shown in Fig. 6. The Thorium (IV) removal efficiency was strongly depended on pH of the solution. The removal efficiency decreased with increasing HNO₃ concentration to a maximum value (0.5 M) and then declines slowly. The efficiency remains up to 87% with further increase up to 0.5 M. Hence it has a good adsorption capability in the range of 0.1 to 0.5. The removal efficiency of Th (IV) decreases remarkably with increasing HNO₃ concentration.



Where HA is Cyanex272.

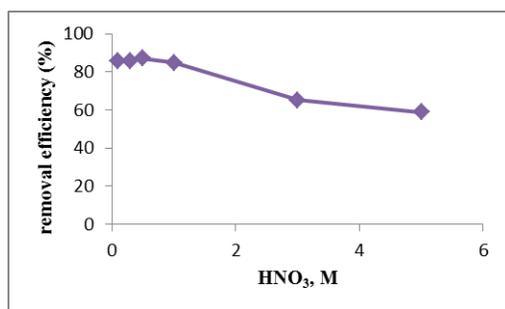


Fig. 6. Effect of the HNO₃ concentration variations on the adsorption of Thorium (IV) ([Th⁴⁺] = 50 mg/L, adsorbents = 5mg, and T=25°C).

In strong acidic solutions (less than 0.5M), more protons will be able to protonate amine groups to form -NH₃⁺ groups on the Cyanex272 surface, reducing the number of binding

sites for the adsorption of Th^{4+} due to electrostatic repulsion, as a result, the removal efficiency of Thorium decreases a little in strong acidic solutions (less than 0.5M). The hydrolysis of Th^{4+} ions plays important role in determining the equilibrium between Thorium (IV) in solution and on adsorbent. It can be explained that pH plays an important role in dissociating proton of functional groups, resulting in more negatively charged functional groups, and the capacity of combination between functional groups and Th (IV) can also be enhanced. However, when the aqueous phase acidity is higher than a certain value, (greater than 0.5 M) OH^- itself has a tendency to combine with Th (IV), and it competes with functional groups on the adsorbent for metal ions, leading to the decrease of the adsorption capacity (Wang and Chen, 2009). The optimal HNO_3 concentration of 0.5 M was selected for further study in the other experiments.

3.3. Effect of Adsorbents Dose on the uptake of Th with Cyanex272-coated magnetic particles.

The effect of adsorbents concentration on the adsorption removal efficiency was studied by contacting a variety of adsorbent dose (1, 2, 3, 4, 5 and 6 mg.L^{-1}) at a constant temperature (25°C) and 0.5 M HNO_3 using 50 mg.L^{-1} of Thorium (IV) concentration for 140 min. The results are shown in Fig. 7. The removal efficiency of Thorium (IV) increased with increasing adsorbents concentration in the aqueous solution. The adsorption surface area gets larger with increasing of the mass of the adsorbents. C272-MNPs adsorbent showed greatest results, even at the lowest concentration (1 mg.L^{-1}), the removal efficiency was more than 55%. The efficiency increases up to 87% when the concentration of the adsorbent is 5 mg.L^{-1} .

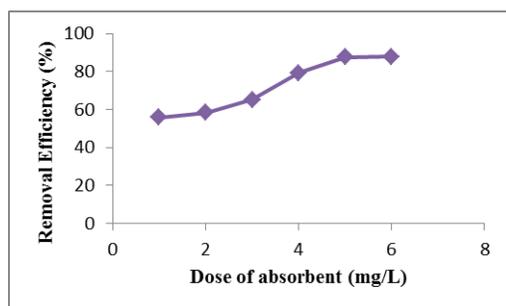


Fig. 7. The adsorption removal efficiency for variable dose of adsorbent, Thorium ($[\text{Th}^{4+}]$ at 50 mg/L , at 0.5 M HNO_3 and $T=25^\circ\text{C}$, 140 min).

3.5. Effect of Thorium Concentration on the uptake of Th with Cyanex272-coated magnetic particles

The effect of Thorium concentration on the adsorption removal efficiency was studied by contacting a fixed dose of adsorbent (5 mg.L^{-1}) for 140 minutes at a fixed temperature (25°C) and 0.5 M HNO_3 using a variety of Thorium concentrations (10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130 and 140 mg.L^{-1}). The results are shown in Fig. 8 and 9. The removal efficiency of Thorium decreased from 87% to 60% with increasing Thorium concentration in the aqueous solution. This phenomenon can be explained since adding more mass of Thorium into the system will increase the initial Thorium concentration in the aqueous solution, but the

amount of the adsorbent remains the same. The adsorption capacity Q , was calculated based on the difference of Thorium concentration before and after adsorption. The adsorption capacity of adsorbents for Thorium increased with increase of Thorium concentration, as the amount of the adsorbent remains unchanged. From the Fig. 8., it can be deduced that the maximum adsorption capacity for Th was about 48 mg per gram adsorbent at Thorium concentration. This gives a removal efficiency of 87%.

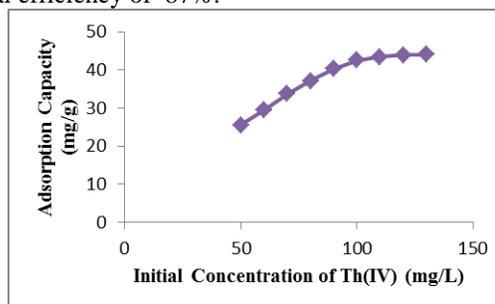


Fig. 8. The adsorption capacity under variable Thorium (IV) concentration; 5 mg adsorbent amount, 0.5 M HNO_3 , and $T=25^\circ\text{C}$, 140 min)

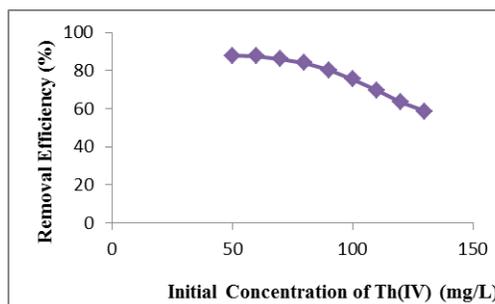


Fig. 9. The adsorption removal efficiency under variable Thorium (IV) concentration adsorbents; 10 mg adsorbent amount, 0.5M HNO_3 , and $T = 25^\circ\text{C}$.

Hudson and Matejka, (1989) applied polymeric microspheres for heavy metal adsorption, and found that the adsorption capacities were just between 14.4 and 24.6 mg/g Erdal et al. (2009) used polyethyleneglycol-methacrylate (PEGMA)-co-vinylimidazole (VI) microspheres as adsorbents and found that its adsorption capacity was only 25 mg/g for heavy metals. Compared with the data mentioned above, the C272-MNPs performs better in the treatment of Th (IV) in solution. It can be further indicated that the C272-MNPs has a good potential as adsorbent for the treatment of other metals.

IV. CONCLUSION

In this work, C272-MNPs was synthesized and characterized as a new adsorbent for Th (IV) adsorption from aqueous solution. The adsorbent was prepared on the surface of Cyanex272-coated magnetic nanoparticles. The batch adsorption experiments have proven that the removal efficiency of Th (IV) adsorbed by C272-MNPs was enhanced on the surface of Cyanex272-coated magnetic nanoparticles. The C272-MNPs was shown to be efficient adsorbent for the adsorption of Th (IV) from aqueous solution at HNO_3 concentration values from 0.1 to 5 M HNO_3 , with maximum

adsorption removal efficiency at 0.5 M. In addition, more than 85% of Th (IV) ions were removed by 5 mg of C272 -MNPs within the first 2 hours, and the time required to achieve the adsorption equilibrium was only 140 minutes.

Magnetic nanoparticles were synthesized rapidly. The application of magnetic nanoparticles in extraction processes allows fast and cost effective extraction from the reaction mixture without filtration or centrifugation, therefore representing a gentle, versatile, scalable, and easy to automate separation process.

REFERENCES

- [1] S.E. Mathews, P. Parzuchoski, A. Garcia-Carrera, C. Gruttner, J.F. Dazol, V. Bohmer, *Chem. Commun.* 5 (2001) 417.
<http://dx.doi.org/10.1039/b009679m>
- [2] M.D. Kaminski, L. Nunez, *Sep. Sci. Technol.* 37 (2002) 3703.
<http://dx.doi.org/10.1081/SS-120014828>
- [3] F.A. Aydin, M. Soylak, A novel multi-element coprecipitation technique for separation and enrichment of metal ions in environmental samples, *Talanta* 73 (2007) 141–147.
<http://dx.doi.org/10.1016/j.talanta.2007.03.007>
- [4] Y.K. Agrawl, P. Shrivatav, S.K. Mnom, Solvent extraction separation of uranium (VI) with crown ether, *Sep. Purif. Technol.* 20 (2000) 177–183.
[http://dx.doi.org/10.1016/S1383-5866\(00\)00110-6](http://dx.doi.org/10.1016/S1383-5866(00)00110-6)
- [5] A.T. Kuhu, *Electrochemistry of Cleaner Environments*, Plenum Press, New York, 1972.
- [6] M.L. Dietz, H.E. Philip, L.R. Sajdak, R. Chiarizia, An improved extraction chromatographic resin for the separation of uranium from acidic nitrate media, *Talanta* 54 (2000) 1173–1184.
[http://dx.doi.org/10.1016/S0039-9140\(01\)00390-3](http://dx.doi.org/10.1016/S0039-9140(01)00390-3)
- [7] A.C. Ladeira, C.A. Morais, Uranium recovery from industrial effluent by ion exchange-column experiments, *Miner. Eng.* 18 (2005) 1337–1340.
<http://dx.doi.org/10.1016/j.mineng.2005.06.012>
- [8] T.P. Rao, P. Metilda, J.M. Gladis, Preconcentration techniques for uranium (VI) and thorium (IV) prior to analytical determination, *Talanta* 68 (2006) 1047–1064.
<http://dx.doi.org/10.1016/j.talanta.2005.07.021>
- [9] A.M. Donia, A.A. Atia, E.M. Moussa, A.M. El-Sherif, M.O. Abd El-Magied, Removal of uranium (VI) from aqueous solutions using glycidyl methacrylate chelating resins, *Hydromet.* 95 (2009) 183–189.
<http://dx.doi.org/10.1016/j.hydromet.2008.05.037>
- [10] Y. Jung, S. Kim, S. Park, J.M. Kim, Application of polymer modified nanoporous silica to adsorbents of uranyl ions, *Colloids. Surf. A* 31 (2008) 162–166.
<http://dx.doi.org/10.1016/j.colsurfa.2007.04.087>
- [11] Bargar, J.R., R. Reitmeyer, J.A. Davis, 1999. Spectroscopic confirmation of uranium(VI) –carbonate adsorption complexes on hematite. *Geochimica et Cosmochimica Acta*, 33: 2481–2484.
<http://dx.doi.org/10.1021/es990048g>