Preparation, characterization and application of $NaHCO_3$ leached bulk U(VI) imprinted polymers endowed with γ-MPS coated magnetite in contaminated water

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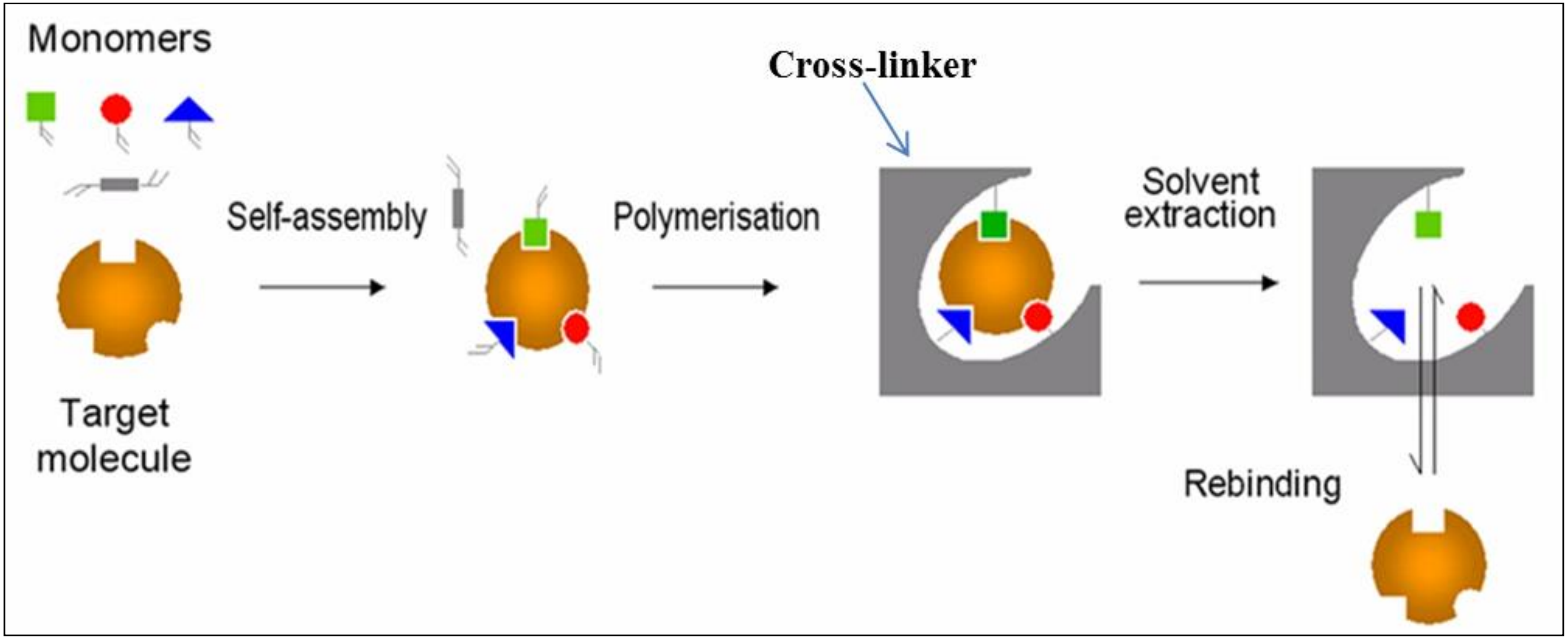
Presentation outline

- Introduction and background
  - Ion imprinted polymers (IIPs)
  - Magnetic IIPs
  - U(VI) target
- Aims and objectives
- Materials and methods
- Results and discussion
  - Synthesis and characterization of magnetic particles
  - Optimization of adsorption parameters
  - Application
- Conclusions

Principle of imprinting of polymers

Molecularly (Ion) imprinted polymers are highly stable polymers that possess recognition sites within the polymer matrix that are adapted to the three-dimensional (3-D) shape and functionalities of an analyte of interest

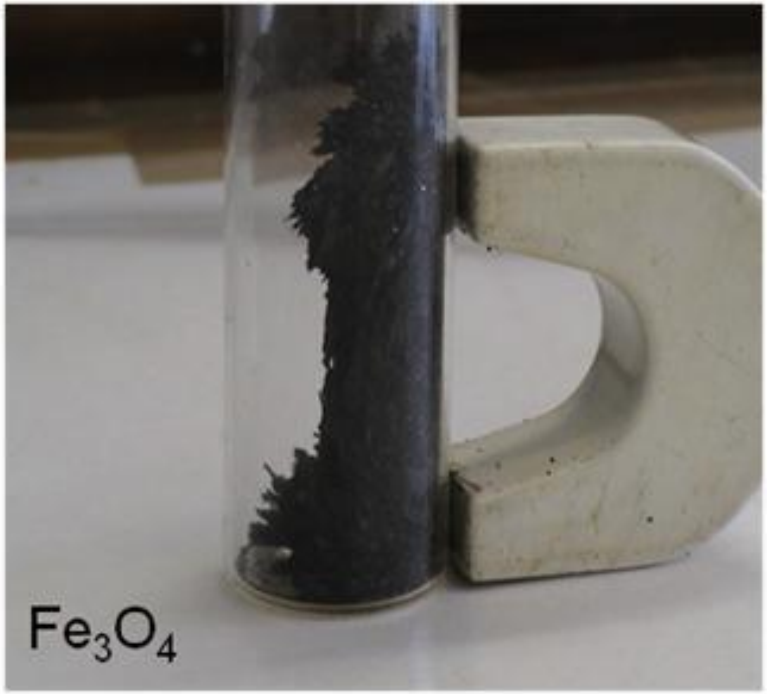


Overview of some application areas

- Selective sorbents in environmental remediation
- Selective stationary phases in chromatography
- Site-mediated synthesis, enzyme mimics/catalysis
- Sensor like devices, antibody-receptor mimics
- Screening combinatorial libraries, drug delivery

Magnetic materials

- Materials that respond to external magnetic field
- They usually have unpaired electrons



Benefits of combining magnetic particles with imprinted polymers

- Magnetic property helps to separate the particles from the sample using a magnetic

- Magnetic property helps to eliminate time consuming and expensive methods such as centrifugation and filtration during sample extraction process

- Selectivity of the particles helps to remove only the chosen analyte from the sample that is of concern (from complex matrices)

Background-uranium

- Used to fuel commercial nuclear power plants (storage of huge amounts of energy)

- Geochemical speciation of uranium influences its solubility, mobility and biological availability in the environment

- Distribution of uranium ions in aqueous solution is dependent on both the solution pH and the total uranium concentration

- At low concentration and pH, U(VI) predominates

Effects of uranium

- Non-renewable resource of nuclear energy
- Radioactive
- Bio-accumulation in food webs
- Excessive exposure cause kidney toxicity
- Glomeruli damage

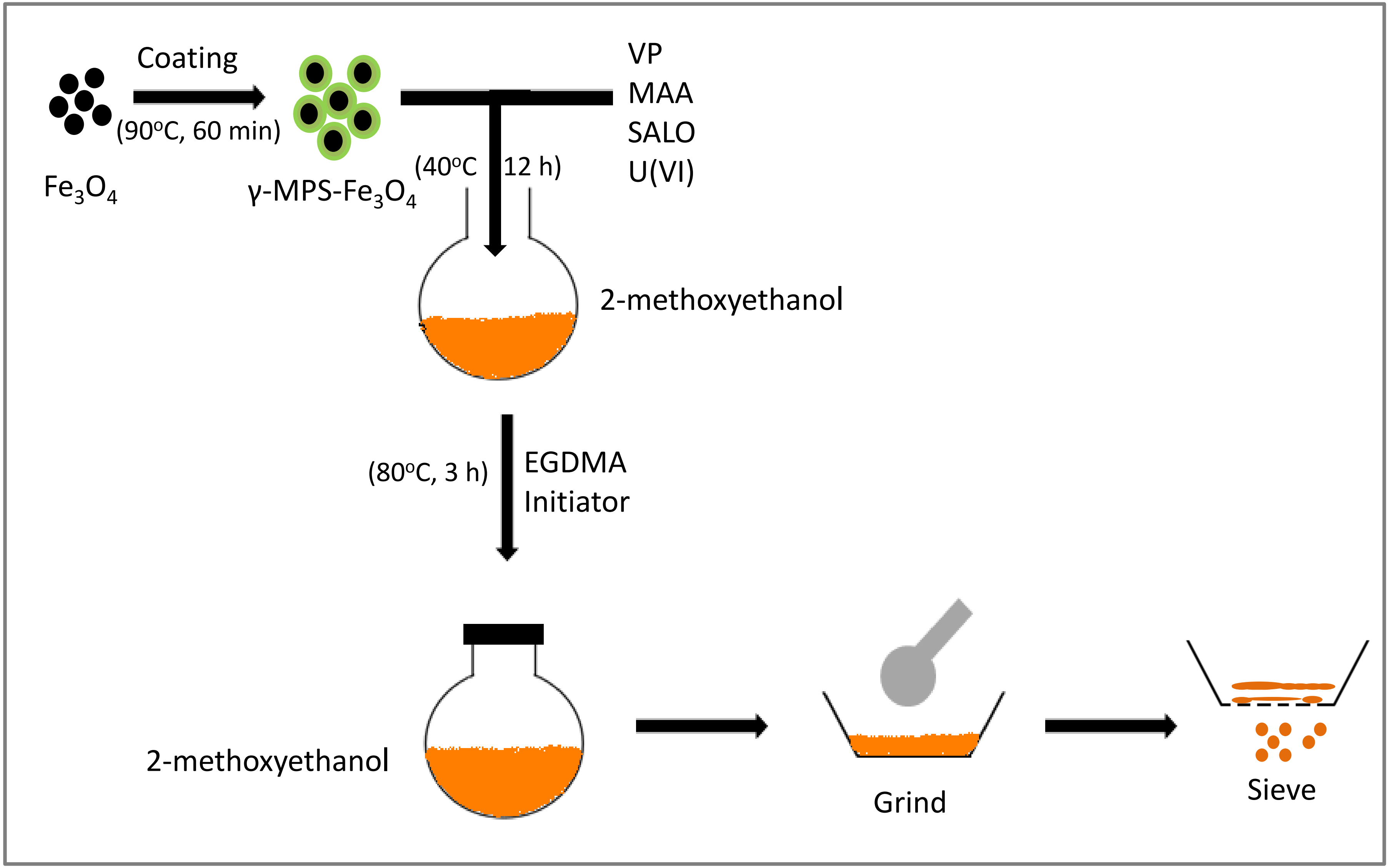
Regulation of dangerous uranium

	Maximum allowable limit ($\mu g\ L^{-1}$)
World Health Organization	9
Health Canada	20
Australian	20

Aims and objectives

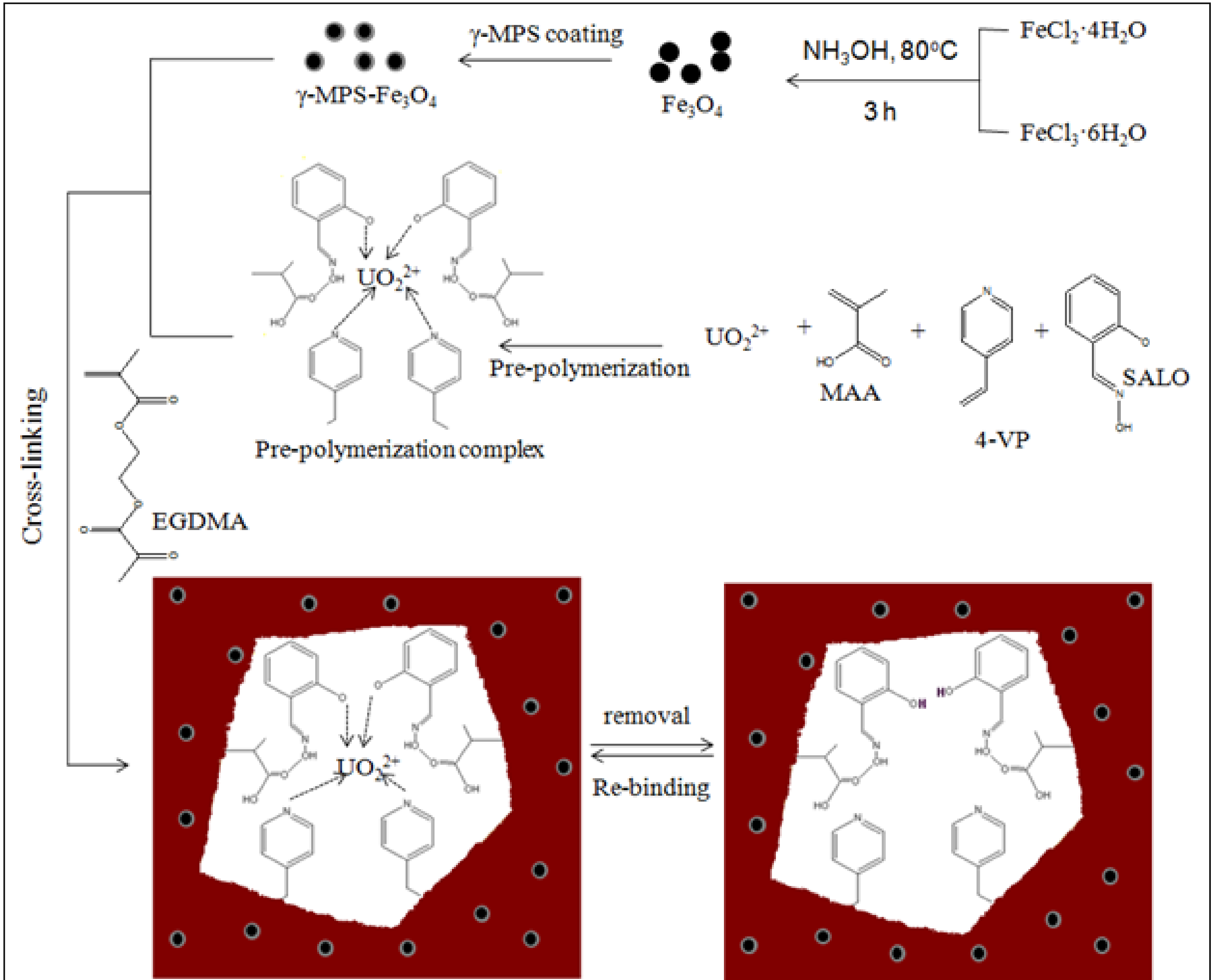
- To synthesize superparamagnetic magnetite
- To functionalize magnetite using γ-MPS surfactant
- To prepare the magnetic nano-composite materials based on ion-imprinted polymers specific for U(VI)
- To characterize the prepared magnetite, functionalized magnetite and magnetic nano-composite polymers selective for U(VI)
- To study the binding behaviour of U(VI) onto the prepared magnetic nano-composite beads from aqueous solutions

Polymerization scheme



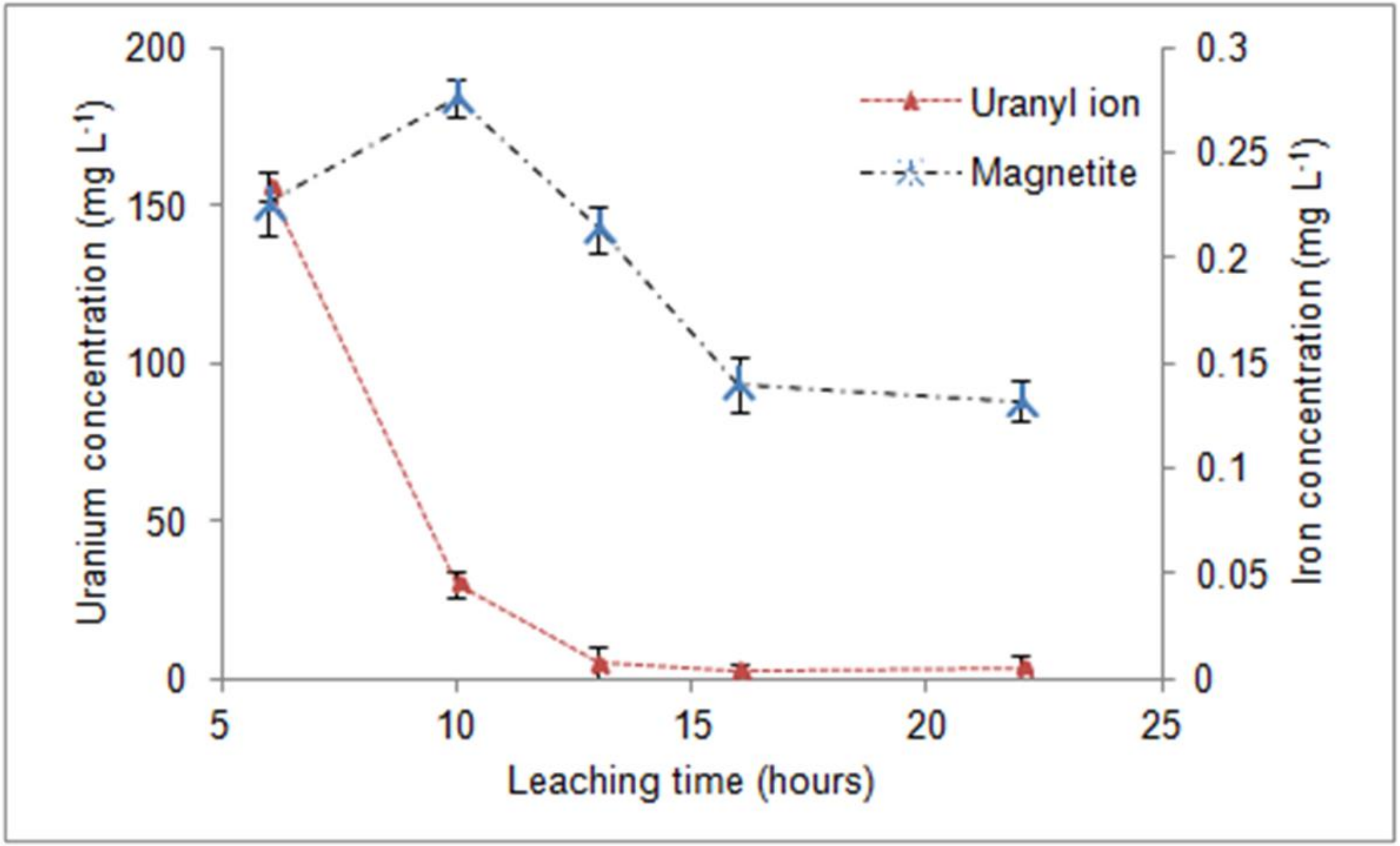
γ-MPS: γ-methacryloxypropyltrimethoxysilane, VP: vinylpyridine, MAA: methacrylic acid, SALO: salicylaldoxime, EDGMA: ethylene glycol dimethacrylate

Schematic diagram for the synthesis of magnetic IIP



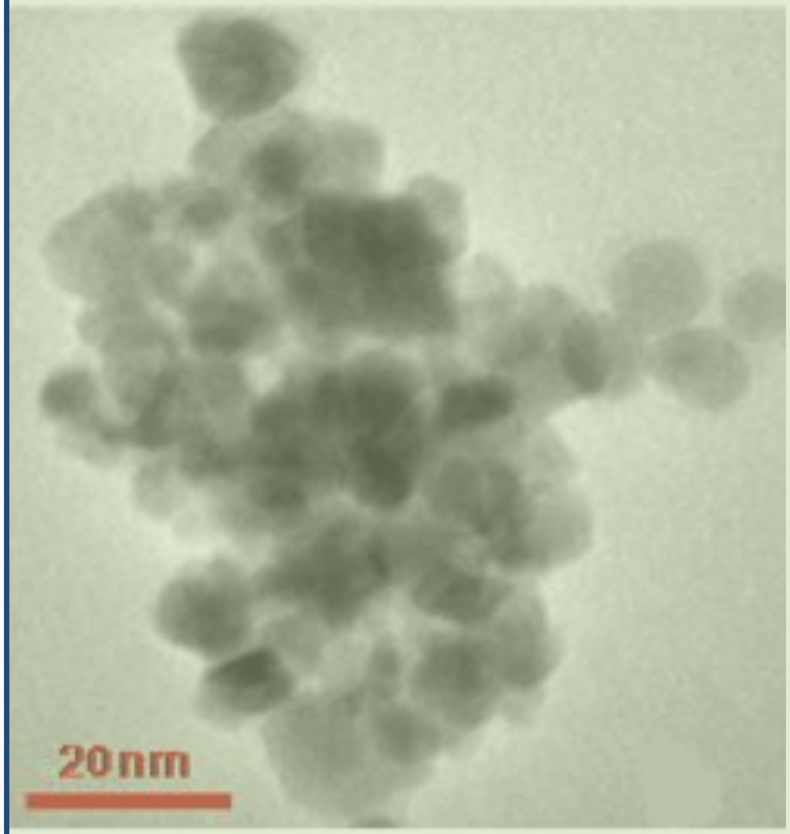
Leaching of U(VI) from magnetic polymers

- Batch extraction approach
- The template was removed using $NaHCO_3$



Morphological and elemental analysis of coated magnetite

Transmission Electron Micrograph (TEM)



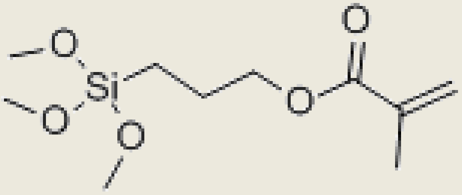
- Spherical particles
- Narrow particle size diameters
- Agglomeration

CHNS elemental analysis

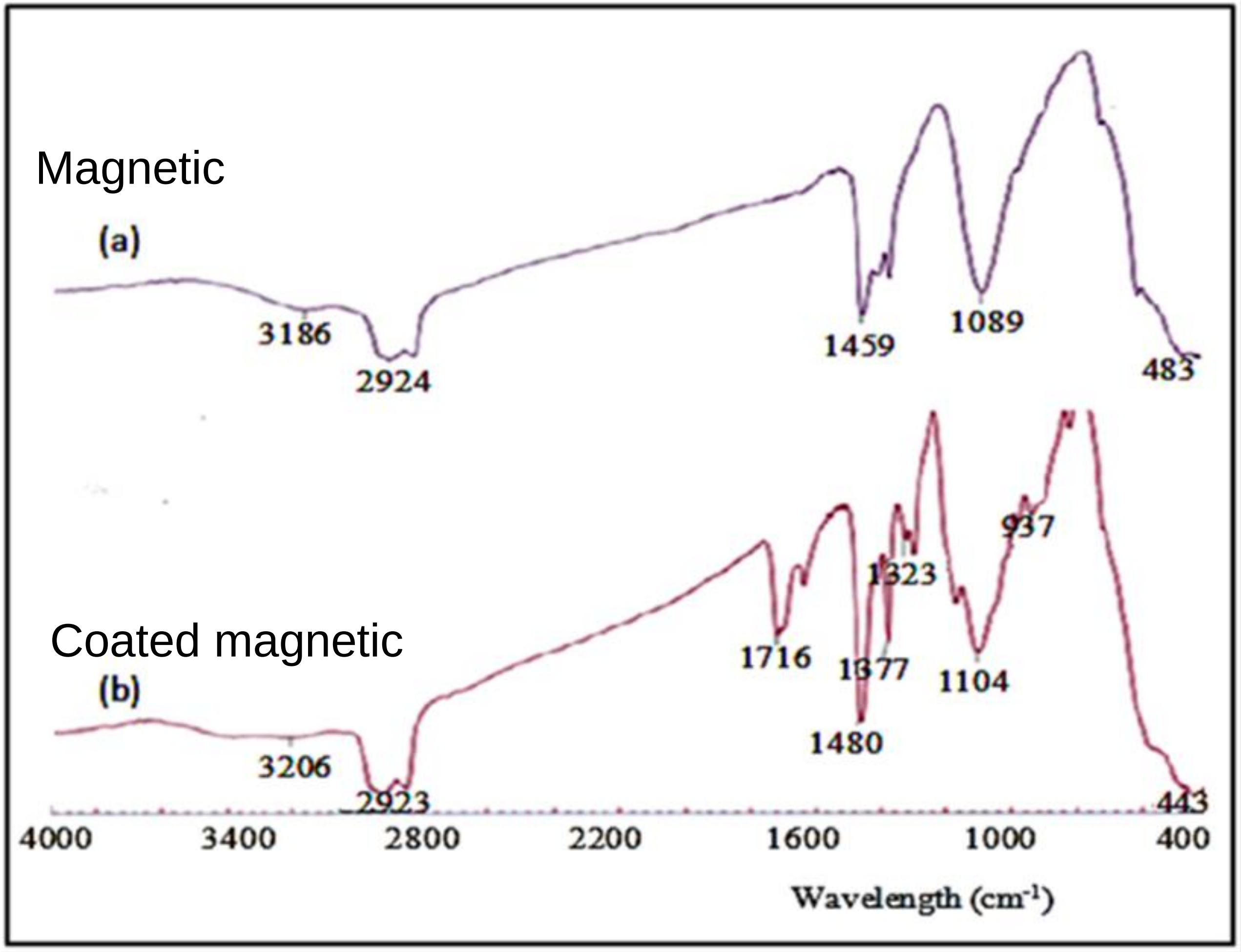
mass (g)	% C	% H	Ligand concentration (mmol g^{-1}) *
2.00	20.16	2.94	16.8
2.00	19.25	2.92	15.8
2.00	18.92	2.84	15.8

*Values for the ligand concentration were all based on the carbon content

Quantitative loading of γ-MPS on magnetic = 16.1 mmol g^{-1}



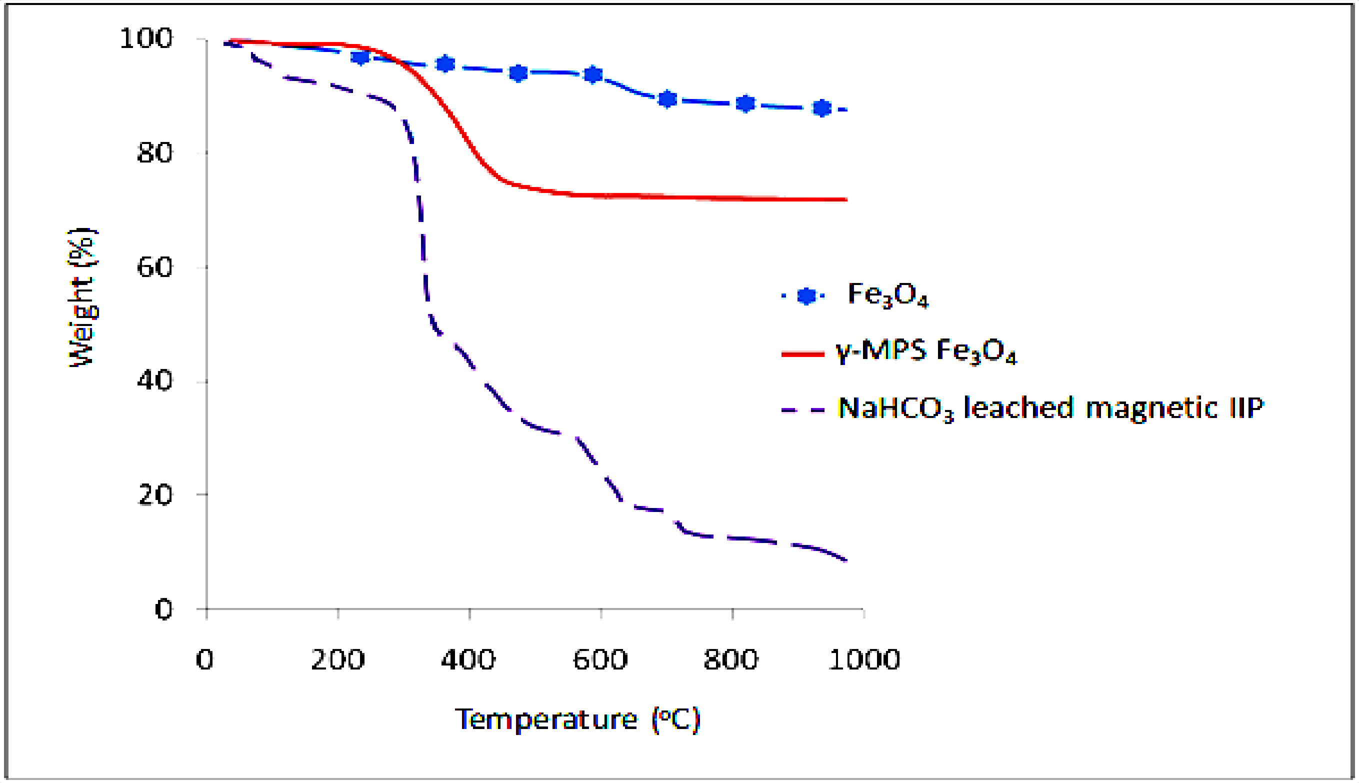
FTIR confirmation of γ-MPS coating of magnetite



- Of note is the OH with a stretching frequency of 3186 cm^{-1}
- Functionalization evident with the band at 1716 cm^{-1}

Thermogavimetric analysis and BET measurements

Thermal stability of magnetic polymers



BET surface area

	BET surface area (m^2 g^{-1})	v_m (cm^3 g^{-1})	c
Unleached magnetic IIP	8.8	2.09	94.86
$NaHCO_3$ leached magnetic IIP	65.2	15.43	129.6

Optimization of adsorption parameters

- Batch sorption experiments
  - Sample pH
  - Sample weight
  - Contact time → (Kinetic modeling)
  - Sample concentration → (Adsorption modeling)

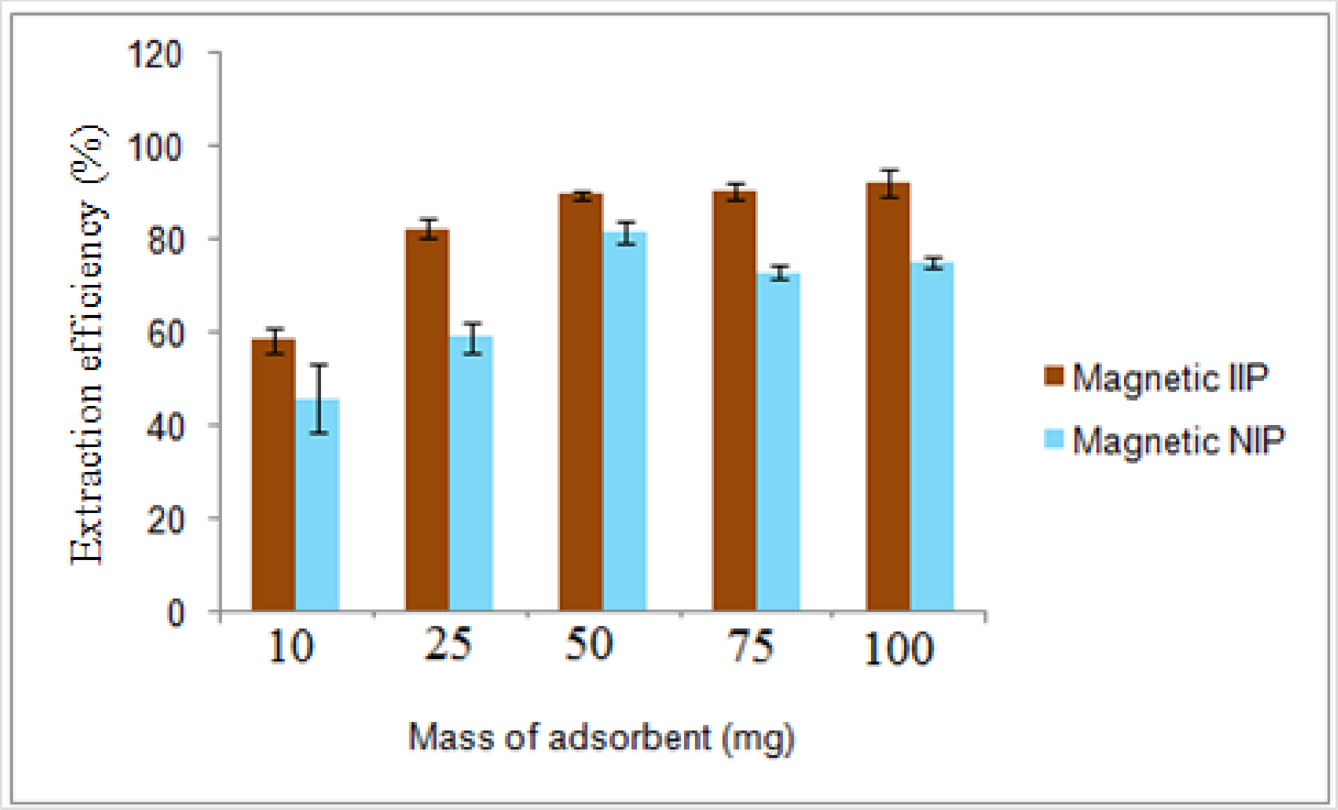
- Magnetic IIP performance

$$\text{Extraction efficiency} = \frac{(C_o - C_e)}{C_o} \times 100\%$$

$$q = \frac{(C_o - C_e)V}{W}$$

where Co (mg L^{-1}) is the initial concentration, Ce (mg L^{-1}) the final concentration, q (mg g^{-1}) adsorption capacity

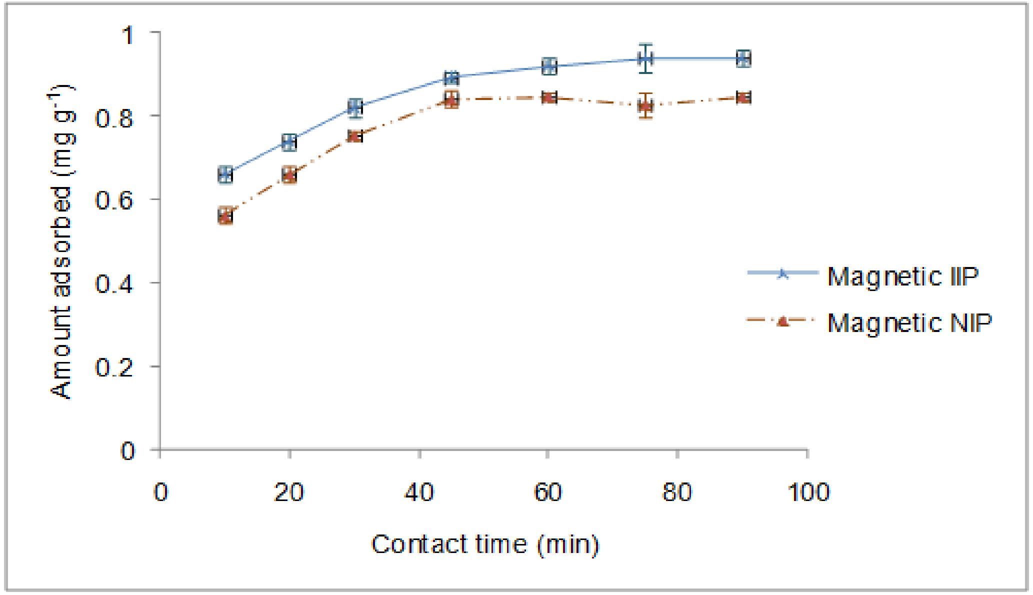
Mass optimization



Experimental conditions: Sample pH, 4; sample volume, 25 mL; uranium concentration, 2 mg L^{-1}; Contact time, 45 min; stirring speed, 1500 rpm; temperature, ambient temperature

- Optimum amount of magnetic IIP = 50 mg
- Selective to U(VI) (Imprinting effect)

Time optimization



- Low uptake capacity of U(VI) by magnetic IIP
- Optimum extraction time = 45 min (Fast mass transfer)

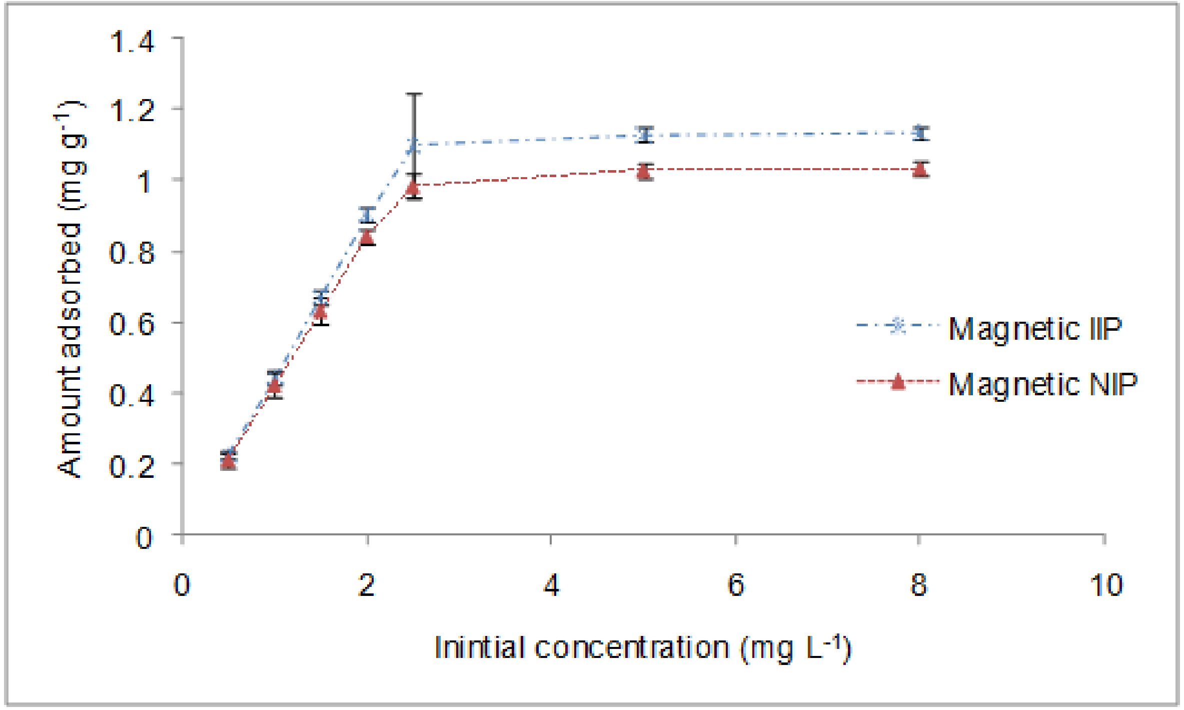
Kinetic modeling

	Pseudo first-order			Pseudo second-order		
Polymer	k_1 (min^{-1})	q_e (mg g^{-1})	R^2	q_e (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2
Magnetic IIP	0.054	1.100	0.885	1.008	0.163	0.9979
Magnetic NIP	0.071	0.478	0.986	0.859	0.163	0.9988

Pseudo-second- order model showed better correlation:

- Based on the linear regression ($R^2 > 0.99$)
- qe values obtained (0.86-1.00 mg g^{-1}) close to experimental values

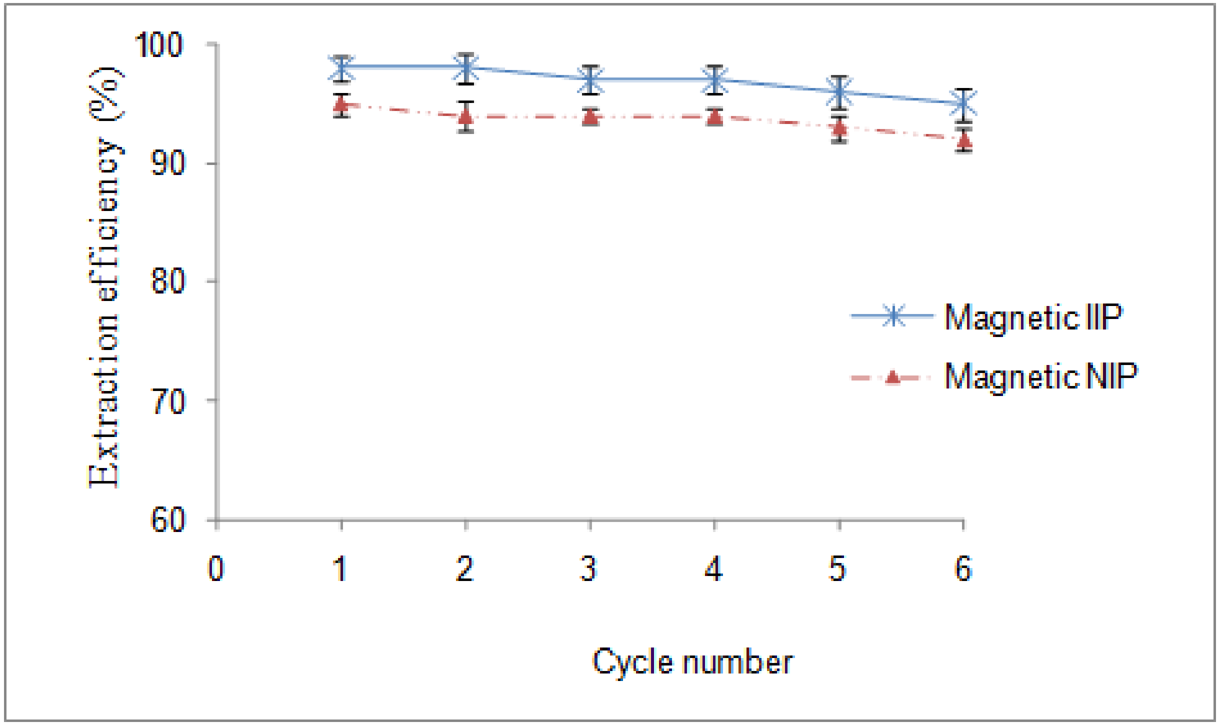
Initial concentration optimization



Adsorption modeling

Polymer	Langmuir constants				Freundlich constants		
	b (L g^{-1})	q_m (mg g^{-1})	R_L	R^2	n	K_f (L g^{-1})	R^2
Magnetic IIP	0.09	67.1	0.85	1.00	1.00	5.77	1.000
Magnetic NIP	0.22	7.4	0.69	0.999	1.07	1.47	0.997

Reusability and stability of magnetic polymers



Adsorption conditions: Amount of materials, 50 mg; solution pH 4; solution volume, 25 mL; contact time, 45 min, U(VI) concentration, 2 mg L^{-1}

Desorption conditions: Solution volume, 25 mL; contact time, 45 min, HCl concentration leachant, 1 mol L^{-1}

Conclusions

- Preparation of magnetic materials promising
- Further assessment of magnetic responses (SQUID and VSM) required
- Both magnetic IIPs and NIPs showed potential in the uptake of U(VI) from contaminated solutions
- Magnetic IIPs had superior performance as compared to the control due to imprinting
- Generally low uptake due to incorporation of the magnetic core

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