

# Selective Adsorption of Uranium (VI) on NaHCO<sub>3</sub> Leached Composite $\gamma$ -Methacryloxypropyltrimethoxysilane Coated Magnetic Ion-imprinted Polymers Prepared by Precipitation Polymerization

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## ABSTRACT

Ion imprinted nano-magnetic composite polymers for selective removal of hexavalent uranium were prepared by a precipitation polymerization technique in the presence of  $\gamma$ -methacryloxypropyltrimethoxysilane ( $\gamma$ -MPS) coated magnetite and other pre-polymerization reagents. The synthesized magnetic polymers were then leached with NaHCO<sub>3</sub> to produce magnetic ion imprinted polymers (IIPs) with fabricated adsorption sites complementary to the uranyl ions in terms of size and shape. Several parameters were investigated to obtain conditions which gave the optimum adsorption of the uranyl onto the magnetic IIPs and their corresponding controls, magnetic ion non-imprinted polymers (NIPs). The optimum amount of magnetic sorbent, initial concentration and contact time were 50 mg, 2.5 mg L<sup>-1</sup> and 45 min, respectively. The adsorption capacity of the magnetic IIP (1.15  $\pm$  0.01 mg g<sup>-1</sup>) was higher than that of the magnetic NIP (0.93  $\pm$  0.02 mg g<sup>-1</sup>). This indicated that the former had a somewhat higher affinity for U(VI) than the later. The magnetic polymers also displayed good selectivity of the order: U(VI) > Ni(II) > Mg(II). After six cycles of use, the magnetic polymers illustrated good stability and reusability.

## KEYWORDS

Complex matrices, magnetic ion imprinted polymers, precipitation, selectivity, uranium.

## 1. Introduction

Major sources of radioactive wastes and contaminants, like uranium, emanate from the production of electrical power and weapons from nuclear fuels, nuclear weapons' tests, fuel reprocessing, and nuclear accidents.<sup>1</sup> These processes generate a lot of uranium waste that has always been a problem for long-term storage.<sup>2,3</sup> Other sources of uranium waste include by-products of mining activities of other minerals such as gold and copper.<sup>4,5</sup> The production of uranium has generally been a by-product of gold or copper mining. Gold and uranium mining are typically accomplished together, as both methods process large volumes of material with very small yields.

In nature, uranium normally occurs in tetravalent and hexavalent form, but the latter is easily soluble in acidic conditions.<sup>6</sup> In oxygen-containing groundwater, uranium is most commonly found in the hexavalent oxidation state, U(VI),<sup>4,7,8</sup> a highly soluble, mobile and therefore troublesome form. Under these oxidizing conditions, the uranyl ion predominates and behaves as a strong acid on the Lewis acidity scale.<sup>9</sup> Uranyl ions show high interaction with a variety of organic and inorganic ligands to form complex species of different stabilities.<sup>9</sup> In systems with high dissolved carbonate concentration, uranyl-carbonate complexes may become dominant<sup>10</sup> and it forms soluble carbonate complexes in solution.<sup>11,12</sup> These stable dissolved ternary complexes can effectively compete for mineral surfaces as reservoirs for U(VI).<sup>13</sup>

Uranium is a well known pollutant and can cause irreversible renal injury and may even lead to death, which prompted the United States Environmental Protection Agency (USEPA) to set the maximum permissible uranium concentration in drinking

water as 30  $\mu$ g L<sup>-1</sup>.<sup>14</sup> Several methods, such as chemical precipitation, solvent extraction, micellar ultra filtration, organic and inorganic ion exchange, and adsorption processes have been described for the removal of U(VI) from aqueous solutions.<sup>15</sup> Adsorption is regarded as one of the most efficacious and economical method because of its low cost and regeneration capabilities.<sup>16</sup> Some sorbents that have been used include activated carbon,<sup>17</sup> hydrogels,<sup>18</sup> clays,<sup>19</sup> silica gels<sup>20</sup> and hydrous oxides.<sup>21</sup> However, most of these reported methods are not selective. In trace analysis, and other fields, a sorbent that specifically extracts specific targets is desired. Ion imprinting is such a technique for creating recognition sites for a specific analyte in a synthetic polymer.<sup>22</sup> Sadeghi and Mofrad,<sup>23</sup> Singh and Mishra,<sup>24</sup> Milja *et al.*,<sup>25</sup> among others, have applied ion imprinted polymers (IIPs) for the removal of uranium from aqueous samples.

Loaded imprinted polymers cannot be efficiently separated from the biological or environmental samples by the traditional filtration and centrifugation.<sup>26,27</sup> Endowing magnetic nano-particles into the polymer matrix of IIPs will allow these sorbents to be easily separated from aqueous solution but not much has been reported on the preparation of such materials.<sup>28-0</sup> Previously, there was an attempt in our group by Pakade *et al.*<sup>31</sup> to use ion-imprinted polymers prepared by bulk polymerization for uranium uptake. The polymer used, however, was not magnetic and a totally different reagent combination was used. Recently, Tavengwa *et al.*<sup>32</sup> reported a bulk polymerization approach for the synthesis of magnetic particles for uranium which involved grinding of the resultant polymer. The main objectives of the present study were to prepare uranyl ion imprinted and non-imprinted magnetic polymer particles

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through precipitation polymerization, and ultimately, investigate their selective removal of toxic uranium from contaminated solutions. Precipitation polymerization is more advantageous over bulk polymerization in that no grinding of polymers is involved. Grinding has been criticized for breaking up the active sites.<sup>33,34</sup>

## 2. Materials and Methods

### 2.1. Materials and Instrumentation

Pre-polymerization reagents, ethylene glycol dimethacrylate (EGDMA), methacrylic acid (MAA), 1,1'-azobis(cyclohexanecarbonitrile), salicylaldehyde (SALO), 4-vinylpyridine (4-VP), 2-methoxyethanol and  $\gamma$ -methacryloxypropyltrimethoxysilane ( $\gamma$ -MPS) were purchased from Sigma Aldrich (Steinheim, Germany).  $\text{NH}_4\text{OH}$  washing solvent, methanol,  $\text{NaHCO}_3$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  were also purchased from Sigma Aldrich (Steinheim, Germany). The imprint, uranyl nitrate ( $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) was bought from BDH Chemical Ltd, (Poole, England). Stock solutions of  $1000 \text{ mg L}^{-1}$  were prepared by dissolving the appropriate amounts of the following analytical grade dried salts in 1 volumetric flasks:  $\text{U}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . These solutions were then acidified with 0.05 % (v/v)  $\text{HNO}_3$  and working solutions were prepared daily from the stock solutions.

Genesis End-on-Inductively Coupled Plasma Optical Emission Spectrometry – ICP-OES from Spectro Genesis (Kleve, Germany) was used to measure the metals concentration in multi-elemental solutions. Atomic Absorption Spectrometry (AAS) measurements were done on a PG-990 AAS (Leicestershire, UK) with pyrolytically coated HGA-76 graphite furnace tubes used as sample holders. Deionized water was prepared from a Millipore system (Massachusetts, USA) and all pH measurements were performed on a 766 Calimatic pH meter equipped with a Shott N61 pH electrode from Knick (Berlin, Germany). In batch adsorption studies, a Laser Photo/Contact Tachometer DT-1236L from Lutron (Taipei, Taiwan) was used to measure the rotational speeds of the magnetic stirrers. Surface morphological information of magnetic IIPs and NIPs was obtained using a scanning electron microscope (SEM) JOEL Model JSM 6700F (Tokyo, Japan). A Veeco/Digital Instruments Dimension 3100 Scanning Probe Microscope (Santa Barbara, USA) was used in AFM-tapping mode in the study of surface morphology of magnetic polymers.

### 2.2. Synthesis of Magnetic U(VI) Polymers and Leaching of the U(VI)

Methods described by Thorek *et al.*<sup>35</sup> and Kan *et al.*<sup>36</sup> were used for the synthesis of magnetite and its coating with  $\gamma$ -MPS, respectively. Magnetic polymers were synthesized with 270 mg  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  according to the method outlined by Singh and Mishra<sup>22</sup> with one modification of dispersing 2 g of  $\gamma$ -MPS functionalized magnetite in the ternary complex solution of the pre-polymerization mixture.

Precipitate magnetic polymer sorbent (3 g) was then transferred to a 250 mL volumetric flask and 100 mL of  $1 \text{ mol L}^{-1}$   $\text{NaHCO}_3$  was added. The mixture was stirred gently for 10 h, after which filtration was done under vacuum. The filtrate was retained for metal analysis. A freshly prepared  $\text{NaHCO}_3$  leachant, with the same concentration and volume as above, was added to the magnetic polymer for leaching for an additional 4 h and similarly this was repeated for another 3 h.

Magnetic NIPs were prepared and treated likewise, except that the imprint ion was not included.

### 2.3. Optimization Studies

In order to investigate the effect of sample pH, the uranium solutions were adjusted to pH 2–9, and 25 mL of  $2 \text{ mg L}^{-1}$  of these were then transferred to 30 mL vials where 20 mg of an adsorbent (magnetic IIP and NIP) were added. After this, the uranyl-IIP mixture was allowed to equilibrate for 45 min. The loaded magnetic-IIPs were then separated from the mixture by application of an external magnetic field and the solution analyzed for uranium content. All adsorption experiments were carried out at room temperature.

For the effect of the amount of magnetic polymer, adsorption was carried out in a series of 30 mL vials at room temperature. Each vial was filled with 25 mL of an initial concentration of  $2 \text{ mg L}^{-1}$  solution of uranium. An optimized sample pH was used. The added magnetic polymer mass was varied between 10 to 100 mg. After stirring the solution for 45 min, separation of the solution magnetic polymers was achieved by use of a magnet, and the analyzed for uranium content.

In order to establish the optimum contact time of the magnetic polymers and  $2 \text{ mg L}^{-1}$  of uranium solution, adsorption of uranium onto the magnetic polymers was investigated at various time intervals (10–90 min). The optimized amount of the polymer was added into 25 mL uranium solution, and this mixture was then mixed at room temperature while stirring. After adsorption, the polymers were separated from aqueous phase by use of an external magnetic field, and the supernatant analyzed for uranium.

For the initial uranium concentration, adsorption was carried out in a series of 30 mL vials at room temperature. Each vial was filled with 25 mL of uranium solution of five varied initial concentrations ranging from 0.5–10  $\text{mg L}^{-1}$ . The pH and amount of the magnetic polymer used were those optimized. After stirring the solution for the optimum period, separation of the magnetic polymers was achieved by use of a magnet, and the solution was then analyzed for uranium.

All experiments were done in batch mode and in triplicate. The concentration of unextracted U(VI) ions in solution was determined by GFAAS and ICP-OES for multi-elemental analysis. These parameters were optimized by varying one parameter while keeping others constant in a sample volume of 25 mL and a stirring speed of 1500 rpm. The performance of the magnetic polymers were determined by calculation of the extraction efficiency,  $E$  (%), and adsorption capacity,  $q$  ( $\text{mg g}^{-1}$ ), given by equations (1) and (2), respectively.

$$\text{Extraction efficiency} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1)$$

$$\text{Adsorption capacity} = \frac{(C_o - C_e)V}{W} \quad (2)$$

where  $C_o$  ( $\text{mg L}^{-1}$ ) and  $C_e$  ( $\text{mg L}^{-1}$ ) are the initial and final concentrations, respectively.  $V$  (L) is the sample volume of the solution used, and  $W$  (g) is the mass of the magnetic polymer used for extraction. The effect of imprinting on selectivity was defined by the distribution coefficient ( $K_d$ ), and expressed mathematically by Equation (3).

$$K_d = \frac{(C_o - C_e)V}{C_e W} \quad (3)$$

The selectivity coefficient,  $K$ , for the binding of hexavalent uranium ( $\text{U}^{6+}$ ) in the presence of a competing ion  $X$  was obtained by Equation (4), while the relative selectivity coefficient  $K'$  is given by Equation (5). These quantities ( $K_d$ ,  $K$  and  $K'$ ) estimate the extent of imprinting on selectivity.

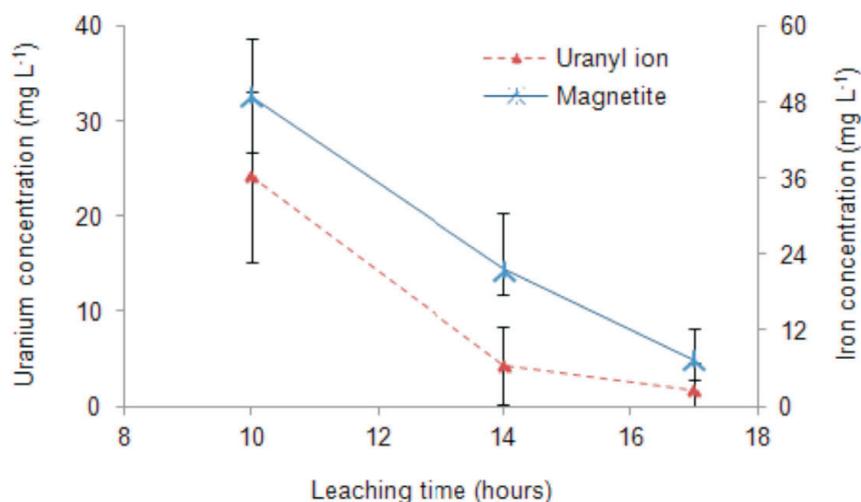


Figure 1 Precipitate magnetic IIP leached with 1 mol L<sup>-1</sup> NaHCO<sub>3</sub> (n = 3).

$$K = \frac{K_d(U^{6+})}{K_d(X)} \quad (4)$$

$$K' = \frac{K_{IIP}}{K_{NIP}} \quad (5)$$

### 3. Results and Discussion

#### 3.1. Preparation and Leaching of Imprinted Polymers

A SALO and 4-VP functional monomer combination was selected in this synthesis because of lone pairs of electrons on oxygen and nitrogen atoms of the former and on nitrogen of the later. O and N atoms are therefore likely to act as donor atoms to the cationic uranyl through ion-dipole interactions.

The expected decrease of the amount of leached uranyl from precipitated magnetic polymers as a function of time is shown in Fig. 1. However, there was a parallel unwanted leaching of the embedded magnetic core from the polymers with 1 mol L<sup>-1</sup> NaHCO<sub>3</sub>. Only the residual magnetite still embedded imparted magnetism to the polymers. It was also observed that the leaching of the uranyl ion was slow, and this is undesirable as the uranyl might bleed out when partially leached polymers are being applied to environmental waste water samples. It was also

noted that bulk polymers tended to lose more of both the uranyl as well as the magnetite than those from precipitation polymerization as was observed in our previous work.<sup>32</sup> This can be attributed to the crushing of the polymers in bulk polymers and that is why the precipitation approach was used in this synthesis. Precipitation polymerization uses more porogen volume than that used in bulk polymerization; the rest of the quantities of the prepolymerization reagents remain the same. Stoichiometrically, 3.4 mg of U(V) was in 3 g of magnetic IIP, and from Fig. 1, the total uranium leached from the three 100 mL leachates amounted to 3.2 mg. This value translated to approximately 94 % of U(VI) having been leached from the magnetic polymer.

#### 3.2. Characterization

The surface morphology of the magnetic polymers was investigated using scanning electron microscopy (SEM). The SEM image in Fig. 2(a) shows irregularly shaped precipitate imprinted polymers. The surface texture exhibited cavities on the surface of the leached magnetic IIP as a consequence of imprinting (Fig. 2(b)). The roughness of the surface is important as it promotes the mass transfer rate of uranyl ions toward the polymer surface. The formed cavities further increase the sorption capacity of the sorbent.

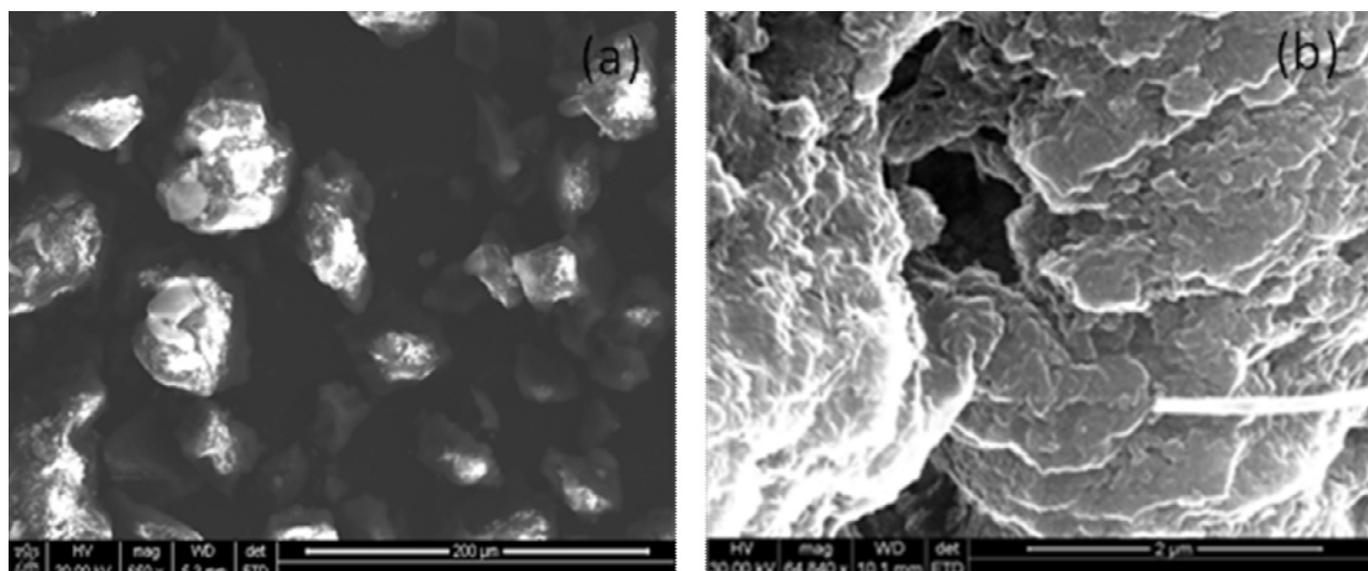


Figure 2 SEM micrographs of (a) unleached and (b) leached magnetic ion imprinted polymers.

Imaging of unleached magnetic IIPs using tapping mode atomic force microscopy (AFM) proved difficult, as the tip was repelled from the magnetic surface it was supposed to image. However, imaging of the leached magnetic polymers was successful. This was made possible by the fact that some magnetite was lost during leaching; hence the residual magnetite did not have sufficient power to repel the AFM probing tip. Figure 3 shows a three-dimensional AFM image of  $\text{NaHCO}_3$  leached polymer and it clearly shows the pores formed by the leaching of the uranyl ions from the polymer surface.

### 3.3. Influence of Sample pH

The charge density on the magnetic polymer surface is one of the main factors affecting the extraction of analytes and it strongly varies with pH. Sample pH variation was investigated (Fig. 4) at room temperature (rt.) under the following experimental conditions: amount of the magnetic polymer, 50 mg; sample volume, 25 mL; uranium concentration,  $2 \text{ mg L}^{-1}$ ; contact

time, 45 min; stirring speed, 1500 rpm. As seen from Fig. 4, the initial adsorption of  $\text{UO}_2^{2+}$  by the polymer was low, and then it gradually reached a plateau at equilibrium. At lower pH values, the functional monomers become protonated thereby making the adsorption sites unavailable for the adsorption of uranyl ions. However, at  $\text{pH} > 4$ , and due to the repulsive electrostatic interactions, the positively charged uranyl ion became preferentially adsorbed ahead of the hydroxyl ions, which were repelled from the adsorption cavities with functional monomers carrying lone pairs of electrons. At higher pH value, it is known that the  $\text{UO}_2^{2+}$  may hydrolyze and generate a series of species such as  $\text{UO}_2(\text{OH})^+$ ,  $(\text{UO}_2)_2(\text{OH})_2^{2+}$  and  $(\text{UO}_2)_3(\text{OH})_5^+$ .<sup>37</sup>

### 3.4. Influence of the Amount of Polymer Materials

Different amounts of the magnetic polymer materials ranging between 10 and 100 mg were used for the binding of U(VI) when these experimental conditions were used: sample pH, 4; sample volume, 25 mL; uranium concentration,  $2 \text{ mg L}^{-1}$ ; contact time,

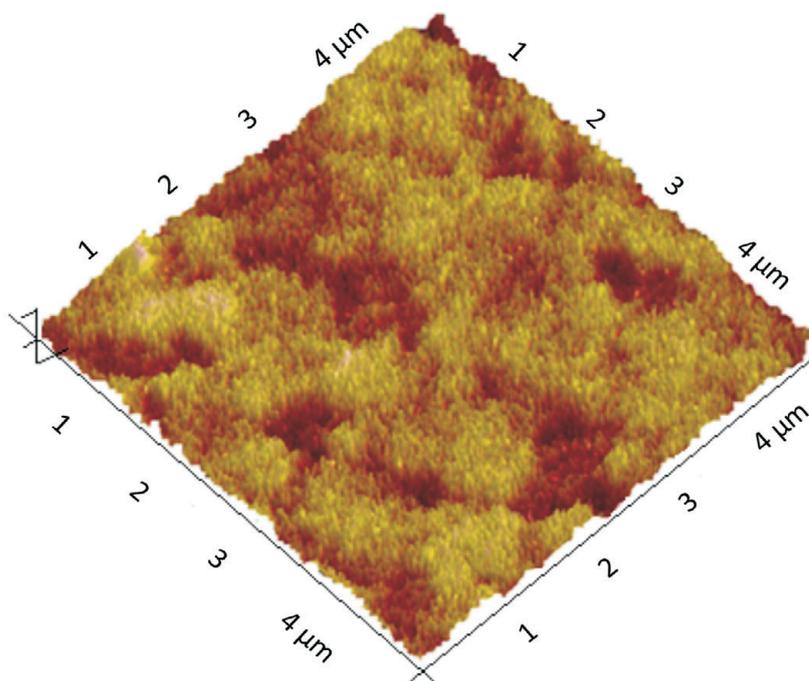


Figure 3 A three-dimensional AFM image of  $\text{NaHCO}_3$  leached polymer.

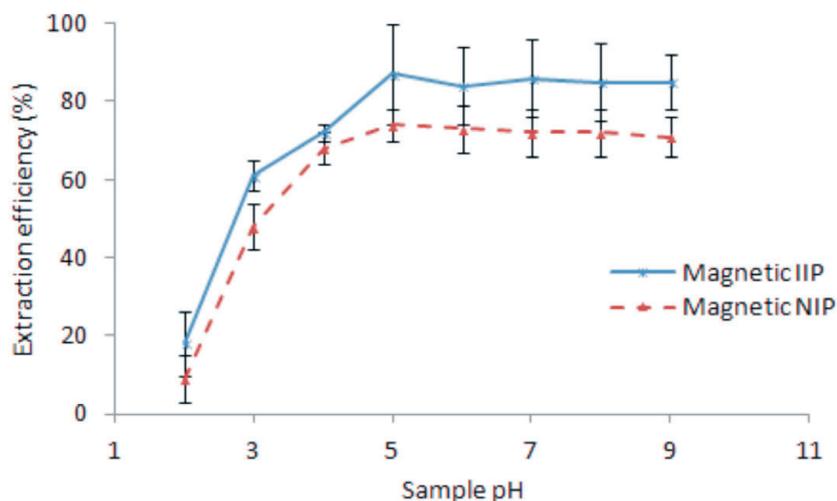


Figure 4 Effect of sample pH on the uptake of uranium by magnetic polymers ( $n = 3$ ). [weight of magnetic polymer, 50 mg; sample volume, 25 mL; uranium concentration,  $2 \text{ mg L}^{-1}$ ; contact time, 45 min; stirring speed, 1500 rpm; temperature, rt.].

45 min; stirring speed, 1500 rpm; temperature, room temperature. A minimum amount of 50 mg of magnetic IIP was required for >80 % extraction of 2 mg L<sup>-1</sup> of uranium from 25 mL of aqueous phase (Fig. 5). The higher extraction efficiency of magnetic IIP (>90 %) compared to its corresponding NIP (70 %) using 50 mg of magnetic polymer material was attributed to the imprinting effect. The results showed that more specific binding sites in the IIP provided higher affinities than the non-specific sites. From the 20 to 200 mg range investigated by Sadeghi and Mofrad<sup>23</sup>, there was no significant difference between 100 and 200 mg of IIP particles in enrichment of uranyl ions and consequently, 100 mg of IIP particles was considered optimum. They synthesized their polymer through formation of ternary complexes involving uranyl ion, with piroxicam and 4-vinylpyridine (VP) as chelating agent.

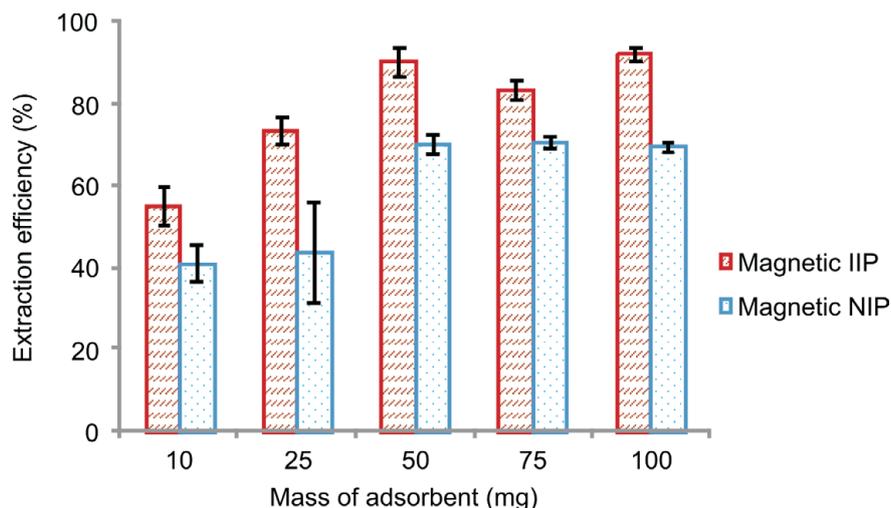
### 3.5. Influence of Contact Time

An illustration of the adsorption of U(VI) ions as a function of contact time is shown in Fig. 6. The batch adsorption was done under the following conditions: A sample pH of 4, sample volume of 25 mL, 2 mg L<sup>-1</sup> uranium concentration, 50 mg polymer weight at a stirring speed of 1500 rpm at room temperature. The adsorption increased with increasing contact time as expected. The adsorption equilibrium time for U(VI) onto the magnetic polymers was found to be 45 min. Singh and Mishra<sup>24</sup> investi-

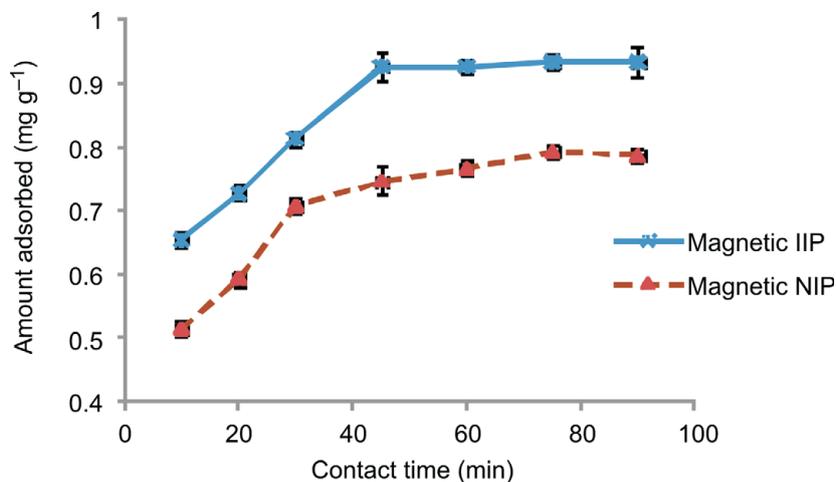
gated the effect of stirring time for the pre-concentration and elution of uranium(VI) at pH 5 using 100 mg of polymers and showed that 10 min was enough and it was used in their subsequent studies. The binding kinetics of uranyl on the prepared polymers was therefore slower compared to that reported by Singh and Mishra<sup>24</sup>.

### 3.6. Influence of Concentration

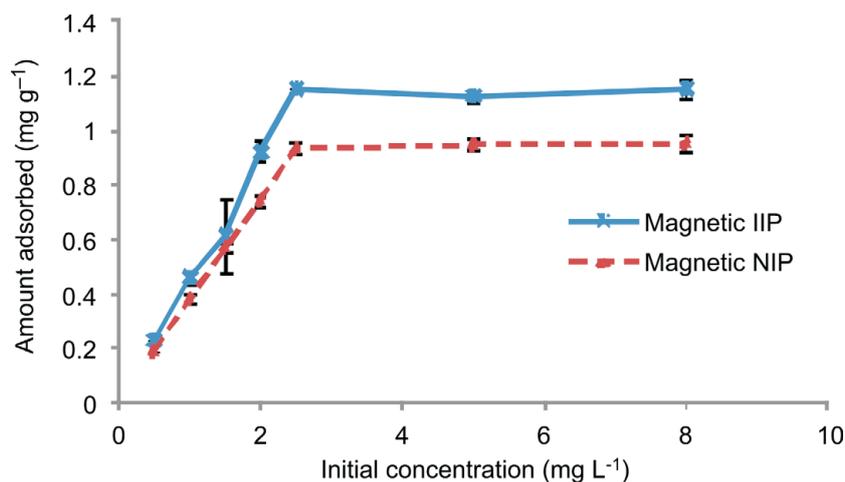
As can be seen from Fig. 7, the initial concentration of U(VI) in solution varied from 0.5 to 8 mg L<sup>-1</sup>. The following experimental conditions used at room temperature: sample pH, 4; sample volume, 25 mL; polymer weight, 50 mg; contact time, 45 min; stirring speed, 1500 rpm. The amount of U(VI) adsorbed per unit mass of adsorbent increased from 0.23 to 1.15 mg g<sup>-1</sup> and 0.19 to 0.93 mg g<sup>-1</sup> for the magnetic IIP and NIP, respectively. With this contact time, any increase of U(VI) concentration accelerated the diffusion of U(VI) ions from the bulk solution onto the fabricated adsorption sites of the magnetic polymers due to the increase in the driving force of the concentration gradient. The maximum adsorption capacity was found to be around 1.15 mg g<sup>-1</sup> and 0.93 mg g<sup>-1</sup> for the magnetic IIP and NIP, respectively. Magnetic ion-imprinted polymers generally have lower adsorption capacities than ion imprinted polymers (Table 1). This may be due to the fact that that magnetite embedded at the centre and within the polymer matrix prevent deep cavities or pores found in ion



**Figure 5** Extraction efficiency obtained by varying the mass of magnetic polymers ( $n = 3$ ). [pH, 4; sample volume, 25 mL; uranium concentration, 2 mg L<sup>-1</sup>; contact time, 45 min; stirring speed, 1500 rpm; temperature, r.t.].



**Figure 6** Contact time effect on the uptake of uranium by magnetic polymers ( $n = 3$ ). [pH, 4; weight of magnetic polymer, 50 mg; sample volume, 25 mL; uranium concentration, 2 mg L<sup>-1</sup>; stirring speed, 1500 rpm; temperature, r.t.].



**Figure 7** Effect of initial concentration on the uptake of uranium by magnetic polymers ( $n = 3$ ). [pH, 4; weight of magnetic polymer, 50 mg; sample volume, 25 mL; contact time, 45 min; stirring speed, 1500 rpm; temperature, r.t.].

imprinted polymers. This also explains why they normally have fast mass transfers.

### 3.7. Selectivity Studies

Competitive adsorption of the binary mixtures  $\text{UO}_2^{2+}/\text{Ni}^{2+}$  and  $\text{UO}_2^{2+}/\text{Mg}^{2+}$  were investigated in an equilibrium-adsorption batch system and the results are summarized in Fig. 8. At room temperature, the following experimental conditions were used: sample pH, 4; sample volume, 25 mL; polymer weight, 50 mg; contact time, 45 min; stirring speed, 1500 rpm and the concentration of all ions was  $2 \text{ mg L}^{-1}$ . For both binary mixtures,  $\text{UO}_2^{2+}$  was observed to be adsorbed more as compared to its competitors and the performance of the magnetic IIP was always higher than that of the corresponding control due to imprinting.

Data for metal removal capacity in terms of  $K_d$ ,  $K$ , and  $K'$  for the binary competitive binding experiments is summarized in Table 2. The distribution ratios of the Mg(II) and U(VI) were 133 and 2441, respectively, and for Ni(II) and U(VI) they were 206 and 2778, respectively. Based on these values, the selectivity order of ions adsorbed onto magnetic polymers can be deduced as:  $\text{U(VI)} > \text{Ni(II)} > \text{Mg(II)}$ .  $K$  values of U(VI) binding in the presence of Ni(II) ions were found to be 13.5 and, 18.4 for Mg(II)

meaning the Ni(II) was a stronger competitor than Mg(II). The more similar  $K$  values for the magnetic NIPs meant they had inferior selectivity due to the absence of fabricated adsorption sites in the magnetic polymer matrix and only non-specific interactions with the U(VI) ions and its competitors were involved.

### 3.8. Stability and Reusability of Magnetic IIPs

The magnetic IIP and NIP were used to extract U(VI) from solutions using the optimum conditions in batch mode as previously reported in other experiments described in sections 3.3–3.6. HCl was then used to strip the adsorbed U(VI) before the material was filtered and the recovered magnetic IIP used in the next adsorption cycle. HCl was shown to elute the magnetite, hence the reduction of magnetic responsive of the polymers. Since there was only a 2 % and 3 % extraction efficiency loss (data not shown) for the magnetic IIP and NIP, respectively, after the sixth cycle, they can be used repeatedly.

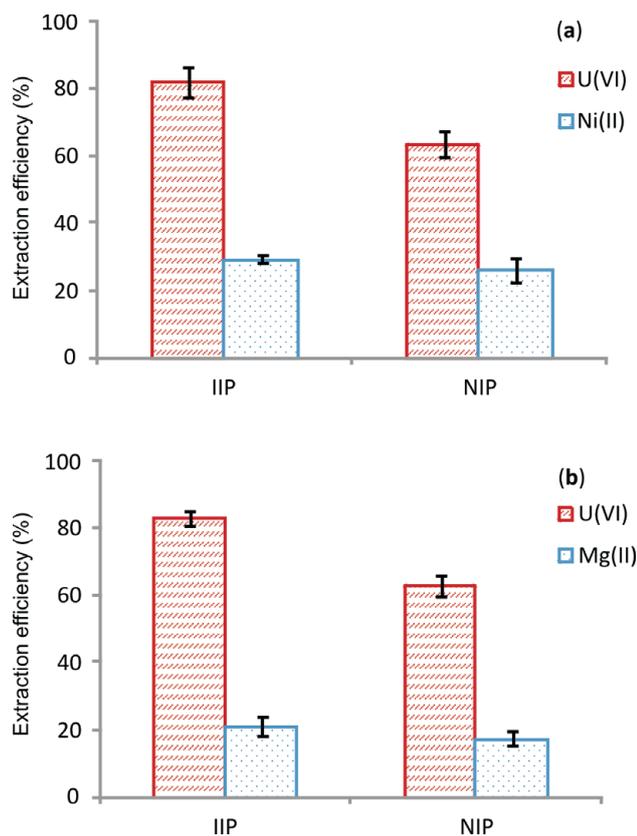
### 3.9 Application of Magnetic IIP to Wastewater Samples

The applicability of the proposed method was tested in real wastewater from a treatment water plant (WWTP). After collecting the wastewater sample, filtration was performed using

**Table 1** Performance comparison of different U(VI) ion imprinted polymer sorbents (magnetic and non-magnetic).

Functional monomer	q/mg g <sup>-1</sup>	t/min	pH	Sorbent dosage/mg L <sup>-1</sup>	Reference
<b>Non-magnetic imprinted polymers</b>					
Salicylaldoxime and 4-vinylpyridine	151 <sup>¥</sup>	10	5	100	Singh and Mishra <sup>24</sup>
Aniline and 8-hydroxy aniline quinoline functionalized	22410 <sup>¥</sup>	30	7	4	Milja <i>et al.</i> <sup>25</sup>
1-(prop-2-en-1-yl)-4-(pyridin-2-ylmethyl)piperazine and methacrylic acid	120	20	4–8	667	Pakade <i>et al.</i> <sup>31</sup>
4-vinylpyridine	134	180	7	2500	Anirudhan <i>et al.</i> <sup>38</sup>
5,7-dichloroquinoline-8-ol-4-vinylpyridineterary	34	10	5–7	100	Gladis and Rao <sup>39</sup>
<b>Magnetic imprinted polymers</b>					
Chitosan	8.6	30	3.5	5000	Wang <i>et al.</i> <sup>28</sup>
Salicylaldoxime and 4-vinylpyridine	1.2	45	4	2000	Tavengwa <i>et al.</i> <sup>40</sup>
2,4-dioxopentan-3-yl methacrylate	15.3	720	–	20	Zhang <i>et al.</i> <sup>41</sup>
Salicylaldoxime and 4-vinylpyridine	1.15	45	4	2000	This work

<sup>¥</sup> Converted from mmol g<sup>-1</sup>.



**Figure 8** Extraction efficiencies of the ions extracted by magnetic polymers from  $2 \text{ mg L}^{-1}$  binary mixtures of solutions of (a) U(VI)/Ni(II) and (b) U(VI)/Mg(II) ( $n = 3$ ).

$0.45 \mu\text{m}$  filters to remove all the solid particles. The wastewater was then subjected to batch adsorption procedures, using the optimized conditions. The result are reported in Table 3 and show that the proposed method shows promise for the determination of U(VI) with average extraction efficiencies of 82 % and 64 % obtained for the magnetic IIP and NIP, respectively in spiked samples.

**Table 2** Distribution coefficient, selective coefficient and relative coefficient values for the magnetic polymers in binary mixtures.

Adsorbent	$K_d/\text{mL g}^{-1}$		K	K'	$K_d/\text{L g}^{-1}$		K	K'
	U(VI)	Ni(II)			U(VI)	Mg(II)		
Magnetic IIP	2778	206	13.5	2.7	2441	133	18.4	2.3
Magnetic NIP	874	176	5.0	–	851	105	8.1	–

**Table 3** Application of magnetic polymers on unspiked and spiked wastewater sample. Experimental conditions: Sample pH, 4; solution volume, 25 mL; sorbent mass, 50 mg for the magnetic polymers ( $n = 3$ ).

Sample	Uranium concentration/ $\text{mg L}^{-1}$				% Recovery	
	Spiked	Determined		Magnetic IIP	Magnetic NIP	
		Magnetic IIP	Magnetic NIP			
WWTP	–	<DL*	<DL*	–	–	
	1.00	0.82 (0.06)	0.63 (0.04)	82	63	
	5.00	4.15 (0.01)	3.25 (0.02)	83	65	
	10.0	8.10 (0.08)	6.40 (0.09)	81	64	

\* Below detection limit and SD values in brackets.

#### 4. Conclusions

Influences of sample pH, amount of magnetic sorbent, contact time and initial concentration were investigated. The performance of the magnetic IIP, in terms of uranium extraction, was always superior to that of the corresponding controls. The imprinting effect was evident from the selectivity studies where the order of selectivity was U(VI) > Ni(II) > Mg(II). Experimental results obtained show that the magnetic polymer has potential for selective extraction and pre-concentration of U(VI) ions in the presence of other ions. However, the performance of magnetic IIPs in real samples was not so good. Though selective, the magnetism of the sorbent was reduced due to loss of magnetite. The application of the imprinting technique can be extended to natural sorbents which can be endowed with magnetic particles instead of synthetic polymers to reduce costs.

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