

Magnetic Gels for Uranium Recovery from Wet Phosphoric Acid

by

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Submitted to the Department of Chemical Engineering in partial fulfillment of the requirements
for the degree of

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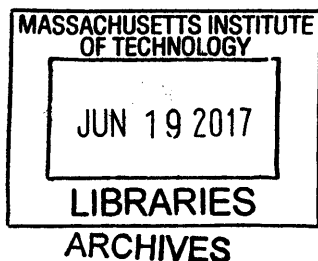
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ABSTRACT

Incorporation of uranium recovery into wet phosphoric acid (WPA) processes can potentially supplement a significant portion of the world's uranium production and simultaneously benefit human health and environment by reducing radiological and toxic contamination of the phosphate fertilizer products. Liquid-liquid extraction as conventional uranium recovery methods applied in industrial suffers from various processing challenges, such as large consumption of combustible carriers, incomplete demulsification, interference with humic matters and crud formation. The aim of this thesis is to develop novel solid state gel-based materials suitable for recovery of uranium from industrial wet phosphoric acid. The materials developed can serve as the foundation of developing alternative processes to overcome limitations within liquid-liquid extraction for uranium recovery.

Two types of materials -- magnetic organo-hydrogel and magnetic lyogel were developed and tested to be capable of extracting uranium selectively from the OCP phosphoric acid samples. The materials demonstrated sufficient structural stability, magnetic recoverability, similar uranium uptake performance as liquid-liquid extraction. Compared with magnetic organo-hydrogel, the lyogel exhibited reduced amount of extractant loss and better recyclability. Therefore, the magnetic lyogel can serve as the foundation on which novel uranium extraction processes to be designed in the future.

Thesis Supervisor: T. Alan Hatton

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1. MOTIVATION

Uranium is mainly used as a nuclear fuel for generating electricity and providing propulsion for aircraft, ships and so forth. Besides, its radioisotopes have many applications in medical fields such as imaging and treatment of cancer. The recovery of uranium from its ores requires successive hydrometallurgical operations including leaching, solvent extraction/ion exchange, stripping and precipitation^[1]. The final partially refined product with a uranium content exceeding 65% is normally termed “yellow cake”. However, as the result of the depleting uranium ores and rapid development of the nuclear industry worldwide, it is estimated that the current mining of uranium will no longer meet the demand in the next few decades^[2]. Because of this imbalance between supply and demand, there is a big incentive to explore additional sources for uranium production.

Phosphate rocks appears to be one of the most attractive unconventional sources of uranium with the potential to supply a big portion of worldwide uranium production^[3]. The content of uranium in phosphate rocks vary considerably depending on the origin of the ore as shown in Table 1-1^[2]. Among major phosphate rock resources, Morocco phosphate contains the highest content of uranium at a level between 100 and 200 ppm. If this part of the uranium is properly recovered, morocco can produce at least 3000 tons phosphorite uranium annually.

Table 1-1. Uranium content in phosphoric rocks

Uranium Content	Origin				
	Russia	S. Africa (Phlaborwa)	Morocco (Khouribga)	United States (Florida)	Senegal
U ₃ O ₈ (ppm)	11	134	185	101	124

In addition to supply security and diversification, uranium recovery from phosphoric rocks also brings environmental benefits. Phosphate rocks contains about 16 elements that are potentially hazardous to human health, including uranium. Neither beneficiation nor acid leaching is capable of separating uranium out of the phosphoric acid. If uranium follows phosphoric acid into downstream fertilizer production, it will eventually be distributed within the environment and cause severe radiological and toxic threats to human health and even to the entire ecological system. Therefore, it is imperative that effective uranium separation technologies are developed and implemented during phosphoric acid processing to eliminate these risks^[3,4].

2. BACKGROUND

2.1 Uranium Material Flow in the WPA Production Process

WPA production involves leaching phosphate mineral concentrate with hydrochloric, nitric or sulfuric acid from the phosphate rock, which is the only economically viable source of uranium^[5]. Phosphate rocks that contain recoverable uranium in the ppm range are found throughout the world, with Morocco accounting for approximately 80% of the phosphate rock uranium resources^[6]. On the industrial scale, solvent extraction and precipitation processes have been implemented for the uranium recovery from WPA, with the solvent extraction dominating the field. The leaching stage of the WPA process always involves solubilization of various impurities including uranium, cadmium, arsenic, fluorine, etc. into the phosphoric acid, which must then be purified by either extracting the impurities from the WPA leachate, or extraction of the phosphoric acid itself from the leachate. Solvent extraction technology is primarily used to separate and purify uranium from aqueous leachates that have been separated from the gypsum (CaSO_4) and other solids formed in the process of the acid leaching^[6]. The uranium found in the WPA leachate is present as a mixture of its hexavalent and tetravalent forms.

2.2 Recovery of Uranium from WPA by Solvent Extraction Process

Ever since the 1950s, various technologies such as solvent extraction^[2], precipitation^[7], ion-exchange resins^[8-10] have been developed to recover uranium from wet phosphoric acid. Among these technologies, only solvent extraction was widely applied at the industrial scale. In the 1950s through the late 1990s, three solvent extraction processes namely OPPA, D2EHPA/TOPO, and OPAP were implemented industrially in United States, Canada, Belgium, Taiwan and Iraq^[2].

The plant with the highest annual capacity of uranium reported to be 500 t/year^[11] was built by International Minerals & Chemical Corp using D2EHPA/TOPO process.

The extractants employed in these three processes were all organophosphorus compounds, either used individually as cation exchanger or together with a synergistic solvating agent to increase the hydrophobicity of the extracted uranyl complexes as well as to remove the water molecules solvating the metal ion. The chemical structures of these extractants employed in conventional solvent extraction processes are shown in Figure 2-1.

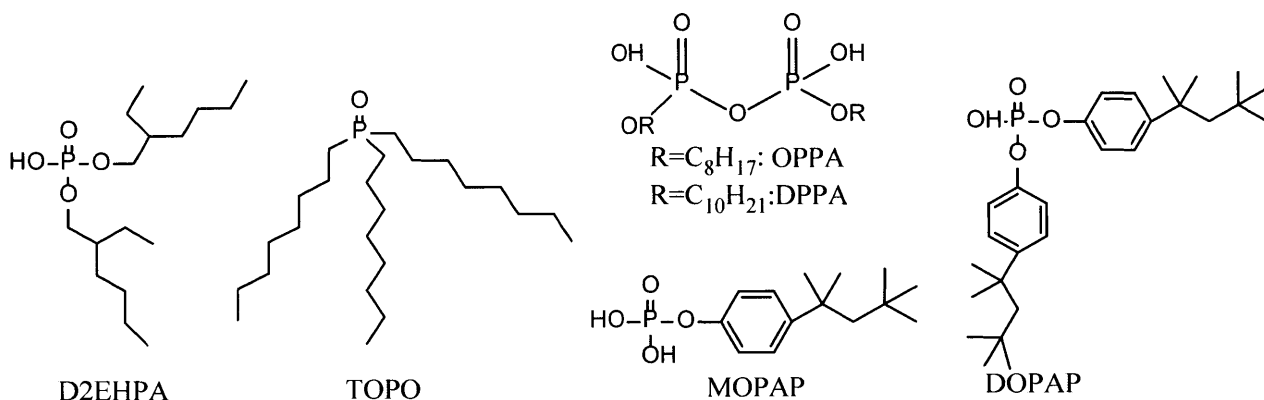
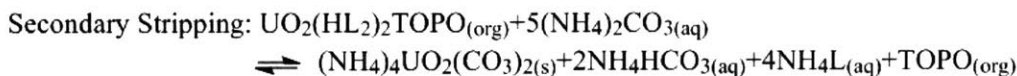
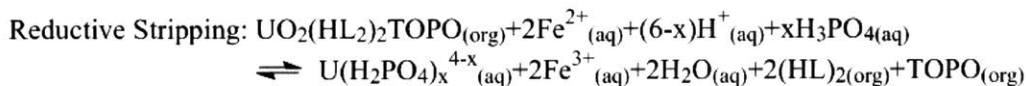
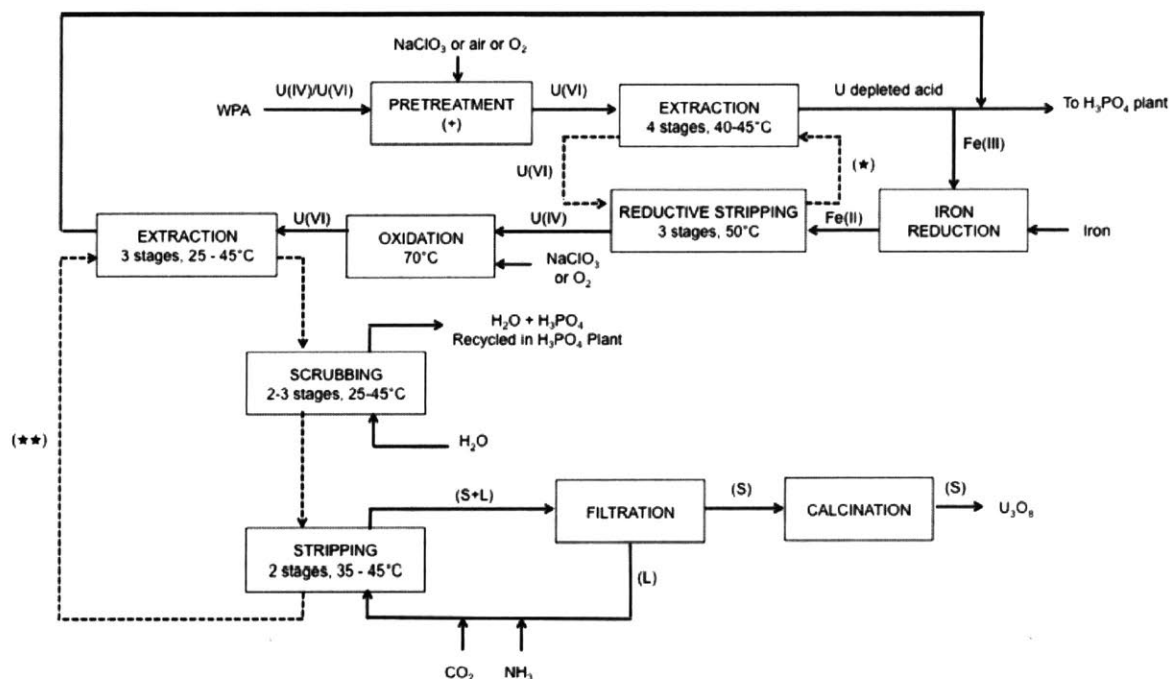


Figure 2-1. Chemical structure of conventional uranium extractants

2.2.1 D2EHPA/TOPO Process

At the end of 1960s, the Oak Ridge National Laboratory developed a two-cycle uranium recovery process using bis(2-ethylhexyl)-phosphoric acid (D2EHPA) and tri-n-octylphosphine oxide (TOPO) diluted in kerosene as the extractant^[12, 13]. In a typical D2EHPA/TOPO process, the uranium from WPA is first oxidized to uranium (VI) by NaClO₃ or air and then extracted by four mixer-settlers. The uranium-laden extract is then reductively stripped by a portion of iron treated phosphoric acid raffinate. After uranium (IV) is reoxidized to uranium (VI), a second cycle of liquid-liquid extraction is implemented with three mixer-settles to recover nearly 99% of

the uranium. The extraction solvent is then scrubbed by water with three mixer-settlers and stripped by ammonium carbonate with another two mixer-settlers. The product precipitated is ammonium uranyltricarbonate $(\text{NH}_4)_4\text{UO}_2(\text{CO}_3)_3$, which is then filtered, washed with ammonium hydroxide and calcined to U_3O_8 . The flowsheet of the D2EHPA/TOPO process and related chemical reactions during extraction and stripping are shown in Figure 2-2.



HL: the cation exchanger extractant D2EHPA

Figure 2-2. Flowsheet of the Oak Ridge D2EHPA/TOPO process and related reactions. (*) 0.5M D2EHPA+0.125M TOPO in kerosene, (**) 0.3M D2EHPA+0.075M TOPO in kerosene

2.2.2 OPAP Process

The OPAP process (Figure 2-3) utilizes a mixture of mono- and dioctylphenyl phosphoric acid (MOPAP and DOPAP) diluted in kerosene to extract uranium from WPA^[14, 15]. In this process, the uranium is first reduced to uranium (IV) by iron powder and further extracted by 0.3-0.4mol/L OPAP diluted in kerosene at 40-45°C in four mixers-settlers. The extract laden with uranium then undergoes oxidative stripping in three mixers-settlers by a stripping solution containing 10M H₃PO₄ and sodium chlorate. Even though OPAP extractant chelates uranium more strongly than D2EHPA/TOPO, its selectivity towards iron (III) is low. Consequently, the OPAP process is often accompanied by a second liquid-liquid extraction stage using a mixture of 0.3M D2EHPA and 0.075M TOPO as in the Oak Ridge process to achieve sufficient separation of uranium from iron. And there is a potential risk of contamination of the second extraction loop by entrainment losses from the first extraction loop.

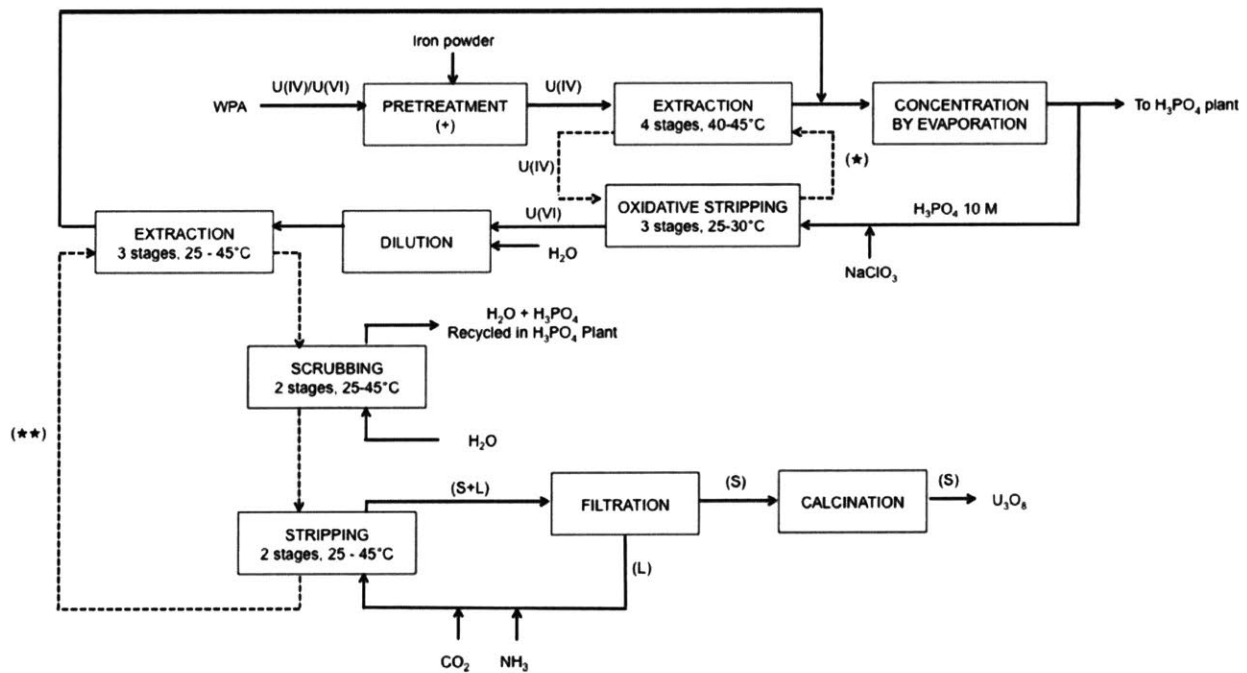


Figure 2-3. Flowsheet of the OPAP process (*) 0.3-0.4M OPAP in kerosene, (**) 0.3M D2EHPA+0.075M TOPO in kerosene

2.2.3 OPPA Process

Didecylpyrophosphoric acid (DPPA) and dioctylpyrophosphoric acid (OPPA) (Figure 2-1) are commonly used in the industrial OPPA process for uranium recovery from WPA^[16]. The uranium is reduced to uranium (IV) first before getting extracted by 3 vol.% OPPA diluted in kerosene in four mixer-settlers. The uranium laden solvent was then reacted with hydrofluoric acid to precipitate hydrated uranium tetrafluoride ($UF_4 \cdot 2H_2O$). Further purification of $UF_4 \cdot 2H_2O$ is necessary to obtain nuclear grade uranium product. A typical purification process includes nitric acid leaching, solid/liquid separation, solvent extraction using tributyl phosphate (TBP), scrubbing with water and stripping with ammonia to produce ammonium diuranate $(NH_4)_2U_2O_7$. The distribution ratio of uranium (IV) between the organic phase containing OPPA diluted in kerosene and WPA is 3-4 times higher than that obtained with OPAP and about 10-25 times higher than that obtained with D2EHPA/TOPO^[17]. Despite the high distribution ratio of uranium, the readily degradation of OPPA by hydrolysis into monoalkylorthophosphoric acids significantly limits the application of the process^[18].

2.2.4 Development of New Extractants

Considerable research has been focused on developing new synergistic extractants (i.e., cation exchanger and solvating agent) with improved selectivity and efficiency to chelate low concentration uranium from WPA.

For the study related to cation exchangers, researchers have mainly focused their attention on phosphorus compounds including bis(2-ethylhexyl) phosphinic acid (B2EHPA)^[19], (2-ethylhexyl) phosphonic acid mono-2-ethylhexyl ester (PC88A)^[20] and bis(2-ethylhexyl) dithiophosphoric acid (D2EHDTPA)^[21]. Some researchers also synthesized phosphoric acids with oxygen atoms

introduced in the hydrophobic chains of the cation extractant, such as D2EHOEPA and BiDiBOPP (Figure 2-4)^[22]. The uranium extraction efficiency of these new cation exchangers in a mixture with TOPO are compared against conventional D2EHPA-TOPO pair and the results are shown in Figure 2-4. Studies illustrated that the replacement of phosphoric acid-type cation exchanger by its phosphinic and phosphonic homologues dramatically reduced the affinity towards uranium while introduction of an ether function in the hydrophobic part of the extractant increases the distribution ratio. The highest distribution ratio was achieved by replacement of the phosphoric group in the extractant by the dithio group (D2EHDTPA). However, the application of this extractant is limited by its low chemical stability in acidic media^[23].

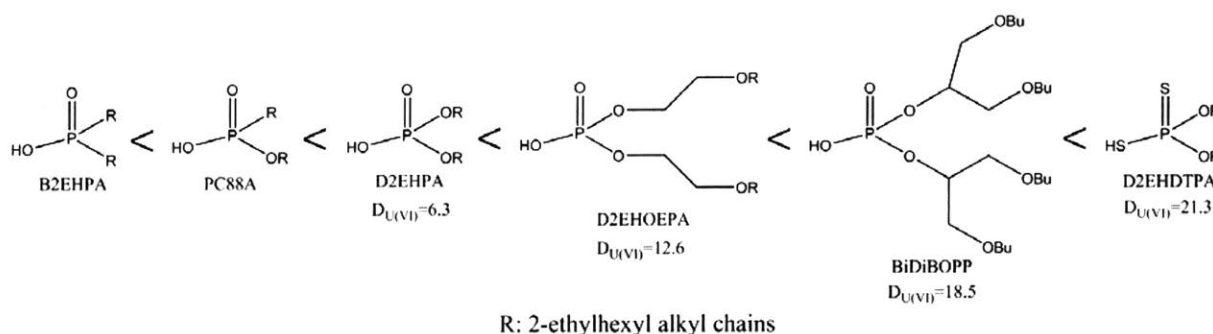


Figure 2-4. Uranium chelating performance of various cation exchangers. $D_{U(VI)}$ obtained between 6M phosphoric acid solution and 0.5M cation exchanger + 0.125M TOPO diluted in kerosene)

Studies related to the solvating agents were mainly focused on substitution of TOPO in the D2EHPA-TOPO pair with tributylphosphate (TBP)^[24], dibutyl butylphosphonate (DBBP)^[25], tributyl phosphine oxide (TBPO)^[26], tridecylphosphine oxide (TDPO)^[27]. The sequence of their uranium chelating abilities is shown in Figure 2-5. The bonding strength between uranyl ion and the solvating agents were assumed to depend on the electron-donor power of the phosphoryl

oxygen atom^[28], which explained why phosphate (TBP) and phosphonate (DBBP) type of extractant exhibited lower distribution ratio than their phosphine oxide homologues. Besides, the increase in the length of the alkyl chain of trialkylphosphine oxide will increase the basicity of the phosphoryl oxygen and therefore improve its affinity towards uranium. Researchers also demonstrated that substitution of TOPO with HMOPO^[29] in which one oxygen atom is introduced into one of the alkyl chains of the phosphine oxide increased the distribution ratio of uranium by 1.5 while introducing oxygen atom at all of the three alkyl chains would result in a twice lower chelation efficiency^[27].

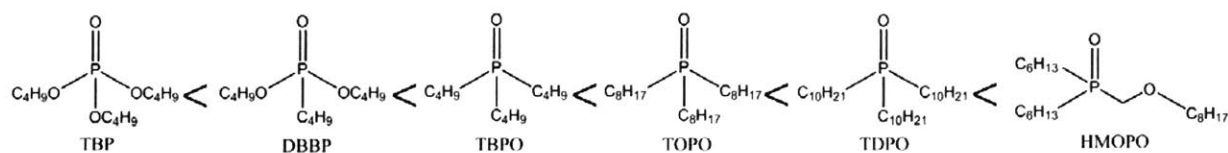


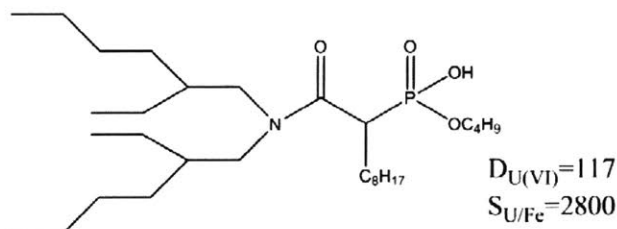
Figure 2-5. Uranium chelating performance of various solvating agents

Based on the result of these research, the Cogema (a nuclear fuel reprocessing plant in La Hague) investigated the uranium extraction performance using BiDiBOPP/HMOPO and achieved 4 times higher uranium concentration in the organic phase than the case with D2EHPA/TOPO^[29]. However, the selectivity of this new synergistic extractants towards iron (III) in the WPA was much lower than D2EHPA/TOPO, which resulted in 2.5 times higher iron content in the extraction solvent. Additional washing by phosphoric acid and sulfuric acid was necessary to scrub out the iron entrained. Comparison between the distribution ratios of uranium (VI) and selectivity towards iron (III) of the two extractant mixtures are summarized in Table 2-1.

Table 2-1. Comparison between D2EHPA/TOPO and BiDiBOPP/HMOPO

Cation Exchanger (0.5M)	Solvating Agent (0.125M)	Solvent	$D_{U(VI)}$	$D_{Fe(III)}$	$S_{U/Fe}$
D2EHPA	TOPO	kerosene	4.47	0.04	112
BiDiBOPP	HMOPO	kerosene	21.3	0.47	46

More recently, researchers discovered a carbamoylphosphonic acid type extractant (BDEHCNP) that is capable of obtaining 90 times higher uranium recovery efficiency and 150 times higher selectivity towards iron (III) from 5M phosphoric acid containing 250ppm U(VI) and 2500ppm Fe(III)^[30]. The extractant with a concentration of 0.25mol/L diluted in dodecane was utilized to perform the extraction and the stripping of uranium from the organic phase was achieved by simply contacting the extracting solvent with ammonium carbonate solution. The structure of this new type of extractant and its uranium extracting performance are shown in Figure 2-6.



Butyl-*N,N*-bis(2-ethylhexyl)carbamyl nonyl phosphonate (BDEHCNP)

Figure 2-6. Chemical structure and uranium extraction performance of BDEHCNP

2.2.5 Challenges with Solvent Extraction

There are several challenges remaining in the development of processes to recover uranium from WPA by solvent extraction.

An important issue with solvent extraction is the interference of humic materials liberated from the phosphate rock during acid leaching^[11]. When phosphoric acid containing humic matters is contacted with kerosene, the humic acid is partly extracted and an oily, viscous emulsion known as “gunk” forms on the interface between aqueous and organic layers. The gunk collected at the interface of the mixer-settler results in not only high losses of expensive extractant, but also low kinetics of extraction and larger size of equipment. To avoid build-up of the gunk, humus is removed from the acid at additional cost by using activated carbon columns before extraction.

Due to limitation in interfacial area as well as mass transfer in conventional extraction process, large amount of organic phase is utilized to achieve sufficient stage efficiency. As an example, the flow ratio applied in the D2EHPA/TOPO process is between 1 and 1.5 (O/A)^[11]. Considering the capacity of the phosphoric acid produced on-site, operating with such a phase ratio means significant consumption of kerosene which will end up as secondary organic waste. Additionally, processing large quantity of kerosene would require bulky equipment and induce safety concerns to the process. As a result, novel extraction processes with enhanced mass transfer and interfacial area needs to be developed to reduce the amount of solvent.

Other issues to be considered when developing new extraction processes include emulsification, cross contamination of WPA with organic solvents and extractants, and formation of third phase caused by the limited solubility of the metal-ligand complex in the nonpolar phase^[31].

2.3 Recovery of Uranium from WPA by Ion-Exchange Resin

The use of solid ion-exchange resin for the recovery of uranium from WPA has also become attractive in the past few years. Compared with liquid-liquid extraction, ion-exchange processes have the potential to treat WPA containing uranium at very low concentration. Additionally, the

chelating efficiency is less sensitive to temperature and therefore no additional cooling of the WPA is required. Finally, there is no solvent contamination issues with ion exchange.

Bayer AG synthesized a series of composite resins impregnated with D2EHPA/TOPO and D2EHPA/TBP but their capacity to recover uranium from WPA was tested to be limited (1-3g of U/kg resin) and the rate of uptake was very low^[10]. Researchers later found that Duolite ES467, a macroporous copolymer of styrene-divinylbenzene with amino phosphonic functional groups, was capable to achieve 4-6 times higher uranium loading^[32]. A pilot plant was built at the Nagev Nuclear Research Center^[11] to verify and confirm laboratory results with Duolite ES467 on a larger scale. The related process was called the Israeli process, its flowsheet as well as the chemical structure of the resin utilized are shown in Figure 2-7. In the Israeli process, the uranium (VI) and iron (III) in WPA were first reduced by iron powder to uranium (IV) and iron (II), the stream was then filtered and directed through the ion-exchange column where extraction took place. The absorbed uranium was then oxidized with raw phosphoric acid after which the resin was washed by water and neutralized by ammonia. Stripping of the absorbed uranium was finally conducted with aqueous ammonium carbonate solution and yellow cake was then precipitated and purified. Preliminary economic analysis showed that the overall expense of the Israeli process was approximately half of an equivalent solvent extraction plant^[10].

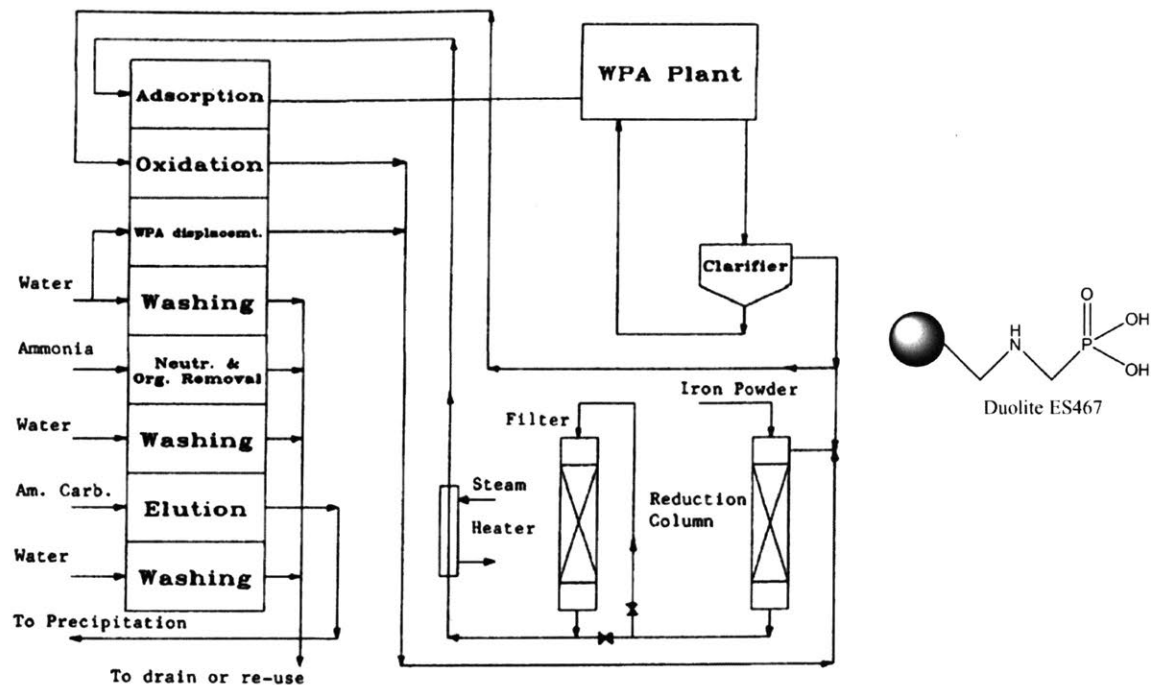


Figure 2-7. Flowsheet of the Israeli process and chemical structure of the Duolite ES467 resin

Kabay et al.^[8] evaluated the uranium extraction ability of various chelating ion-exchange resins containing phosphonic acid groups (RSPO), phosphinic groups (Diaion-CRP200), aminophosphonic acid groups (Purolite S940, Lewatit OC 1060), silica-based diphosphonate groups (Actinide-CU) as well as sulfonic and gem-diphosphonic acid groups (Diphonix). Among all these resins, only Actinide-CU gave quantitative adsorption of uranium (28%) from concentrated phosphoric acid (40%). Even so, the resin barely reached saturation after 24hrs in contact with the acid, suggesting slow kinetics in uranium uptake.

Several advances in developing new ion-exchange resins and processes have been done recently. Dow Chemical used Amberlite IRC747 resin to recover uranium from WPA and achieved higher uranium loading and elution efficiency than Duolite ES467. Charlot et al.^[33] grafted a tridentate carbamoylphosphonate ligand within the pores of mesoporous silica (SBA15). The hybrid

material was distinguished by high available surface area due to its inorganic framework and high selectivity of uranium towards iron in a range of H_3PO_4 concentration up to 1 mol/L. However, the uranium extraction capacity of this material was tested to be 10 times lower than resins studied by Kabay *et al.* Urtek^[34] developed a different ion-exchange resin process for uranium recovery from WPA where iron (III) present in the WPA was precipitated by using ammonia before uranium extraction. It was reported that this process was capable of producing U_3O_8 at 20-30 \$/lb, whereas conventional solvent extraction was operating at a cost of 40-80\$/lb.

Despite the considerable research focused on developing efficient extractant-loaded resins for uranium recovery, no continuous ion exchange processes has been developed and implemented in industry due to several limitations. First, the resins developed so far does not possess sufficient chemical stability in concentrated WPA and is susceptible to degradation. Besides, most of the resin possess higher ionic affinity towards common impurities present in WPA such as Fe^{3+} and Al^{3+} . Once poisoned with these competing ions, the capacity of the resin will be dramatically decreased. Additionally, as the resin beads will float on WPA due to their lower density, packed bed operation is often required and problems such as channeling and plugging are likely to occur and affect the performance. Finally, since most of the resins developed are hydrophobic in nature, the accessibility of uranyl to complexation sites embedded inside the organic backbone of the commercial resins is limited.

2.4 Magnetically Assisted Chemical Separation (MACS) of Uranium

The concept of magnetically assisted chemical separation (MACS) was introduced first by Argonne National Laboratory. The process utilized poly bis-acrylamide coated magnetite particles with an absorbed layer of octyl(phenyl)-N,N-diisobutylcarbamoymethylphosphine

oxide (CMPO) diluted with tributyl phosphate (TBP) for separation and recovery of americium and plutonium from nuclear waste solutions^[35]. The particles loaded with target molecules could be magnetically collected from the extracting medium and then stripped with a small amount of liquid before the particles were transferred back for reuse in the next cycle of extraction. Following this work, considerable research have been conducted on developing magnetic nanoparticle-polymer hybrid materials which are functionalized with appropriate ligands to recover uranium in aqueous solutions such as nitric acid, hydrochloric acid, sea water, ground water and blood.

In 2003, the Argonne National Laboratory used the same polymer coated particle and load it with CMPO, TBP, TOPO and D2EHPA to extract uranium from nitric and hydrochloric acid at different concentrations^[36]. The equivalent distribution ratio achieved by the MACS particles was three orders of magnitude higher than those attained by solvent extraction and this was explained by a hypothetical synergistic interaction between the acrylamide polymer and the absorbed extractants. The higher distribution ratio achieved by the MACS might translate into better separation over solvent extraction with less extractant necessary.

Different from the material used by Argonne National Laboratory where extractants are physically adsorbed on the particle surface, the majority of the MACS particles developed used chemical grafting of the chelating agent on the surface of magnetic nanoparticles. More recently, magnetic chitosan resins and composites incorporating graphene, carbon nanotubes, metal oxide (TiO₂ and MnO₂), and fungus were also investigated as promising uranium separation materials. Table 2-2 summarizes some of the representative designs in functional magnetic hybrid materials for uranium recovery from aqueous solutions and the corresponding conditions.

Table 2-2. Design of MACS particles for uranium recovery from aqueous solutions

Magnetic material	Coating (polymer, extractant etc.)	extraction media	Ref
Fe ₃ O ₄	3-aminopropyl trimethoxysilane (APTMS)	pH 7.0	37&38
Fe ₃ O ₄	poly(vinyl phosphonic acid)	pH 7.0	39
Fe ₃ O ₄	amidoxime modified TEOS based silica gel	pH 5.0	40
Fe ₃ O ₄	APTMS modified with calix[4]arenes containing different chelating groups	pH 5.5	41
Fe ₃ O ₄	silica and nickel-ethylene glycol	pH 6.0	42
Fe ₃ O ₄	TiO ₂	pH 6.0	43
Fe ₃ O ₄	calcium silica hydrate	pH 5.0	44
Fe ₃ O ₄	silica modified with 3-aminopropyl triethoxysilane (APS) and quercetin	ground water mineral water	45
Fe ₃ O ₄	tetraethyl-3-amino-propane-1,1-bisphosphonate	blood	46&47
Fe ₃ O ₄	fungus	nuclear waste water	48
Fe ₃ O ₄	MnO ₂ and graphene oxide	pH 6.0	49
CoFe ₂ O ₄	MWCNT	pH 6.0	50
Fe ₃ O ₄	chitosan crosslinked by glutaraldehyde	pH 5.0	51
Fe ₃ O ₄	chitosan modified with triethylene-tetramine	pH 6.0	52

Although chemical functionalization of magnetic nanoparticles has been proposed in many papers for decontamination of uranyl ion from aqueous solutions, this approach has not yet been studied for selective uranium recovery from WPA to the best of our knowledge.

2.5 Previous Work in the Research Group on Recovery of Uranium from WPA

Previously in Hatton Group, different types of functionalized magnetic nanoparticles was developed to recover uranium from 6M H₃PO₄ as well as industrial grade WPA which was synthesized according to the formula provided by the OCP group (the “OCP fluid”).

Table 2-3. Composition of the OCP fluid

H ₃ PO ₄	H ₂ SO ₄	NaF	Fe ₂ (SO ₄) ₃	Al ₂ (SO ₄) ₃	Temperature
6 mol/L	0.86% (w/v)	0.9% (w/v)	0.7% (w/v)	0.35% (w/v)	80°C

Lev et al.^[53] synthesized a composite material comprising magnetic chromium dioxide as the core and poly(vinylbenzyl chloride) grafted with CMPO as the shell. The particle was observed to be stable in the phosphoric acid solution and quantitative uranium separation from 6M H₃PO₄ was achieved (Figure 2-8). The reusability of the particle was tested and no further loss in extraction efficiency was observed after first cycle conditioning.

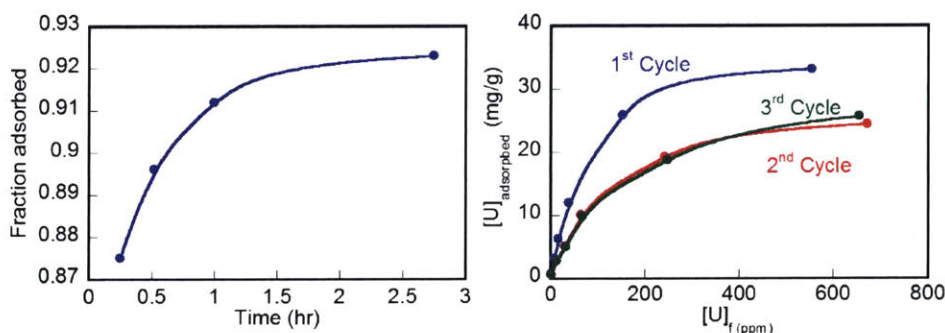


Figure 2-8. Uranium extraction performance of CrO₂-PVBC-CMPO particle

However, this particle couldn't survive the condition in the OCP fluid as the chromium dioxide dissolved and lost all magnetic properties after one week. To provide protection for the particles, Lev developed a highly crosslinked polymeric system comprising four monomers: 2,2'-diallylbisphenol A, 1,1'-(Methylenedi-4,1-phenylene)bismaleimide, vinylbenzyl chloride, and divinylbenzene. The coating of chromium dioxide nanoparticle with the polymer was conducted by using suspension polymerization and CMPO was incorporated subsequently by nucleophilic substitution reaction. The particle exhibit some but limited capability for uranium recovery from the OCP fluid. This is probably due to low loading of CMPO and limited accessibility of the uranyl binding sites embedded in the hydrophobic terpolymer network.

In order to overcome the aforementioned limitations, Lev and I cooperated together in developing a new composite material in which the magnetic core comprised of carbon coated iron nanoparticles was grafted with poly (vinylbenzyl chloride) functionalized with CMPO. The particles were tested to be sufficiently stable in the OCP fluid and easier to be dispersed than the terpolymer encapsulated particles. However, the uranium extraction ability in the OCP fluid by this kind of particle was still limited. One possible explanation is the low surface grafting density of the extractant. CMPO loading was tested to be 0.4mmol/g with this particle, which was slightly higher than the terpolymer coated particle (0.32mmol/g) but much lower than the CrO₂-PVBC-CMPO particle (1.135mmol/g). Besides, the effectiveness of CMPO in extracting uranium from OCP fluid where competing species (Fe³⁺, Al³⁺) are present at concentrations much higher than uranyl ions requires further investigation.

The results from previous work call for further development of new designs that can enable us to achieve 1) easy and efficient incorporation of whatever extractant tested to be selective in uranium recovery from the OCP fluid 2) improved accessibility of the uranyl binding sites 3)

chemical and colloidal stability in the OCP fluid 4) reusability of the solid extractant by repeated separation and resuspension of the particles.

3. URANIUM EXTRACTION WITH MAGNETIC ORGANO-HYDROGEL

3.1 Material Design

Encapsulation of nanoemulsions within a hydrogel matrix was previously studied in Prof. Doyle's lab for controlled crystallization^[54], orthogonal encapsulation and release^[55, 56]. Inspired by this design, the first kind of magnetic gel we developed for uranium recovery from phosphoric acid was magnetic organo-hydrogel. In this design, extractants were immobilized in a hydrogel matrix as nanoemulsion droplets through inter-droplet attractions induced by polymer bridging, while magnetic nanoparticles were physically incorporated throughout the gel network to enable magnetic separation and recycling of the resulting material. A schematic illustration for this composite hydrogel particle is shown in Figure 3-1.

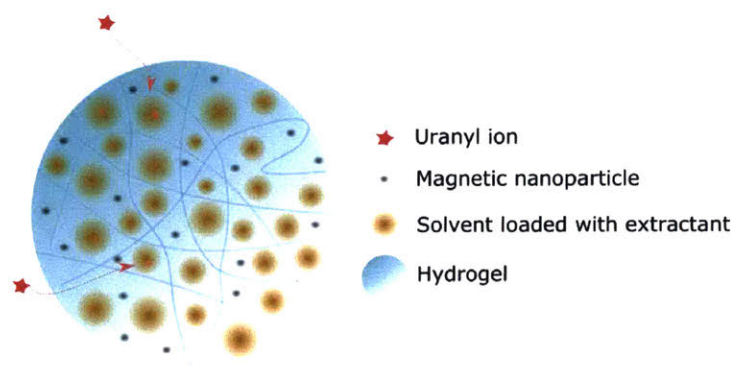


Figure 3-1. Structure of the magnetic organo-hydrogel

Compared to the original way of utilizing magnetic nanoparticles where extractants were chemically grafted on the particle surface, a significant advantage of the “organo-hydrogel” concept is that it enables encapsulation of commercially available extractant without chemical modifications, even synergistic extractants such as D2EHPA/TOPO which molecularly lacks a handle for chemical grafting. Another benefit offered by this design is that the capacity of

extraction is no longer limited by the grafting density of the extractant on the surface, since each of the encapsulated nanodroplets can serve as a reservoir of extractant. Additionally, in terms of magnetic collection, the magnetic gel beads are more favorable than individual magnetic nanoparticle due to the following two reasons. First, the aggregation of magnetic nanoparticles can be suppressed significantly when they are immobilized in a gel and second, the resuspension of the gel beads can be achieved easily with stirring even when the magnetic particles incorporated are not purely superparamagnetic and may have remanent magnetization upon removal of the magnetic field.

Using this kind of material, many challenges encountered in the conventional liquid-liquid extraction process for uranium recovery can be solved, just as the original concept of functionalized magnetic nanoparticles. In conventional liquid-liquid extraction process, large quantity of kerosene carrier is often used to reduce the viscosity of the extractant stream and enhance the diffusion of the extractants in the organic phase. Our organo-hydrogel design requires zero consumption of kerosene diluent since the highly viscous mixture of extractants can be transported together with the hydrogel particles and diffusion within each nano-droplet is also enhanced by reducing its size to nanometer scale. Experiments have shown that a mixture of D2EHPA and TOPO without kerosene can be prepared by mixing an appropriate amount of TOPO powder with three times its weight liquid D2EHPA followed by gentle heating to 80°C. The mixture was tested to be immiscible with water, allowing generation of oil-in-water nanoemulsion which could be further frozen by polymerization. Another challenge in solvent extraction is the formation of stable emulsions which are very hard to demulsify. This is often undesirable since it induces problems such as loss of extractant and product contamination by entrained solvent droplets. With this new design, nanoemulsion droplets are immobilized in the

hydrogel and can be magnetically separated from the product stream without the time-consuming emulsion breaking step. Finally, organic impurities such as humic substances in the phosphoric acid often leads to operational problems such as crud formation. With our design, this issue can be solved since humic acids are biopolymers in nature and their diffusivity through the hydrogel network is very low. Therefore, within the timescale of extraction, the diffusion of polymeric humic acid through the hydrogel network is negligible.

In this study, all prepared materials were tested for their structural characteristics. Chemical stability and uranium extraction performance of the materials were evaluated using the OCP phosphoric sample labeled as A3.

3.1.1 Demo: Proof of Concept with D2EHPA-TOPO-Alginate Organo-Hydrogel

To demonstrate the hydrogel's ability to encapsulate magnetic nanoparticles and organic nanodroplets, we synthesized a magnetic organo-hydrogel using calcium alginate as the monomer. The procedures to prepare such material are as follows: 0.5mol/L D2EHPA and 0.125mol/L TOPO diluted in kerosene were prepared as the organic phase. The organic extractant solution was then emulsified in 2% (w/w) alginate solution containing 1% (w/w) Lutensol AT25 and 5% (w/v) carbon coated iron magnetic nanoparticles. The emulsion was dripped dropwise into a stirring CaCl_2 solution by a 34-gauge needle. The droplets containing nanoemulsion and nanoparticles underwent gelation as soon as they contacted the gelling bath. The resulting particles were observed to be 1-2 mm in diameter and able to move under magnetic field. The magnetic response of the resulting organo-hydrogel beads is illustrated in Figure 3-2.



Figure 3-2. Magnetic response of the organo-alginate hydrogel

In later studies we switched from D2EHPA-TOPO-Alginate organo-hydrogel to D2EHPA-TOPO-PEGDA organo-hydrogel for the following three reasons:

- 1) Alginate hydrogel is a physical gel cross-linked by chelation between the polymer backbone and calcium ion, its mechanical strength is weaker than a chemically linked gel. From practical point of view, a stronger gel such as PEGDA is better applicable in a real industrial process.
- 2) Alginate hydrogel contains large quantities of calcium ions which may undergo ion exchange reaction with many metal ions present in the wet phosphoric acid. This would not only introduce foreign calcium ions to the product stream but also reduce the selectivity due to co-extraction of impurity ions. On the contrary, PEGDA forms a gel network which requires no foreign metal ions as cross-linkers.
- 3) The chemical stability of PEGDA hydrogel was quite good. It was tested in the OCP A3 sample at 80°C for 24 hours without any observable structural degradation.

3.2 Uranium Extraction with Magnetic Organo-Hydrogel Beads Prepared by the Dripping Method

The first technique developed to synthesize these magnetic organo-hydrogel beads was called the “dripping method” in which oil-in-water emulsion droplets were generated by gravity, just as water dripping from the faucet. Droplets were dripped into a silicone oil bath which is exposed to UV irradiation to initiate photo polymerization in the droplet. A typical synthesis procedure includes the following four steps:

- 1) Prepare a mixture of di-(2-ethylhexyl) phosphoric acid and trioctylphosphine oxide with a molar ratio of 4:1 by gentle heating to 80°C.
- 2) Use ultra-sonication to prepare oil-in-water emulsion comprised of extractant mixture, poly(ethylene glycol) diacrylate (PEGDA) aqueous solution, magnetic nanoparticles (1mg/ml), Pluronic F-68 surfactant (5vol%) and Daracure 1173 photo initiator (5vol%)
- 3) Use syringe pump to generate emulsion droplets through a 34-gauge needle and drip them dropwise into a stirring silicone oil bath which is exposed under UV irradiation.
- 4) Wash the magnetic organo-hydrogel beads thoroughly with deionized water and wipe off excess water on the surface.

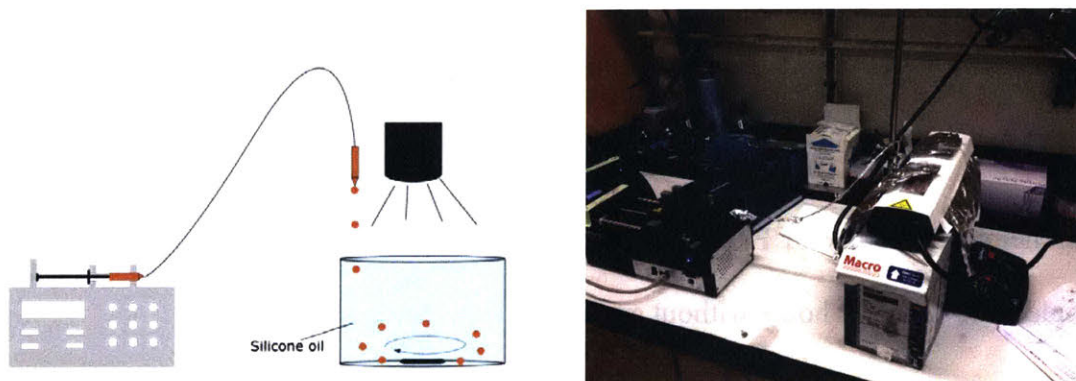


Figure 3-3. Schematic illustration and experimental set-up for synthesis of magnetic organo-hydrogel beads by the dripping method

To investigate if there was any loss of extractant or magnetic nanoparticles during the synthesis process, we performed elemental analysis on the emulsion (before photo-polymerization) and the gel beads (after photo-polymerization). By comparing phosphorous and iron content in these two samples (Table 3-1), we could conclude that there was no significant loss of either the extractant or magnetic nanoparticles during the gel preparation process.

Table 3-1. Elemental analysis on P and Fe before and after photo-polymerization

	Phosphorus (wt %)	Iron (wt %)
Emulsion	3.16 ± 0.5	0.03 ± 0.02
Organo-Hydrogel	3.81 ± 0.4	0.05 ± 0.01

The resulting organo-hydrogel beads were characterized by optical microscopy, SEM and confocal fluorescence microscopy. The magnetic organo-hydrogel beads had an average diameter around 1mm (Figure 3-4), which was similar to the size of the droplets when dripping off the needle tip. From the SEM images, porous structure on the particle surface was observed (Figure 3-5), which could be attributed to the evaporation of oil extractant droplets near the surface of the beads in the SEM vacuum chamber. Further examination on the intersection of the gel beads revealed that poly-dispersed extractant droplets with sizes ranging from sub microns to 100 microns were immobilized within the gel network (Figure 3-6). Compared with the original nanoemulsion size measured directly after ultra-sonication by DLS (around 320nm), there is a difference in the droplet size distribution which could be a result of coalescence during the synthesis process. Furthermore, by controlling the environmental humidity and temperature, we observed some morphology changes (Figure 3-7) as the organo-hydrogel beads began to

dehydrate. More specifically, several oil droplets previously separated by an aqueous layer started to coalesce into one big droplet. This change of morphology was irreversible and often undesirable since extractant could be expelled from the gel beads as the hydrogel start to collapse upon drying. By mixing fluorescence dye with the extractant prior to emulsification and examining the prepared gel particles under confocal microscope, we obtained the fluorescence image which revealed that the extractant droplets were evenly distributed within the organo-hydrogel beads (Figure 3-8).

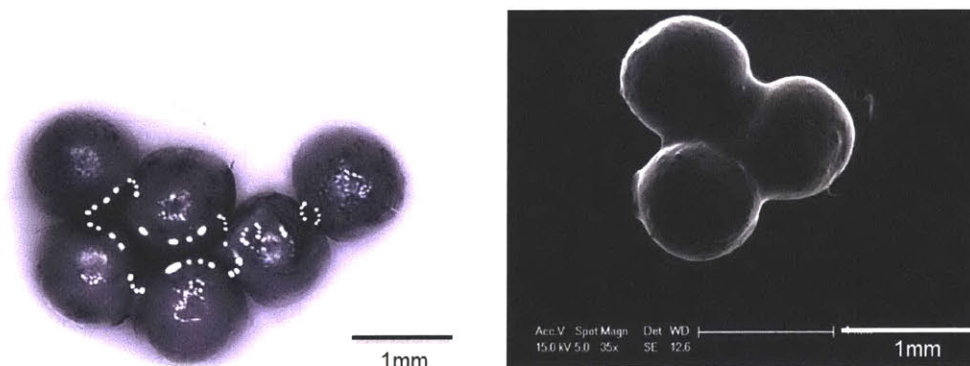


Figure 3-4. Particle overall morphology



Figure 3-5. Particle surface morphology

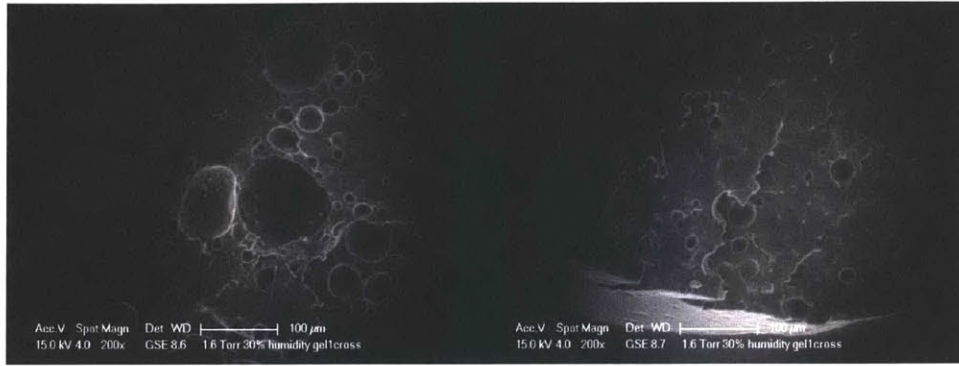


Figure 3-6. Particle inner morphology

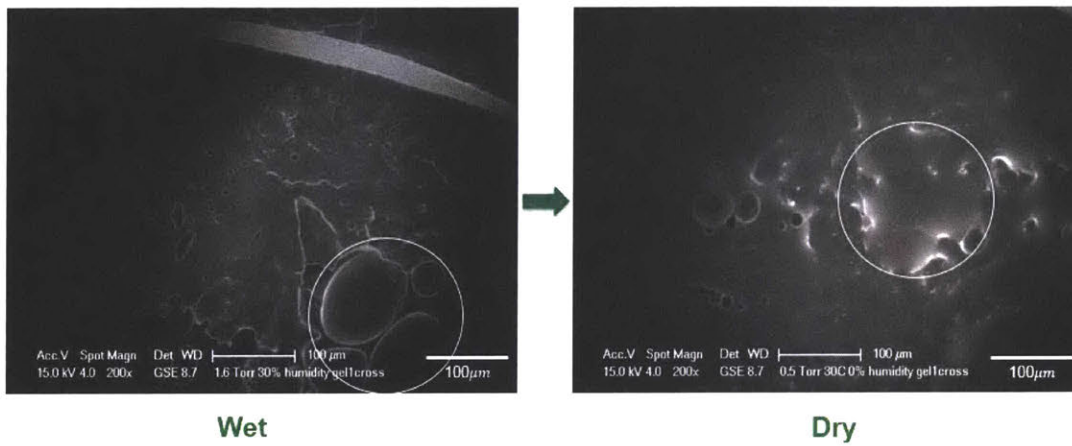


Figure 3-7. Morphology change with dehydration

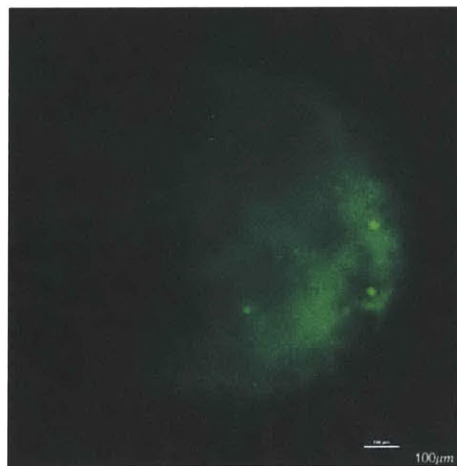


Figure 3-8. Confocal images of the gel particles

All the following uranium extraction experiments were conducted in industrial phosphoric acid sample obtained from OCP labeled as A3. Prior to extraction, gel particles were preserved in aqueous solution to prevent undesirable dehydration. Right before extraction, the particles were wiped several times to get rid of excess water on the surface.

A comparison between gel extraction and liquid-liquid extraction showed that there was no perceptible formation of crud in the case of gel extraction. On the contrary, a brownish layer of crud formed at the interface between phosphoric acid and D2EHPA-TOPO mixture (Figure 3-9). This further proved that using gel extraction could help reduce crud formation.



Figure 3-9. Comparison between gel extraction and liquid-liquid extraction

Equilibrium extraction studies were performed at three different temperatures (40 °C, 60 °C and 80 °C) and the results were plotted in Figure 3-10. The loading of magnetic organo-hydrogel was fixed at 1g/5ml. The extraction time was 48 hours which was long enough to reach equilibrium. A programmed shaker provided vigorous shaking to ensure well mixing. The resulting isotherm showed that the extraction coefficient decreased with increasing temperatures, the trend of which was in accordance with previous studies on D2EHPA-TOPO in liquid-liquid extraction. Using the van't Hoff equation 3.1, we could calculate the standard enthalpy change to be about -17.8 kJ mol⁻¹, the entropy change to be -24.9 J mol⁻¹ K⁻¹ and the overall Gibbs free energy change at 80 °C to be -9 kJ mol⁻¹. The negative enthalpy change indicated that the extraction reaction was

exothermic in nature, the negative value of entropy change could be related to the loss of translational and rotational entropy of extractant upon complexation in the bulky extracted species, negative entropy change also suggests the presence of few water molecules in the extracted metal complexes^[57], the negative ΔG° attests to the extraction being thermodynamically favorable. Since the initial concentration of uranium in this study was not high enough for the material to reach saturation adsorption, no plateau was observed in these isotherms.

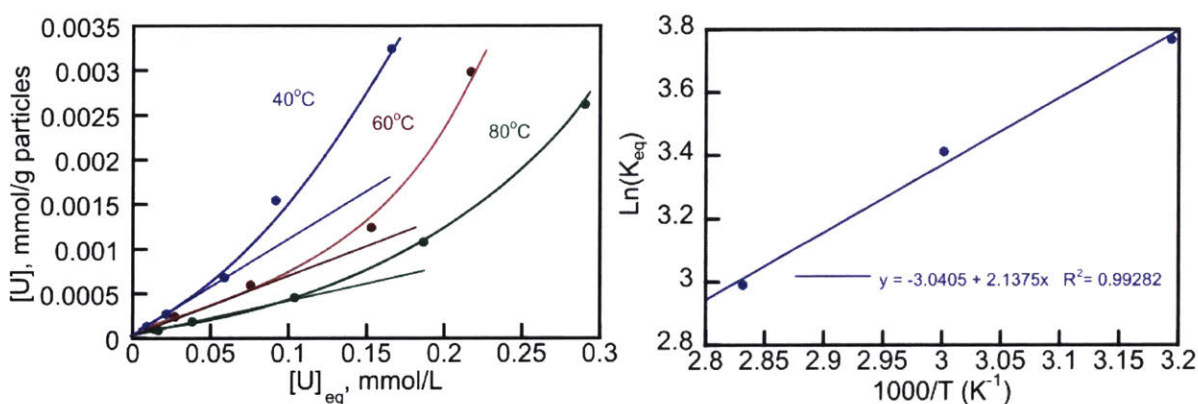


Figure 3-10. Temperature dependent extraction performance

$$\ln K_{eq} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (3.1)$$

Compared to equilibrium extraction studies, kinetics of adsorption was more crucial for designing effective uranium extraction process with these materials. Therefore, we investigated different combination of extractants, extractant loading ratio, concentration and molecular weight of PEDGA and their effects on extraction kinetics in order to figure out the optimum formula to prepare the gel particles. The results are shown in the following figures.

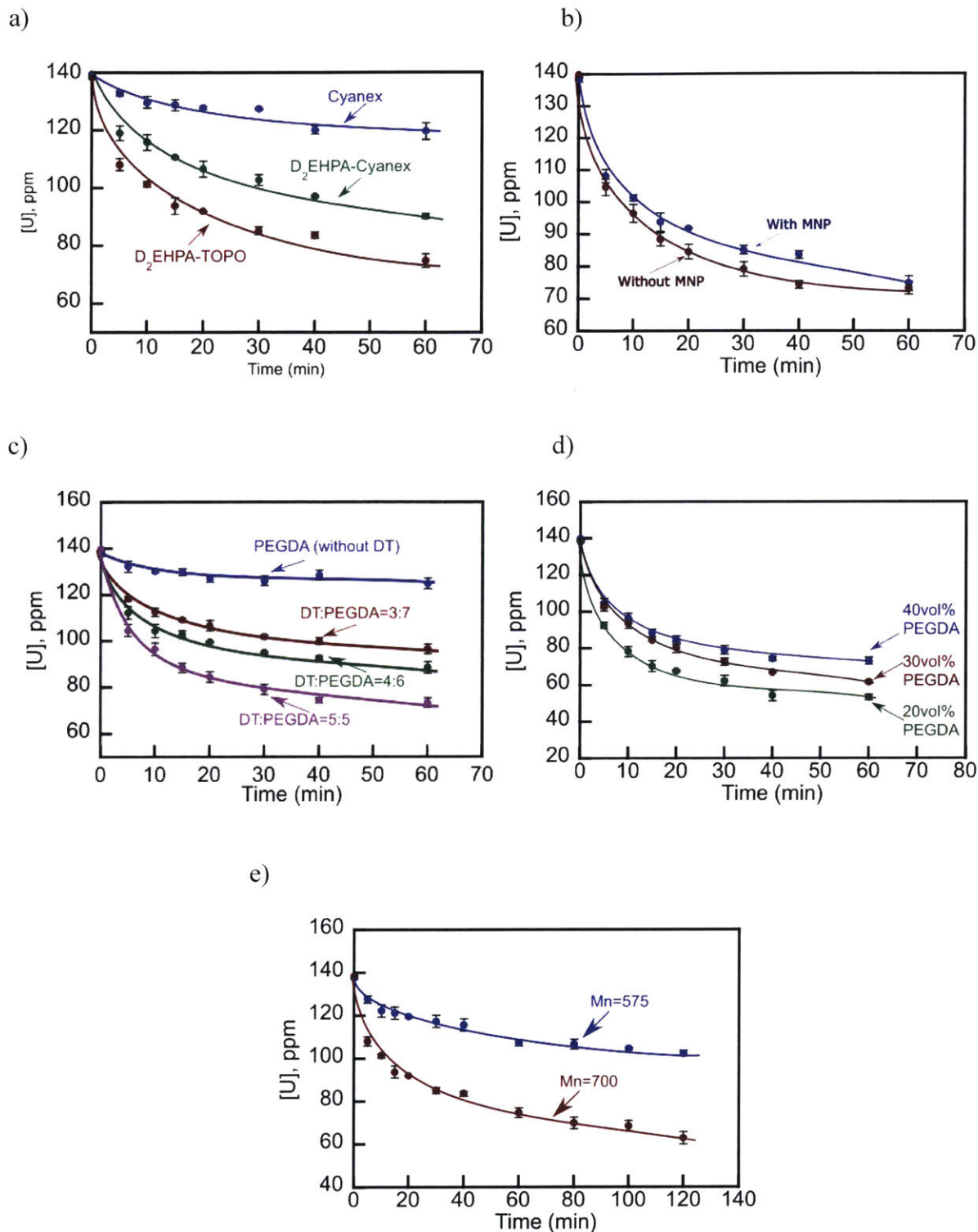


Figure 3-11. Extraction kinetics of magnetic-organohydrogel prepared by the dripping method

Figure 3-11 a) compares the extraction performance between D2EHPA-TOPO, D2EHPA-Cyanex, and Cyanex alone. Since Cyanex is essentially a liquid mixture of organophosphorus compounds structurally similar to TOPO, using Cyanex itself without D2EHPA does not induce any synergistic effect and would not work as well as D2EHPA-TOPO pair. In previous studies, researchers have tried different synergistic pairs of phosphine oxide and D2EHPA. They discovered that only TOPO works reasonably well with D2EHPA. Therefore, this could explain why D2EHPA-TOPO gave better kinetics than a mixture containing D2EHPA and different kinds of TOPO-like phosphine oxides.

Figure 3-11 b) shows that incorporation of magnetic nanoparticles slightly decreases the rate of uranium uptake. One possible explanation is that nanoparticles within the gel network could introduce additional diffusion resistance for uranyl ions to penetrate through the hydrogel.

Figure 3-11 c) demonstrates the effect of extractant loading on uranium extraction kinetics. As expected, uranium uptake capacity increases with loading of the extractants, pure PEGDA hydrogel could barely extract uranium from the A3 phosphoric acid sample. However, the maximum extractant loading should not exceed 50% by volume in order to prevent phase inversion.

Figure 3-11 d) and e) reveals that different PEGDA concentration and molecular weight could have an impact on extraction performance. In general, with higher PEGDA concentration or lower molecular weight, the resulting hydrogel would have higher crosslink density and smaller mesh size. Highly cross-linked hydrogel had enhanced mechanical strength but lower through-gel diffusivity and thus slower uptake kinetics. In light of the structural stability which is usually a major concern for real process application, on the safe side, 40vol% PEGDA with molecular

weight 700 was selected as the aqueous phase for preparing organo-hydrogel beads. There was no perceptible extractant loss nor deterioration of the structural integrity of this kind of gel beads under vigorous shaking.

Several kinetics models including first order kinetics model, pseudo-second-order kinetics model (equation 3.2), shrink core model, intra-particle diffusion model and Elovich model were considered. Among these models, pseudo-second-order kinetics gave the best fit of the kinetics data (Figure 3-12). This observation implies that interfacial chemical reaction between uranium and D2EHPA-TOPO is not a first order reaction and could be a significant rate-controlling step. Another important factor to consider is intra-particle diffusion. As will be explained later, the rate of metal ions to diffuse through the hydrogel determines the extraction performance by affecting the amount of the extractant that can be utilized within the time frame of extraction.

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \quad (3.2)$$

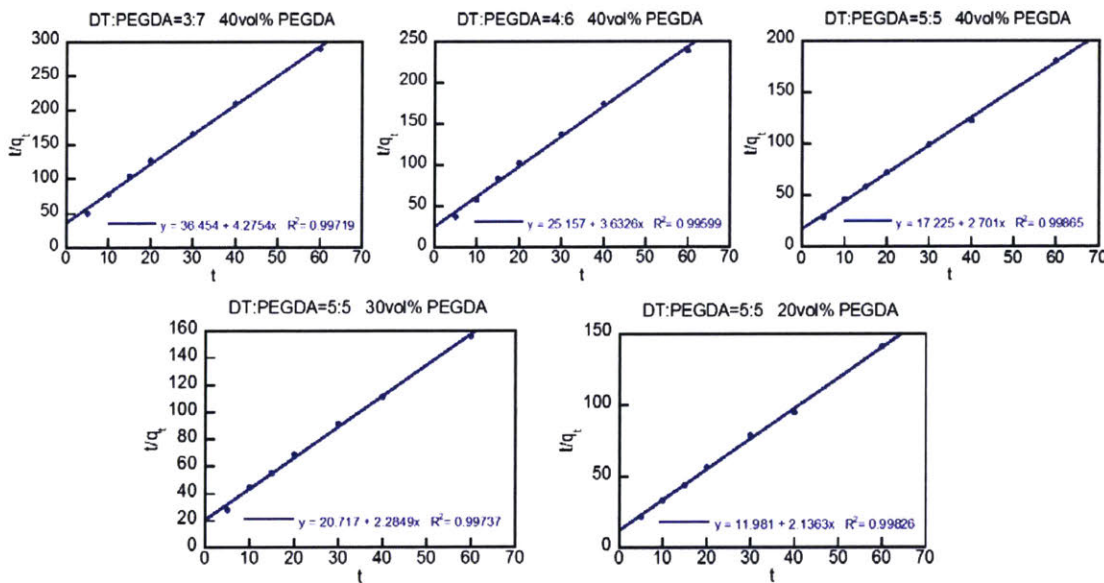


Figure 3-12. Pseudo-second-order kinetics model for extraction

Stripping experiments were performed by using 1.0 mol/L ammonium carbonate solution at a particle loading of 1g/5ml. From the data we could observe that it took about 2 hours for stripping to reach equilibrium, and by that time about 75.2% of the uranium previously extracted was stripped off the gel particles. To perform recycling experiments, particles were washed with deionized water several times and then dried for next cycle extraction. The capacity decreased in the second cycle extraction but the difference was roughly the amount of uranium remained in the organo-hydrogel after first cycle stripping (Figure 3-13).

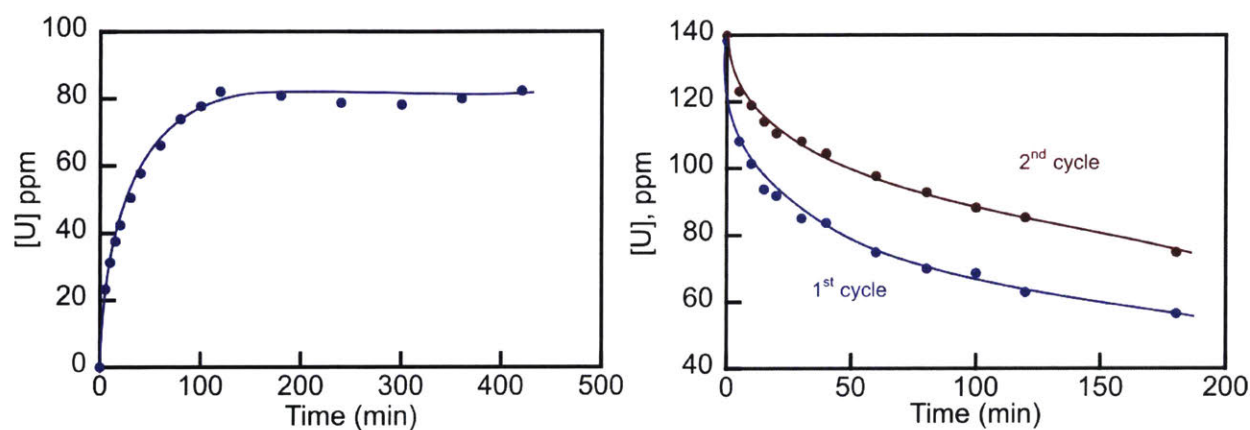


Figure 3-13. Stripping and recycling of organo-hydrogel beads

3.3 Uranium Extraction with Magnetic Organo-Hydrogel Beads Prepared by Microfluidic Device

The organo-hydrogel can be assumed as a gel consisting of successive onion type shell layers, the thickness of each layer depends on the size of droplet in that layer. Each of the nanodroplets immobilized in the hydrogel network acts as a trap for uranyl ions. Unless all the droplets in a particular layer are saturated, no ion can penetrate to the inner layers. This is because the rate of supplying new uranyl ions is often limited as a result of slow intra-particle diffusion. Therefore, every layer acts as an ionic shield for the inner layers. For extractant droplets that are located

near the center of the organo-hydrogel beads, the resistance for uranyl to diffuse to the interface is often very high. Therefore, in order to improve the utilization of the extractant and enhance uranium uptake kinetics, it is desirable to prepare smaller gel beads so that the shielding effect could be reduced. Besides, using smaller beads can enhance mixing and increase surface contact area which would also be beneficial for extraction.

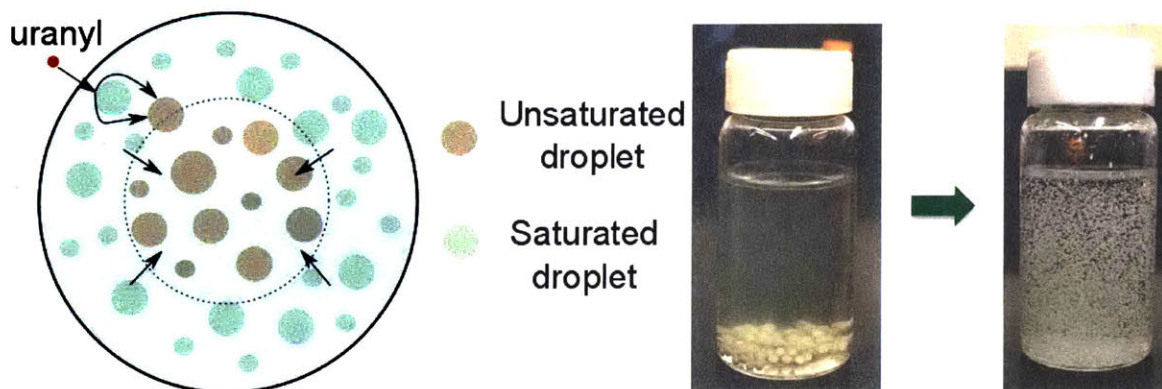


Figure 3-14. Shielding effect and mixing improvement by micro organo-hydrogel beads

Previously we used a dripping method to prepare organo-hydrogel beads and their size was about 1-1.5 mm in diameter. In order to fabricate smaller beads, we used a microfluidic device with flow-focusing pattern in which the inner phase flowed through a hole of $150\mu\text{m}$ while droplets broke off as the outer phase squeezed and exerted shear force on the inner stream. In our experiments, the dispersed phase was chosen to be the emulsion containing D2EHPA-TOPO, and the continuous phase was chosen to be silicone oil. Silicone surfactants Dow Corning 749 was added to the continuous phase to prevent coalescence of the droplets. After generated at the intersection, the droplets flowed through the collection tube which was exposed to UV irradiation in order to initiate photo-polymerization of PEGDA. The residence time during which

droplets underwent liquid-to-solid transformation was about 10 seconds. The beads obtained were then washed with 3-[hydroxy(polyethyleneoxy)propyl]heptamethyltrisiloxane solution and separated from silicone oil by magnet. The microfluidic set-up for preparation of the micro magnetic organo-hydrogel beads is shown in Figure 3-15.

Flow rates of the two phases were controlled by Harvard syringe pumps and was set about 5-10 $\mu\text{l}/\text{min}$ for the dispersed phase and 60-100 $\mu\text{l}/\text{min}$ for the continuous phase. Increasing the flow rate of continuous phase would generate more shear to the dispersed phase and produce smaller droplets. Similarly, decreasing the inner diameter of the collection tube also helps to reduce the size of the droplets.

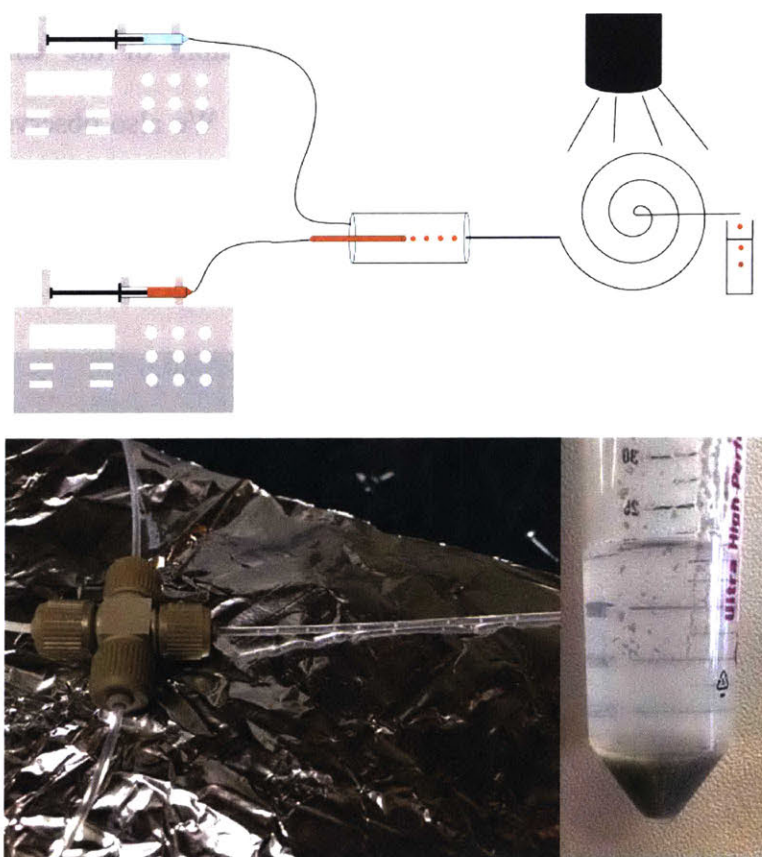
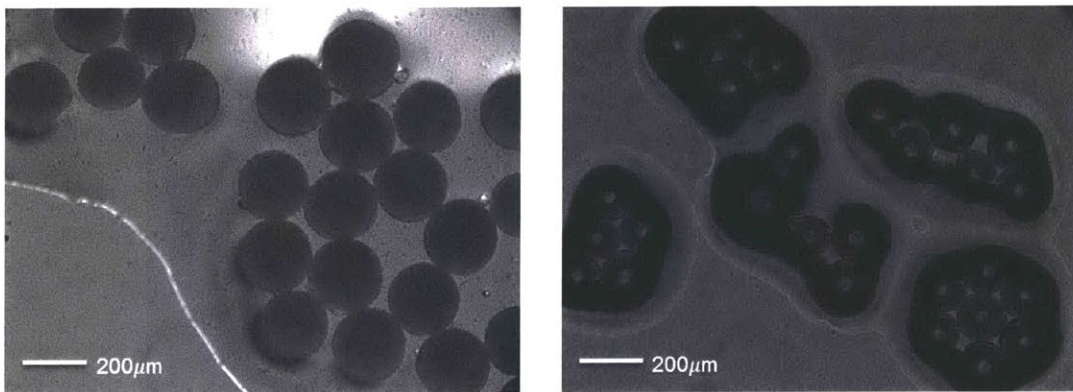


Figure 3-15. Microfluidic device for fabricating small organo hydrogel beads

Organo-hydrogel beads prepared by microfluidics were characterized by optical microscopy (Figure 3-16). Typical size range of the beads was between 100-400 microns, depending on the size of the collection tube and the flow rates. When exposed to air, small organo-hydrogel beads tend to dehydrate more quickly compared to their bigger counterparts. Upon dehydration, shrinking behavior of the hydrogels was observed and a layer of viscous extractant mixture comprising D2EHPA and TOPO began to form on the surface of the beads. The extractants were expelled because of the shrinking of the hydrogel. To achieve better preservation of the extractant encapsulated in the gel network, it is crucial to keep the beads in a hydrated condition.

From the SEM images (Figure 3-17), we can observe that the beads had narrow size distribution around 150 microns in diameter and the surface was not smooth but decorated with many submicron-sized bumps. These bumps were good indicators of the emulsified extractant nanodroplets that are encapsulated in the hydrogel network. We also observed porous structure on the surface, which was generated when the PEGDA hydrogel surface layer broke under vacuum during the SEM sample preparation process.



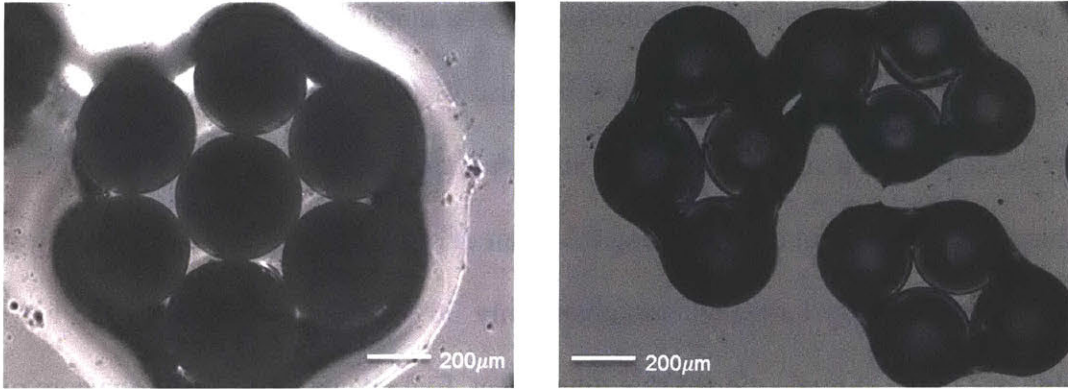


Figure 3-16. Optical images of small organo-hydrogel beads (left: wet gel; right: dry gel)

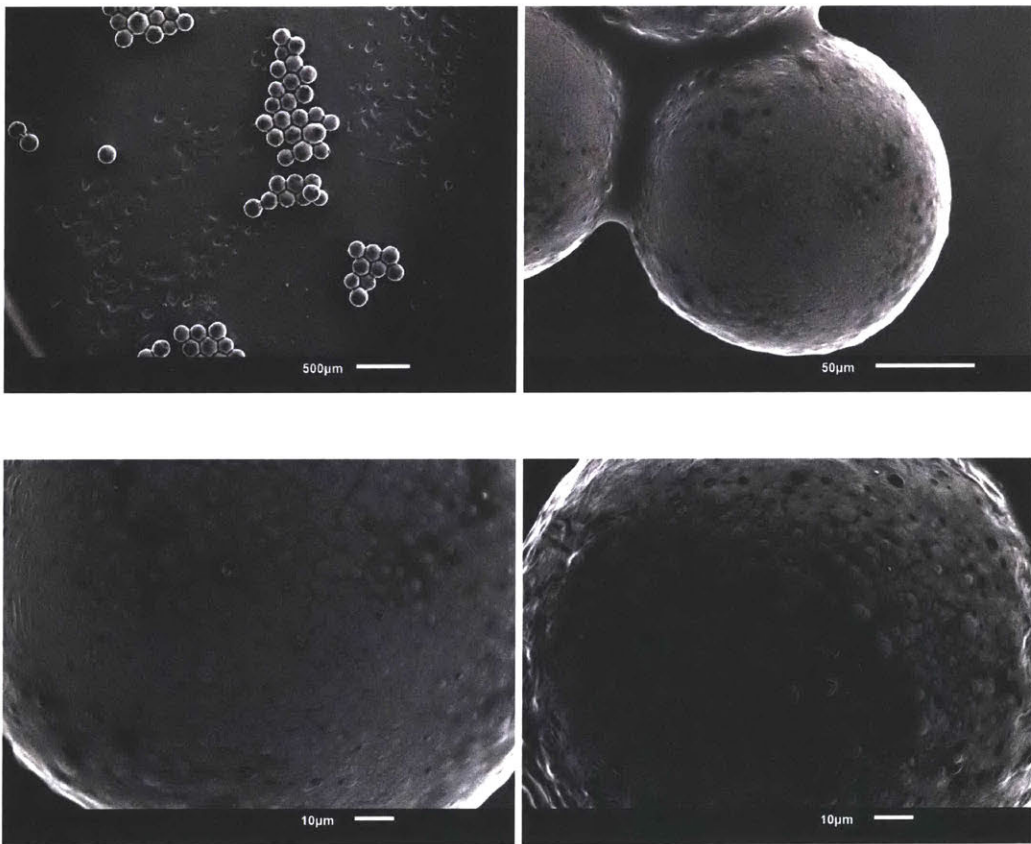


Figure 3-17. SEM image of small-organohydrogel beads

Using the same formula, comparison was made between gel particles generated by the dripping method and gel particles generated by microfluidics. As indicated in Figure 3-18 a), at the same

dosage, gel beads obtained by microfluidics achieved a much better uranium uptake kinetics than the ones prepared by the dripping method because of their reduced size. Besides, decreasing PEGDA concentration from 40 vol% to 20 vol% further enhanced the uptake kinetics. Figure 3-18 b) showed that one gram of big gel and 0.3 gram of small gel achieved similar performance in uranium extraction. This indicated that about only 30% of the extractant in the big gel was accessible due to the aforementioned shielding effect. Extractants located near the core of the big gel beads could not be utilized in the period of extraction studies.

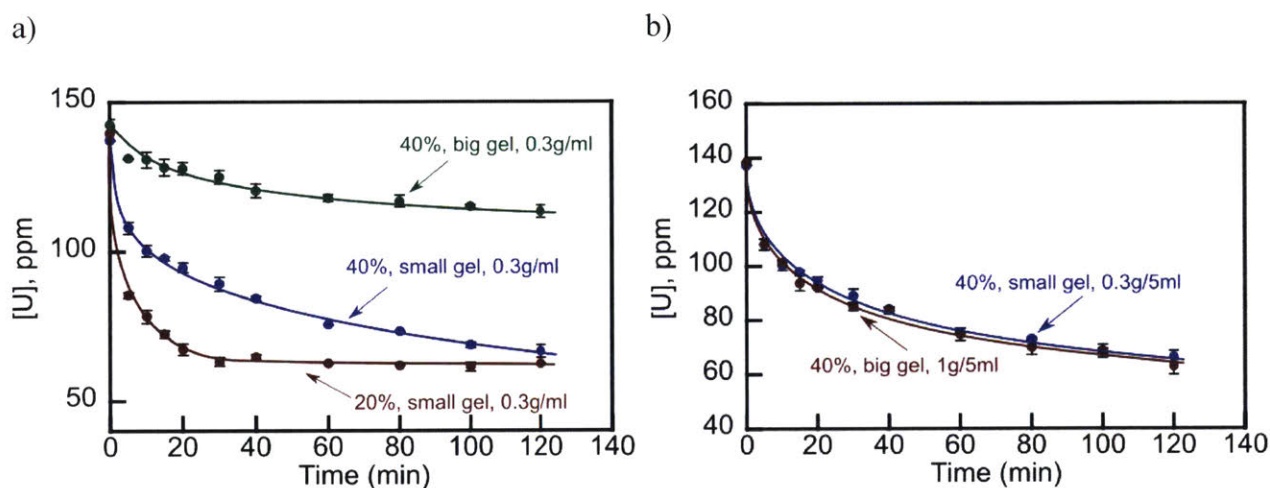


Figure 3-18. Comparison between small gel extraction and big gel extraction

In principle, solvent extraction always gives better uptake kinetics than organo-hydrogel due to absence of intra-particle diffusion resistance. However, by reducing the size of our organo-hydrogel beads as well as tuning the PEDGA composition, we could approach 80% of solvent extraction efficiency (Figure 3-19).

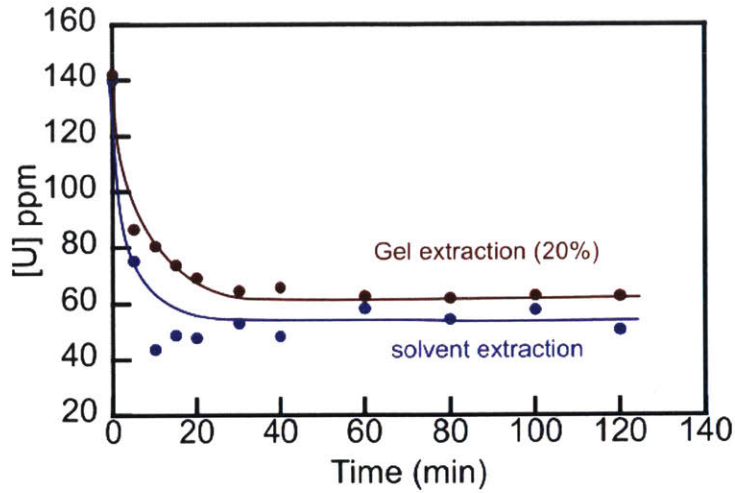


Figure 3-19. Comparison between small gel extraction and liquid-liquid extraction

The distribution coefficient of the small organic hydrogel with 40% PEGDA was calculated to be about 39 using the following equation:

$$K_d = \frac{C_e(l)}{C_e(gel)} \quad (3.3)$$

Where K_d denotes the distribution coefficient, $C_e(l)$ denotes the equilibrium concentration of uranium in the liquid phase, $C_e(gel)$ denotes the equilibrium concentration of uranium in the gel particle. Both concentrations have units of mg/L. The obtained value of distribution coefficient is in the same range as what was previously reported for liquid-liquid extraction, indicating similarity in the performance of equilibrium absorption between these two approaches.

Another commonly reported distribution coefficient was defined as milligrams of uranium extracted per gram of particle:

$$K_d = \frac{(C_0 - C_e)V}{m_{gel}} \quad (3.4)$$

In the above equation, C_0 denotes the initial concentration of uranium in the liquid phase, C_e denotes the equilibrium concentration of uranium in the liquid phase, V represents the volume of the uranium solution, m_{gel} denotes the mass of the gel particles used in the extraction experiment. The corresponding distribution coefficient calculated using equation 3.4 was about 1.18 mg/g.

Stripping experiments were performed with 1.0 mol/L ammonium carbonate solution at a dosage of 0.3g/2ml. We observed that gels with decreased sizes exhibited much faster stripping kinetics than their bigger counterparts. It only took 5 minutes for the small gels to reach adsorption equilibrium (Figure 3-20). We also observed that the PEGDA concentration did not make a difference for stripping, which was probably due to that fact that diffusion through the gels was greatly facilitated as the size of gel particles decreased. As a result, about 70% of the uranium was stripped off at equilibrium, the incompleteness in the stripping could be attributed to the reversibility of the stripping reaction.

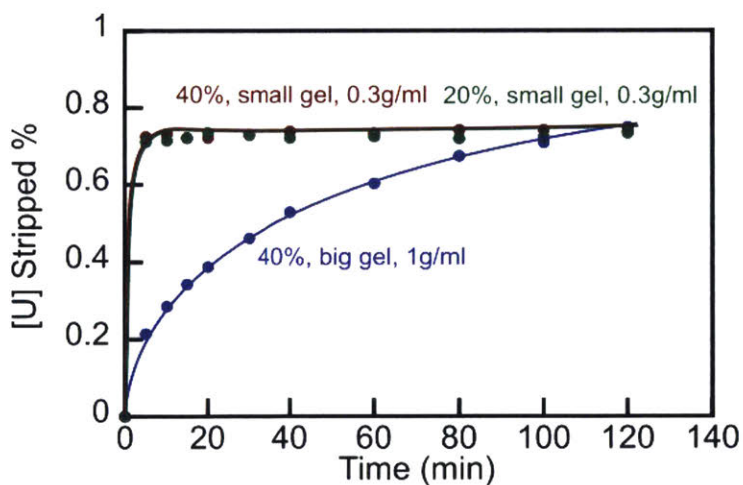


Figure 3-20. Comparison of stripping behavior between the small gel and the big gel

The stripped PEGDA gel was then washed thoroughly with DI water several times and dried before recycling. During recycling experiments, a decrease in extraction and stripping capacity

was observed (Figure 3-21). Besides, PEGDA concentration had an effect in the recyclability of the gel beads (Figure 3-22). We noticed that although 20% PEGDA gel achieved better extraction kinetics than 40% PEGDA gel in the first cycle extraction, it performed worse in the second cycle extraction. This could probably due to leakage or loss of extractant during washing and drying. More specifically, washing of small microdroplets that exists on the outer surface of organo-hydrogel beads, inherent leakage due to porosity, change of polymeric matrix by the ammonium carbonate, and attritions and mechanical stress arising from the vigorous shaking process could all contribute to extractant loss. Since 20% PEGDA gel was weaker in mechanical strength than 40% PEGDA gel, there would be less remaining extractant available for the second cycle extraction after the stripping process. This could explain why 20% PEGDA gel performed worse in the second cycle extraction.

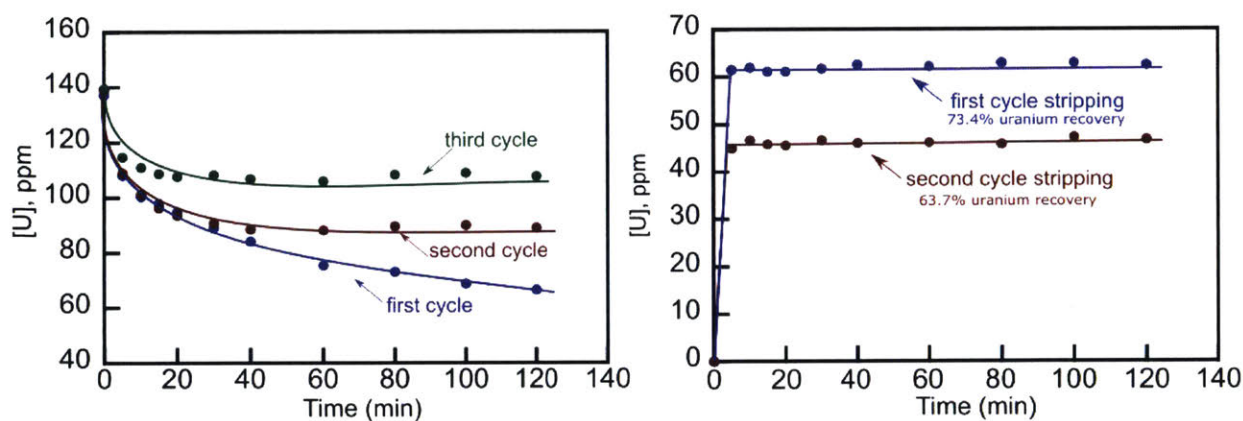


Figure 3-21. Recycling experiments with 40% PEGDA gel

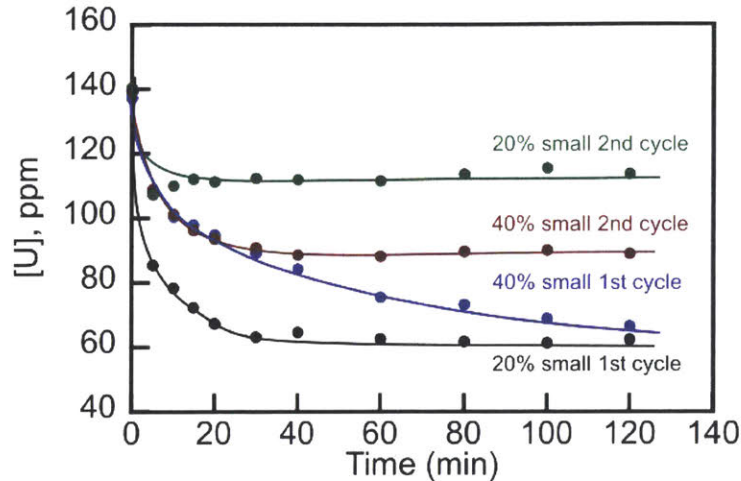


Figure 3-22. Effect of PEGDA concentration on recycling

Another issue that could attribute to reduced extraction capacity was the co-extraction of impurity metal ions. As indicated by OCP, we tested the selectivity of the material by investigating synergistic extraction of uranium with Vanadium, Iron and Chromium in the OCP sample A3 (Figure 3-23). The concentrations of various metal ions before and after extraction were listed in Table 3-2. From the results, we could conclude that by using PEGDA as inert network and D2EHPA-TOPO as extractant, the extraction was selective towards Uranium. However, since the concentration of iron in OCP phosphoric sample was one order of magnitude higher than the concentration of uranium, the uptake of iron was still higher than uranium. During stripping process, about 80% of uranium was stripped off the gel particles but only 25% of iron was removed. Therefore, the remaining irons in the gel beads could consume a lot of extracting sites and led to a decrease in uranium uptake capacity during recycling.

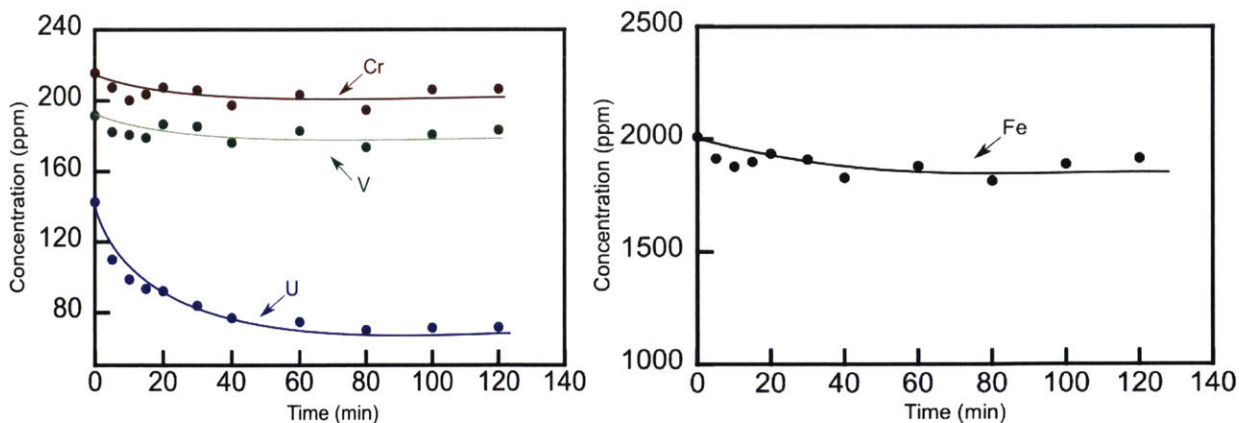


Figure 3-23. Synergistic extraction of U, Cr, V, and Fe

Table 3-2. Selectivity of D2EHPA-TOPO-PEGDA organo-hydrogel

	U	V	Cr	Fe
Initial Concentration (ppm)	142.8	191.4	215.6	2012
Final Concentration (ppm)	71.0	183.3	206.5	1917
Extracted %	50.3%	4.2%	4.2%	4.7%

3.4 Conclusions

Chemically stable organo-hydrogel beads were developed and prepared by two different methods: dripping method and microfluidics. The materials were demonstrated to be capable of extracting uranium from OCP phosphoric sample. Performance of extraction, including thermodynamic isotherms, kinetics and selectivity were evaluated. Comparison were made between gel beads prepared by two different methods and significant improvement in extraction and stripping kinetics was observed with particle size reduction. Stripping and recycling performance of the

particles were also studied. The optimum formula to fabricate the organo-hydrogel is shown in the following table.

Table 3-3. Optimum formula of magnetic organo-hydrogel

	PEGDA molecular weight	PEGDA concentration	Magnetic nanoparticle loading	Pluronic F-68	Darocur 1173	D2EHPA: TOPO (mole)	Oil to aqueous ratio (vol)
Formula	700	40vol%	1mg/ml	5vol%	5vol%	4:1	1:1

In order to reduce extractant loss so as to improve recyclability, it is recommended that the gel particles should be kept hydrated all the time. Besides, PEGDA concentration could be further increased to produce mechanically stronger gels for the application.

4. URANIUM EXTRACTION WITH MAGNETIC LYOGELS

4.1 Material Design

The magnetic organo-hydrogel described in the previous chapter was tested to be sufficient in extracting uranium and exhibited fast kinetics in both extraction and stripping. However, a decrease in the capacity of extraction during recycling of the particles was observed, which was most likely related to a loss of extractant in the recycling process. One possible reason for the extractant loss could be the incompatibility in the nature of the hydrogel and organophosphorus extractants that were encapsulated within the gel network. As demonstrated in the previous chapter, the hydrogel underwent repetitive shrinking and swelling during the washing and drying steps, and thereby the extractant droplets originally trapped in the gel network were likely to be expelled from the hydrogel beads. To enable recyclability of the material and prevent extractant expulsion, it is desirable to design a material where the extractants are chemically compatible with the polymer network in which they are incorporated. Additionally, while carbon-coated iron is sufficiently stable in nitric acid, the nanoparticles can eventually dissolve in 6M phosphoric acid in the presence of sulfuric acid at an elevated temperature after 7 days. This is also an important issue since the condition is very similar to the streams generated in the OCP phosphoric acid production process. Herein, we also aimed at creating materials with enhanced magnetic stability.

The enhancement of stability of our materials could be achieved by embedding the carbon-coated iron nanoparticles into hydrophobic polymeric material that is highly acid-stable and yet contains a conventional organophosphorus extractant such as D2EHPA or TOPO. In order to achieve stability of the extractant in the organic gel (lyogel), the polymer and extractant should

form a “homogeneous” phase that does not exhibit phase separation for extended periods of time, even upon exposure to an aqueous acid solution, washing and drying. A unique polymeric system which possesses such property can be obtained by modifying the polymer by substitution with a radical of a substance compatible with the specific extractant^[58]. Specifically in this study, we used a halopolymer poly(vinyl chloride) (PVC) as the backbone polymer, covalently modified the polymer with dithio-functionalized molecules that closely resemble properties of the chosen extractant with D2EHPA and Cynaex 923, a liquid TOPO analogue. The resulting modified polymer can form stable gels with such liquid organic extractants. Additionally, dithio-containing molecules was previously reported to have the ability to chelate uranium^[59,60], which further motivates the choice of material.

4.2 Polymer Synthesis

Synthesis of poly(vinyl chloride) functionalized with dithioalkyl moieties by nucleophilic substitution has been reported previously^[61-65]. In this work, we chose diethyldithiocarbamate (DEDTC) and diethyldithiophosphate (DEDTP) (Figure 4-1) as representative examples of dithio-functional compounds that are well-known chelating agents of heavy metals^[66-68].

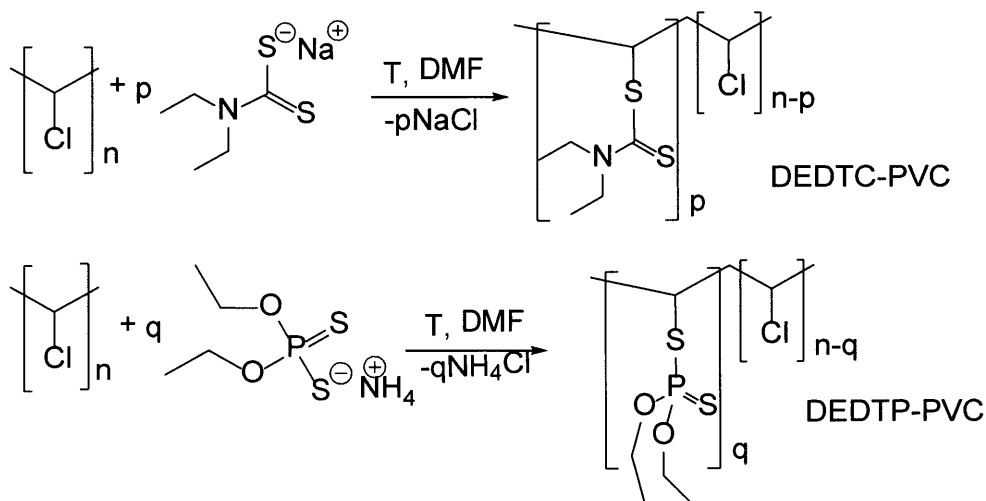


Figure 4-1. Nucleophilic substitution reactions on PVC.

The procedure of conducting the substitution reaction is as follows:

Solution of PVC (MW ~48000, Sigma-Aldrich Chemical Co.), 5-10 wt%, in anhydrous N,N-dimethylformamide (DMF) were deaerated by nitrogen flow for 0.5 h in glass reactors. The reactor was sealed and equilibrated at 75 or 90°C for specified time, then equilibrated at ambient temperature and the polymer was slowly precipitated by dropwise addition of acetone/water (8:2), washed with deionized water repeatedly, snap-frozen in liquid nitrogen and lyophilized. The chlorine substitution degree was expressed as:

$$SD = 100 \times \frac{p}{n} \text{ or } 100 \times \frac{q}{n} \quad (3.5)$$

Where SD is the substitution degree, p and q denote number of substituted unites, n denotes total number of units in the polymer chain. Kinetics of the PVC modification were monitored and the results are presented in Figure 4-2.

It was observed that at about 44 mol% SD, the polymer became insoluble in THF due to the formation of interchain -S-S- crosslinking. Therefore, the reaction time and temperature were optimized to achieve maximum SD, but prior to the onset of the crosslinking resulting in insoluble gels. At 90°C, insoluble gels formed within approximately 1 hour and the gels were brown-yellow and appeared to be difficult to process any further. At 75°C, appropriately large substitution degrees (40-42%) were achieved within 3-4 h and the formed substituted polymer were still solvable in the THF. Therefore, in further studies, DEDTC-PVC and DEDTP-PVC species with a substitution degree about 40-42% were utilized.

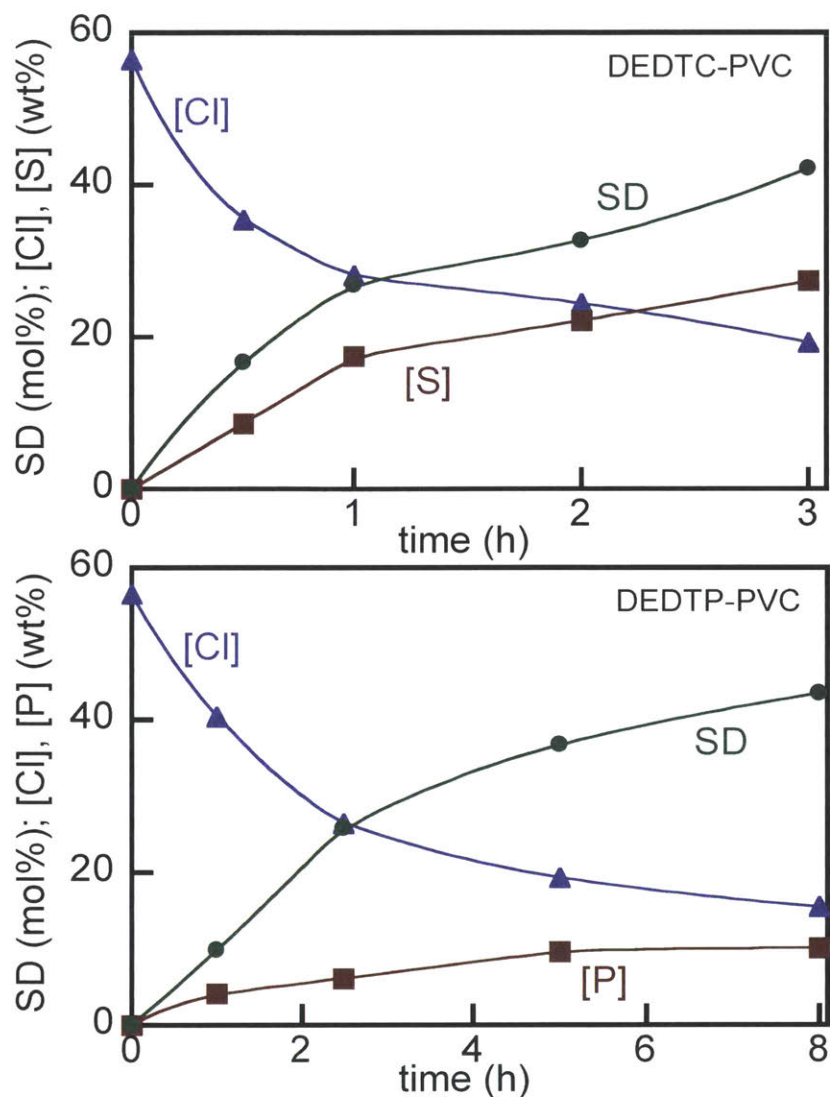


Figure 4-2. Kinetics of PVC substitution with diethylthiocarbamate (DEDTC-PVC) and ammonium diethylthiophosphate (DEDTP-PVC) in DMF at 75°C.

4.3 Preparation of Magnetic Lyogels and Composition Analysis

Magnetic lyogel materials were synthesized by blending weighed amounts of solutions of modified PVC and chosen extractant in THF, followed by addition of weighed amounts of magnetic carbon coated iron (C@Fe) nanoparticles, sonicating of the resulting blend for 15 min, casting of the resulting homogenized blends on Teflon and letting THF evaporates under air flow

for 48-72 h until constant weight. The gel-like soft solids were shredded into irregularly-shaped particles and dried under vacuum.

The C@Fe nanoparticles were obtained from Sun Innovation's Nanomaterial Store. The nanoparticles are fabricated by arc-discharge method, and has a size range between 7 and 50 nm, the mean of the size is about 25 nm. Under SEM observation, the thickness of carbon shell was revealed to be between 2.5 and 3 nm. The nanoparticles are composed of Fe (ferromagnetic), Fe₃C (paramagnetic), some CFe_{15.1}-Austenite (ferromagnetic), and some Fe₂O₃/FeO depending on exposure to air. The elemental iron content in C@Fe nanoparticles was about 77 wt%. The saturation magnetization (M_s) was measured using SQUID to be about 120 emu/g.

Composition of magnetic lyogels prepared in this work was tested by thermogravimetric analysis (TGA) and by elemental analysis using standard methods. Figure 4-3 shows typical TGA thermograms of the initial materials utilized in the lyogel preparation. As is seen, the C@Fe nanoparticles contain approximately 13 wt% carbon, Cyanex decomposition starts at about 230°C, while D2EHPA starts decomposing at 195°C. Modification of PVC by DEDTC and DEDTP results in lower temperature stability of the polymer, which starts degrading at 250-320 °C. Figure 4-4 shows the TGA curves of different types of lyogel materials. The DEDTC-PVC/D2EHPA gel 1 and DEDTC-PVC/D2EHPA gel 2 contained 50 and 69 wt% D2EHPA, respectively. DEDTC-PVC/Cyanex and DEDTP-PVC/Cyanex gels contained 52 and 65 wt% Cyanex, respectively. Combination of TGA and elemental analysis yielded composition that corresponded well to the initial ratio of components set in reaction mixtures.

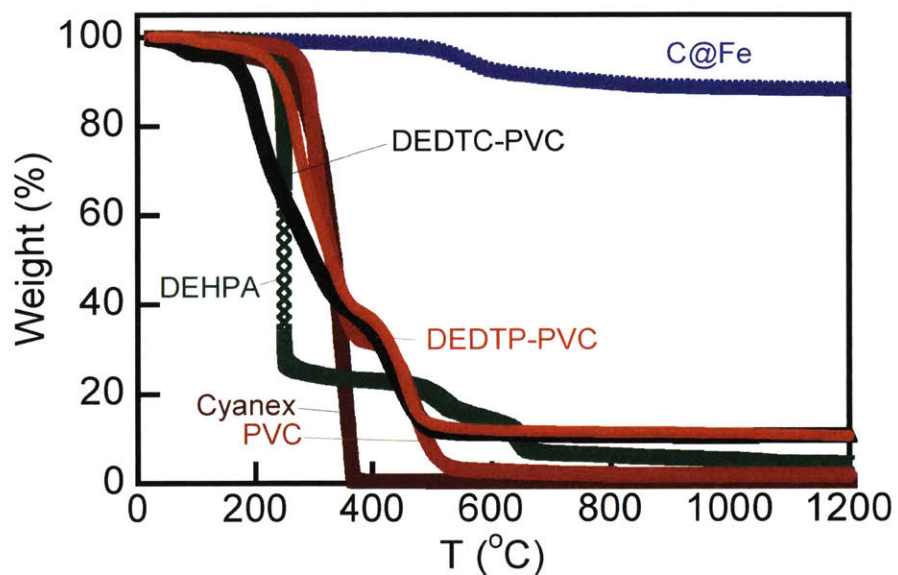


Figure 4-3. Typical TGA thermograms measured in the materials utilized in preparation of magnetic lyogels. Temperature ramp rate, 20°C.

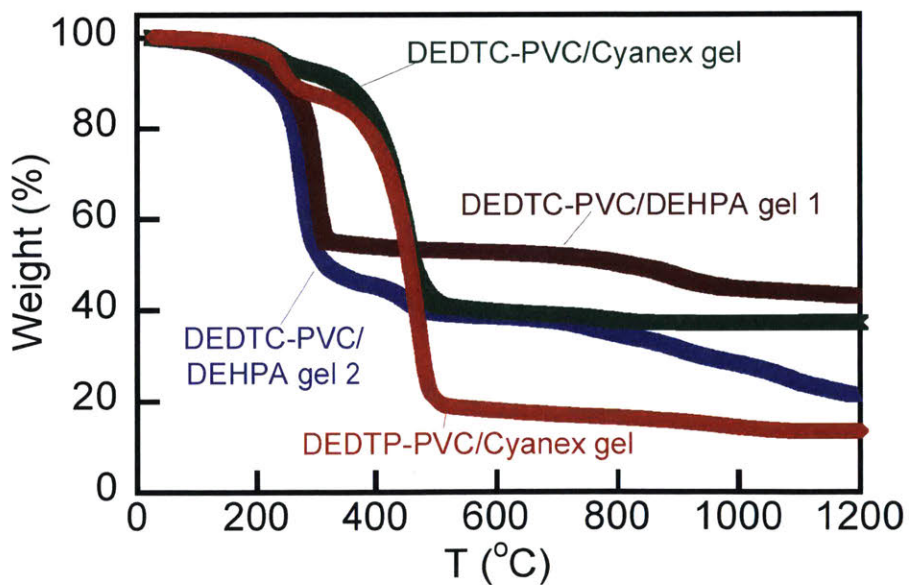


Figure 4-4. Typical TGA thermograms of the lyogel materials. Temperature ramp rate, 20°C.

4.4 Stability of Magnetic Lyogels in the OCP Fluid

Magnetic stability of the composite materials in strongly acidic OCP fluid depends on the preservation of the crystalline structure of Fe without dissolution. The carbon shell of the NP is designed to protect the iron core from oxidation and dissolution in acids, but imperfections in the shell yield to a strong dependence of the magnetic properties on time of exposure and temperature. In this lyogel design, additional protection is offered by incorporating the C@Fe nanoparticles into hydrophobic polymer network composed of acid-resistant modified PVC. To test the magnetic stability of the material, we utilized a synthetic Wet Phosphoric Acid fluid termed “OCP fluid” prepared according to the formula as advised by the sponsor: 6M H₃PO₄, 0.86wt% H₂SO₄, 0.9wt% NaF, 0.7wt% Fe₂(SO₄)₃, 0.35wt% Al₂(SO₄)₃ at 80°C. The density of the OCP fluid was measured using specific gravity bottle to be 1292 g/L.

Magnetization of the prepared lyogel particles strongly depended on the contents of the magnetic nanoparticles. Materials composed of DEDTC-PVC (SD, 41%), D2EHPA as an extractant and Fe@C NP were tested using superconducting quantum interference device (SQUID) before and after the material’s exposure to the OCP fluid for 7 days at room temperature. Typical magnetization-field results are shown in Figure 4-5.

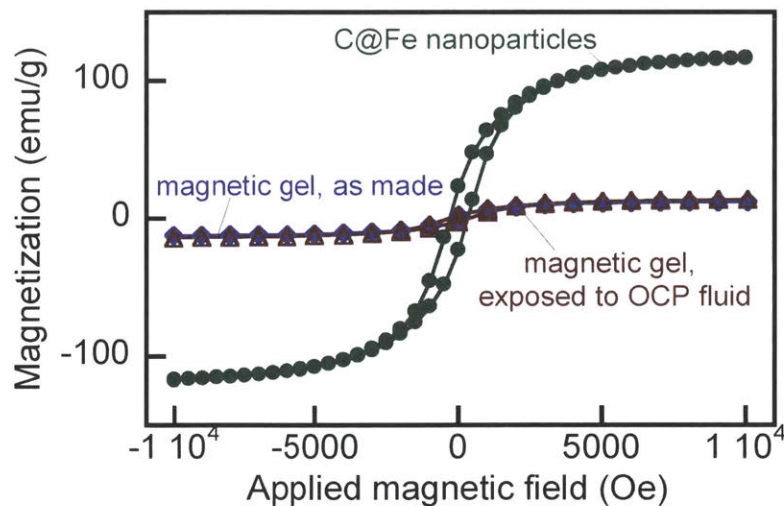


Figure 4-5. Typical magnetization vs field curves of the original C@Fe nanoparticles and magnetic lyogel containing D2EHPA before and after exposed to OCP fluid.

From the above figure, we can observe that the overall magnetization of the lyogels is much less than the magnetic nanoparticles, which is expected because the magnetization is normalized by the total mass of the material. But interestingly, we observed negligible change in the magnetization after exposure to the aggressive OCP fluid, which is indicative of acceptable magnetic stability of the material prepared. It was also observed that the gel particles dispersed in the OCP fluid could move rapidly in magnetic field and be recovered by magnetocollection.

4.5 Equilibrium Uranium Uptake by Magnetic Lyogels

We first investigated adsorption isotherms by the modified PVC polymers alone and magnetic lyogels of various compositions. The isotherms were studied based on 48 hours of equilibration time. The uranium concentration range was chosen to be 0-200 ppm, which is typical range of concentrations found in wet phosphoric acid processes. The maximum uranium concentration of

200mg/L would not lead to the saturation of the binding sites offered by the modified polymer and extractant at the loading dosage chosen for the gel particles (50 mg/ml).

Figure 4-6 depicts typical adsorption isotherms for the materials based on DEDTP-PVC (a) and DEDTC-PVC (b) polymers. As is seen, the dithio-functionalized polymers possessed a significant affinity toward uranium and were able to adsorb it from the highly acidic OCP fluid. In the control experiments with unmodified PVC, we observed no discernible uptake of uranium from the OCP fluid. The dithiophosphate-modified PVC possessed a slightly higher binding affinity toward uranium than the dithiocarbamate-modified PVC, but the former had a strong obnoxious odor and thus, was studied to a lesser extent.

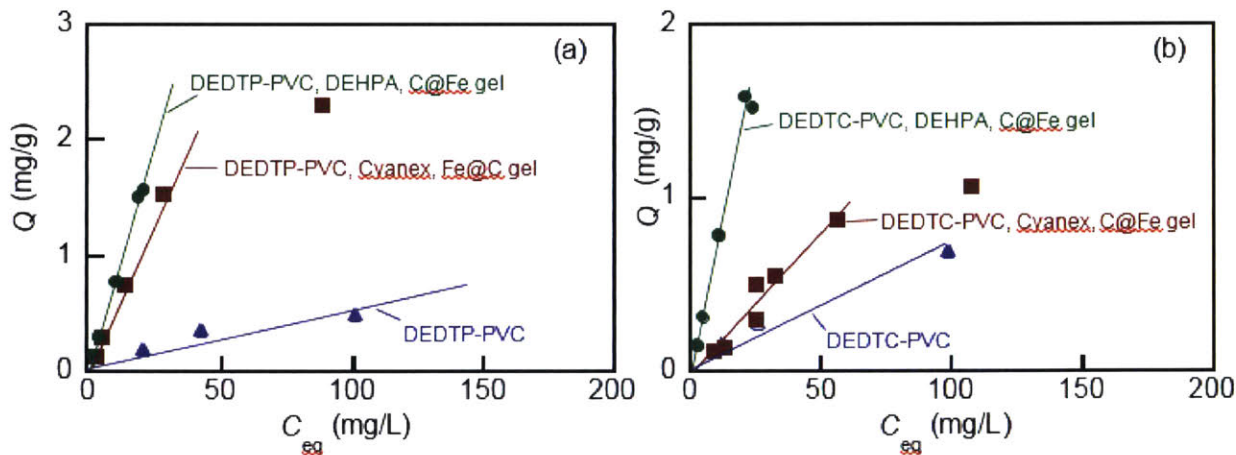


Figure 4-6. Typical uranium sorption isotherms measured with DEDTP-PVC (a) and DEDTC-PVC (b) materials at 25°C. Solutions of uranyl nitrate in the OCP fluid (concentration range, 0-200 mg/L) were equilibrated with weighed amounts of polymers or gel materials for 48 h at room temperature, the solids were separated and uranium concentration (C_{eq} , mg/L) was measured in the supernatant.

As we could not attain the sorbent saturation plateau in the chosen uranium concentration range (Fig.7), it was possible to treat the adsorption isotherms using their initial slope, which is commonly described with Freundlich equation (equation 3.6) developed to reflect upon the adsorption characteristics of a heterogeneous surface [69, 70]:

$$Q_{eq} = K_f C_{eq}^{1/n} \quad (3.6)$$

where Q_{eq} (mg/g) is the amount of uranium adsorbed per gram of material at equilibrium, C_{eq} (mg/L) is the uranium concentration in solution equilibrated with the material, K_f is the Freundlich isotherm constant indicating the sorption capacity, and n is so-called adsorption intensity. The linearized form of Freundlich isotherm was well-applicable to our experimental data (Figure 4-7).

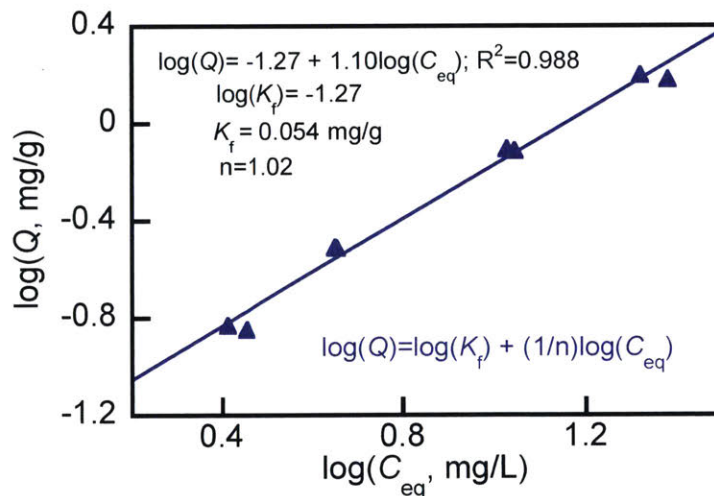


Figure 4-7. Freundlich sorption isotherm for uranium uptake by magnetic lyogel composed of DEDTC-PVC (38.5 wt%), D2EHPA (50.0 wt%) and Fe@C nanoparticles (11.5 wt%).

Because DEDTP-PVC polymer had a strong obnoxious odor and thus, only DEDTC-PVC was studied. The results of equilibrium adsorption experiments of the DEDTC-PVC based magnetic lyogels of various extractant loadings are collected in Table 4-1. The Freundlich adsorption constant (K_f) was measured in triplicate and average standard error was estimated to be 12%. The adsorption intensity n is measured to be close to 1 for all of the material listed in Table 4-1.

Table 4-1. Equilibrium adsorption performance of DEDTC-PVC lyogels

Polymer	Extractant	Extractant content (wt%)	K_f ($\mu\text{g/g}$)
DEDTC-PVC	--	0	29.7
DEDTC-PVC	D2EHPA	50.0	62.9
DEDTC-PVC	D2EHPA	68.8	72.4
DEDTC-PVC	D2EHPA	90.8	108.6

It can be seen from the table that incorporating D2EHPA grants a higher uranium adsorption capacity. As expected, increasing D2EHPA content will augment the uranium sorption capacity and the partition coefficient of the composite material. However, the composite lyogel with 90% of D2EHPA was so soft and pliable that they exhibit to be very tacky and tended to agglomerate when dispersed in the OCP fluid. Therefore, a balance should be found between the uranium uptake capacity and mechanical properties of the lyogel. The optimum sorbent material found during the experiments was composed of DEDTC-PVC (38.5 wt%), D2EHPA (50.0 wt%) and Fe@C nanoparticles (11.5 wt%).

As before, we also studied the effect of temperature on uranium uptake by the lyogel. We chose the optimum composition of the lyogel stated above, performed equilibrium adsorption experiments for 48 hours in a temperature range of 25-80°C. The temperature dependence of uranium adsorption isotherms is shown in Figure 4-8.

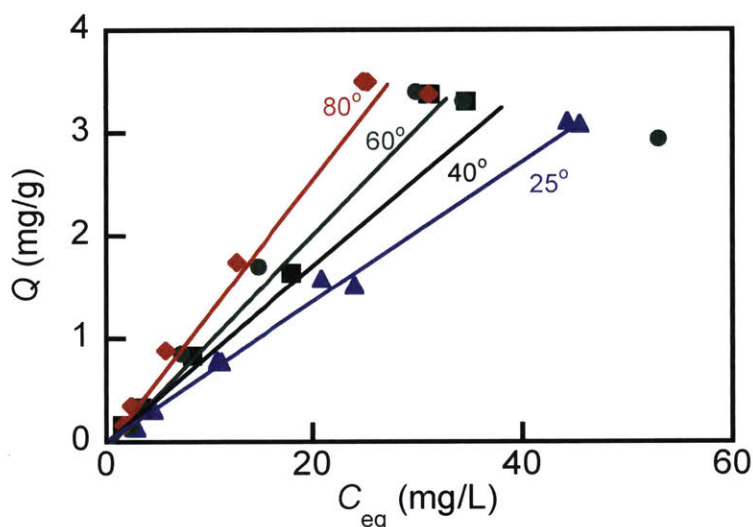


Figure 4-8. Temperature dependence of uranium adsorption isotherms with magnetic lyogel composed of DEDTC-PVC (38.5 wt%), D2EHPA (50.0 wt%) and Fe@C nanoparticles (11.5 wt%), gel loading: 50 mg/mL

As is seen in the figure, the total amount of uranium adsorbed by the lyogel gradually increases with temperature, indicating that the adsorption is an endothermic process. This endothermic nature of metal uptake is consistent with the characteristics of the process of adsorption of rare earths including uranium from aqueous media on specific solid sorbents such as magnetic nanoparticles and ion-exchange resins [71-74]. However, this trend is contradictory to what is observed as an exothermic process in uranium extraction using D2EHPA-TOPO from wet phosphoric acid [75,76] and in the case with organo-hydrogel extraction. Therefore, it appears that

we created a unique material capable of achieving similar capacity of uranium uptake as liquid-liquid extraction from wet phosphoric acid while reversing the thermodynamic nature of uranium binding. The thermodynamic mechanism behind this phenomenon should be studied in depth using molecular simulation and modelling.

4.6 Uranium Recovery from Magnetic Lyogels and Recycling Performance

A challenge in uranium extraction with magnetic organo-hydrogel is the leakage of extractant during the washing and drying steps in the recycling process. One of the purposes of designing this magnetic lyogel is to preserve the ability of the material to extract uranium in successive cycles of extraction and stripping cycles.

The stripping of uranium was extensively investigated in the context of D2EHPA-TOPO liquid-liquid extraction with aqueous ammonium carbonate emerging as an efficient stripping agent. In the present work, we studied uranium stripping from magnetic lyogels prepared using the optimum composition formula: 38.5 wt% DEDTA-PVC, 50.0 wt% D2EHPA, and 11.5 wt% C@Fe nanoparticles. The magnetic lyogels was added to a uranium solution prepared with the OCP fluid and equilibrated for 48 hours. The initial uranium concentration was 200 ppm and the gel loading was 50 mg/ml. The gel particles were then collected by magnet, rinsed with deionized water and air-dried before transferred to a solution containing 1 M ammonium carbonate at a particle loading of 50 mg/ml. The resulting suspensions of lyogels were agitated by rotation at 100 rpm at room temperature for another 48 hours. The particles then were collected by magnet followed by rinsing and air-drying before putting into use of the second cycle of extraction. The supernatants were subjected to uranium concentration measurements by ICP-OES. The performance of uranium stripping and recycling of the lyogel particles is shown

in Figure 4-9. It appeared that the stripped and washed lyogels did not lose their ability to adsorb uranium from the OCP fluid in at least three extraction-stripping cycles. About 78, 82, and 87% of uranium were able to be extracted from the OCP fluid in cycle 1, 2 and 3 respectively, out of which 73, 77, and 82% were stripped off and recovered by using 1 M ammonium carbonate. Additionally, based on gravimetric measurements, 97 to 100% of the lyogel particles were able to be collected in each cycle by magnetocollection. The results proved that the design of magnetic lyogel greatly reduces the loss of extractant during recycling, most probably resulting from the chemical compatibility between the modified PVC backbone and the incorporated extractants. The ability of this material to be recyclable enables the development of economically feasible process for uranium recovery from the wet phosphoric acid.

To further study the extractant leaching from magnetic lyogels, we performed a stability study wherein suspensions of the lyogel particles in 10 mM aqueous sulfuric acid were agitated at 60 °C for 48 hours. The supernatant and the particles were separated by magnet and the supernatant was subject to the phosphorus content by elemental analysis. The resulting phosphorus concentrations were measured to be 0.0012mg/ml. For comparison, the solubility of D2EHPA in analogous sulfuric acid solutions at saturation has been reported in the range of 0.14-0.18 mg/ml at 60 °C^[77]. In conclusion, the magnetic lyogel essentially prevented D2EHPA from leaching out into the aqueous acidic solutions.

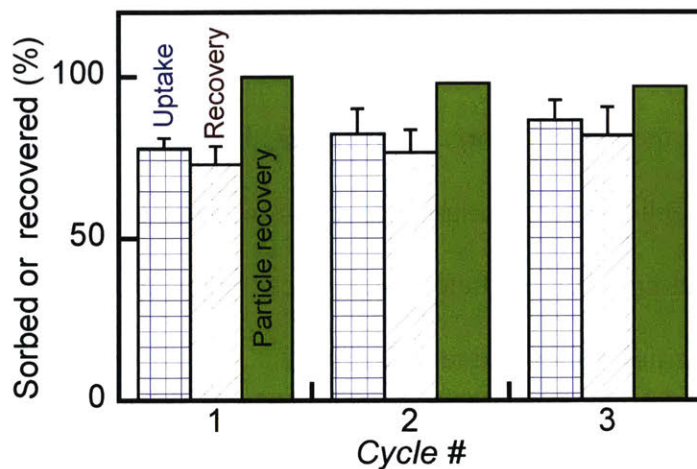


Figure 4-9. Percent of uranium nitrate adsorbed from the OCP fluid and recovered in the stripping experiment with 1 M ammonium carbonate solution and percent of particle recovery measured gravimetrically in three uptake-recovery cycles.

4.7 Conclusions

Magnetic lyogels were synthesized based on poly vinyl chloride modified with dithio-functional molecules which grants compatibility between the polymer backbone and the organophosphorus extractants. As a result, loss of the extractant due to syneresis and leaching were greatly reduced during recycling of the gel particles. Efficient recyclability and reuse of the lyogels in at least three cycles of the equilibrium uranium adsorption-stripping have been demonstrated. The inert organic polymer network also provides additional protection for the carbon coated iron nanoparticles in extremely corrosive environment such as what is represented in the OCP fluid, thereby allowing the composite material to remain magnetic properties in the OCP fluid for extended periods of time. More interestingly, we observed an increase in the equilibrium adsorption capacity of the material at elevated temperature, which is beneficial for its application in the real industrial wet phosphoric processing. As for the kinetics of this type of lyogel,

preliminary research showed that it exhibits similar kinetics with the organo-hydrogel material, with the potential of further improvement by decreasing the sizes of the lyogel particles. In summary, compared to the magnetic organo-hydrogel, the magnetic lyogel has three advantages that make it a better candidate for uranium extraction from wet phosphoric acid: 1) reduction in extractant loss in recycling of the particles 2) enhanced magnetic stabilities in the OCP fluid 3) higher adsorption capacities at elevated temperature.

5. CONCLUSION AND FUTURE WORK

Incorporation of uranium recovery into wet phosphoric acid (WPA) processes can potentially supplement a significant fraction of the world's uranium production and simultaneously benefit human health and environment by reducing radiological and toxic contamination of the phosphate fertilizer products. Traditional approach in industry to recover uranium from WPA was liquid-liquid extraction. However, the process usually generates large amount of waste streams (kerosene) and various problems such as extractant loss due to incomplete demulsification and crude formation. In this study, we investigated into two magnetic solid-state gel materials (magnetic organo-hydrogel and magnetic lyogel) to replace the conventional liquid-liquid extraction process for uranium recovery from wet phosphoric acid (WPA) produced by OCP in Morocco. The challenge within this study was mainly in the design of material that is suitable for operation in the extremely corrosive and chemically complicated environment represented by the OCP fluid and phosphoric acid samples. The magnetic lyogel were developed with properties such as high selectivity towards uranium in the presence of large amount of impurities ions, recoverability by means of magnetocollection, minimized extractant loss and recyclability, high content of the chosen extractant, chemical and magnetic stability in the phosphoric acid environment. The equilibrium adsorption and recyclability were evaluated using the synthetic OCP fluid. The magnetic organo-hydrogel, on the other hand, was proved to be capable of extracting uranium from the real OCP WPA samples with comparable efficiency as the liquid-liquid extraction and fast stripping kinetics. The size of the particles could be tuned by setting appropriate combinations of the flow rates in the microfluidic device which produces the particles. However, this type of material suffers mainly from a loss of extractant in the recycling

process, rendering the current design not as suitable as the magnetic lyogel for industrial application.

In the future study, the magnetic lyogel containing both D2EHPA and TOPO should be tested in the fresh OCP WPA samples. Additionally, the kinetics of adsorption of this type of material could be enhanced by developing novel synthesis method which allows easy manipulation of the size of the gel particles. The interesting phenomenon that the magnetic lyogel exhibits endothermic adsorption behavior as opposed to exothermic nature of liquid-liquid extraction requires further in-depth study using molecular simulation and modelling.

In conclusion, magnetic nanoparticles incorporated in hydrogel and lyogel containing specific extractants were developed with desired properties to extract uranium from the OCP wet phosphoric acid and their uranium extraction performance (isotherm, kinetics and recyclability, etc.) were evaluated. This research led a good foundation for developing novel uranium extraction processes that could be applicable industrially.

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