Synthesis of surface imprinted nanospheres for selective removal of uranium from simulants of Sambhar salt lake and ground water

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ABSTRACT

Imprinted polymer nanospheres for uranium were prepared by complexing uranyl ion on to quinoline-8-ol functionalized 3-aminopropyltrimethoxysilane modified silica nanoparticles followed by surface imprinting with 4-VP (4-vinyl pyridine), HEMA (2-hydroxy ethyl methacrylate) and EGDMA (ethylene glycol dimethacrylate) as the functional monomers and cross linking agent respectively with AIBN (2,2′-azo-bis-isobutyronitrile) as initiator and 2-methoxyethanol as the porogen. Non-imprinted polymer material was also prepared under similar conditions omitting uranyl ion. The above materials were used for solid phase extraction of uranium. Recent realization that its chemical toxicity is dominant than radiation hazards makes decontamination a relevant topic for environmental point of view, particularly in the light of projected global thrust for uranium fuel based atomic power plants. The material offers high retention capacity of 97.1 μmol g^{-1} for 10 mg L^{-1} of uranium that does not require tedious grinding and sieving steps, is water compatible and works in the pH range of 5–7, making it ideal for possible use in decontamination of polluted natural water samples or front end effluents of nuclear power reactors.

1. Introduction

Uranium, since its discovery in 1789 by Martin Klaproth is best known and feared for its involvement in nuclear energy. However, it is only weakly radioactive. The half-life of ^{238}U is 4.468×10^9 years and it emits alpha particles having a low penetration depth which can be arrested by the skin [1]. Uranium has been judiciously utilized for producing electrical energy for centuries without the threat of global warming. On the other hand, uranium(VI) is soluble and mobile and its processing has resulted in widespread environmental contamination [2]. The inhalation of uranium compounds results in its deposition in lungs, which reach kidneys through the blood stream resulting in progressive or irreversible renal injury and in acute cases leading to kidney failure and death. The tolerable daily intake of uranium established by WHO based on Gilman's studies is 0.6 μg/kg of body weight/day [3–5]. The WHO, Health Canada, Australian, and USEPA drinking water guidelines fixed the maximum uranium concentration in drinking water to be less than 9, 20, 20 and 30 μg/L respectively [3,4]. Our society is confronted by global challenges that are coming into clear focus like the need for vast new and sustainable energy sources and the requirements for clean air, water, and food supplies. In all these areas new polymeric materials will play crucial roles [6]. Removal of trace amounts of uranium is essential for environmental cleanup even though it is

being recovered, that can be used for nuclear energy needs. These can be achieved through the strategy of imprinting.

Imprinting is the molding of complimentary binding sites for target molecules into synthetic polymers [7], which relies on the formation of a cross linked polymer in the presence of template [8]. They are remarkably stable against mechanical stresses, high temperatures and pressures, intense radiation and a range of organic solvents, resistant against treatment with acid or base [7]. Bulk polymerization is the most commonly used imprinting technique, but is not amenable to scale up and it has to be grounded and sieved to generate particles of approximately 10–20 μm. This produces highly irregular particles with a loss of up to 80% of the material, the greatest disadvantage being the inaccessible binding sites situated deep inside the bulk of the polymer matrix. Surface imprinting offers a solution to the problem as the cavities are situated at the surface or in the proximity of materials surface, providing the complete removal of templates, good accessibility to the target species, and low mass-transfer resistance [9–11]. Functional nanomaterials have specific and predictable nanostructures imparting unique characteristics to perform a specific function and they have high surface to volume ratio. Imprinted materials are nanostructured at the molecular length scale and respond to challenges in nanoscale chemistry to mimic the biological recognition functions by synthetic chemistry to produce systems of lower complexity.

Ion imprinted polymer with solid phase extraction (IIP-SPE) provides an effective method for pre-concentration and cleanup. The basic principle of SPE is the transfer of analyte from aqueous phase to the active sites of adjacent solid phase by mechanisms such as

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Table 1
Synthesis of uranyl ion imprinted polymers.

UO_2^{2+}:HEMA:EGDMA	Porogen volume (mL)	Temperature (°C)	Morphology
Precipitation polymerization			
PP1 1:8:32	20	80	Micrometer particles (>10 μm)
PP2 1:8:32	40	80	Micrometer particles (>10 μm)
PP3 1:8:32	40	60	Micrometer particles (>10 μm)
PP4 1:8:32	60	60	Micrometer particles (>10 μm)
PP5 1:4:20	4.5	60	Nanospheres (50–80 nm)

All the polymerizations were done with AIBN as initiator and 2-methoxy ethanol as porogen.

physical sorption, complex formation and other chemical reactions on or in the sorbents. A detailed report on the topic is given in the review by Rao et al. [12,13]. Preetha et al. [14] have reported uranium removal from nuclear power reactor effluent but the material works only in weakly acidic pH.

Silica gel has been widely used as an inorganic support in surface imprinting. Shamsipur et al. have reported the preparation of surface imprinted polymer for uranium using "grafting from" method on silica [15]. To the best of our knowledge this is the first attempt for preparation of metal ion imprinted nanospheres. We herein report a method for preparation of uranyl ion surface imprinted nanospheres and the utilization of the material for possible decontamination of ground and Sambhar salt lake water simulants respectively.

2. Experimental

2.1. Apparatus

A Shimadzu UV 2401 PC controlled spectrophotometer (Shimadzu, Japan) and an LI-120 digital pH meter (Elico, India) were used for absorbance and pH measurements, respectively. A Perkin-Elmer A Analyst-100 Flame atomic absorption spectrometer (Perkin-Elmer, USA) was used for determining inorganic species. Sodium and potassium concentration was determined by Flame photometry (Systronics Flame Photometer 128), sonicator (Elma Sonic) was used for sonication. FTIR spectra were recorded using a Prestige-21 IR spectrometer (Shimadzu, Japan). The morphology of the IIP particles was studied using high-resolution transmission electron microscopy (HRTEM) on an FEI, TECNAI 30G2 S-TWIN microscope with an accelerating voltage of 100 kV. Elemental studies CHN Elementar Vario EL III, surface area and pore size analysis was done using a BET surface area analyzer (Gemini 2360, Micromeritics, Norcross, USA).

2.2. Chemicals

Tetraethylorthosilicate (TEOS), 2-hydroxy ethyl methacrylate (HEMA), ethylene glycol dimethacrylate (EGDMA) 4-vinyl pyridine (VP), 2-methoxyethanol, 3-aminopropyltrimethoxysilane (APTMS), and arsenazo III were purchased from Aldrich and used as received. Azo-bis-isobutyronitrile (AIBN, Spectrochem) was purified through re-crystallization in ethanol. Anhydrous toluene was prepared by drying with sodium metal and anhydrous ethanol with magnesium metal. A stock solution of uranium(VI) was prepared by dissolving appropriate amount of $UO_2(NO_3)_2 \cdot 6H_2O$ (Spectrochem) in de-ionized water. Concentrated HNO_3 (5 mL) was added to 100 mL of solution to suppress hydrolysis. 1 mL of 0.1 mol L^{-1} ammonium acetate was used as the buffer.

2.3. Procedure

2.3.1. Determination of uranium by arsenazo III method

To the filtrate obtained after solid phase extraction was added in 5 mL of 1:1 hydrochloric acid, 2 mL of 0.1% arsenazo III solu-

tion and diluted to 25 mL with distilled water. The absorbance of uranium–arsenazo III complex was measured at 656 nm [22].

2.3.2. Synthesis and chemical modification of silica nanoparticles

Uniform silica nanoparticles were prepared by the Stöber method [16,17], which involves the hydrolysis of TEOS with aqueous ammonia in presence of ethanol. 6.3 mL of TEOS was added to 7.5 mL of NH$_4$OH in 105 mL ethanol. The solution was sonicated at a temperature of 35 °C for 4 h. The resulting residue was centrifuged, washed with water and ethanol respectively and dried in an oven at 50 °C. Aminopropyl modification was done by the reported method [10,18]. Appropriate amount of silica was added to 4% (v/v) of 3-aminopropyltrimethoxysilane in dry toluene. The mixture was refluxed for 12 h under dry nitrogen. The APTMS modified silica particles (APTMS-SI) were centrifuged, washed with toluene and dried in an oven at 50 °C. Quinoline-8-ol was grafted on to the amino end group by Mannich reaction. Definite amount of APTMS modified silica was added to 50 mL dry ethanol containing quinoline-8-ol (0.1 mol L^{-1}), formaldehyde (0.1 mol L^{-1}) and glacial acetic acid (0.2 mL) and refluxed for 4 h [19]. The resulting solid (HQ-APTMS-SI) was centrifuged, washed with ethanol, 1 mol L^{-1} HCl and with distilled water respectively and dried at 50 °C.

2.3.3. Synthesis of uranyl ion surface imprinted nanospheres

Different synthesis methods were tried in order to get surface imprinted nanospheres (Table 1). The detailed procedure for the synthesis of nanospheres is given here.

2.3.4. Modified precipitation polymerization

Imprinting of uranyl ion was done by thermal polymerization. 4-VP, HEMA and EGDMA were used as the functional monomers and cross linking agent respectively in the ratio 1:2:4:20 (UO_2^{2+}:4-VP:HEMA:EGDMA) with AIBN as initiator and 2-methoxyethanol as the porogen. 0.1 mmol uranium was used for the synthesis. The pre-polymerization mixtures were dissolved in 60 mL of the porogen and sonicated for 10 min, then cooled to 0 °C (by keeping in a trough containing ice) and purged with N$_2$, appropriate amount of HQ-APTMS-SI was added and sonicated for 10 min. Purged with nitrogen, sealed, and thermally polymerized in an oil bath at 60 °C while stirred for 1 h. The resulting IIP material was washed with methanol and distilled water respectively and then dried. Based on our earlier experience with uranyl IIP materials [12–14], uranyl ion was extracted after stirring 1 g of the material with 100 mL of 1 M HCl for 3 h. This leaching procedure enabled reproducible blank as determined by arsenazo III procedure. Non-imprinted polymer (NIP) was similarly prepared without the uranyl ion. Scheme for the synthesis is shown in Fig. 1.

2.4. Characterization

The functionalization of prepared materials was confirmed using FTIR and elemental analysis and surface area and pore size analysis was also done. Morphology studies were done using HRTEM and SEM.
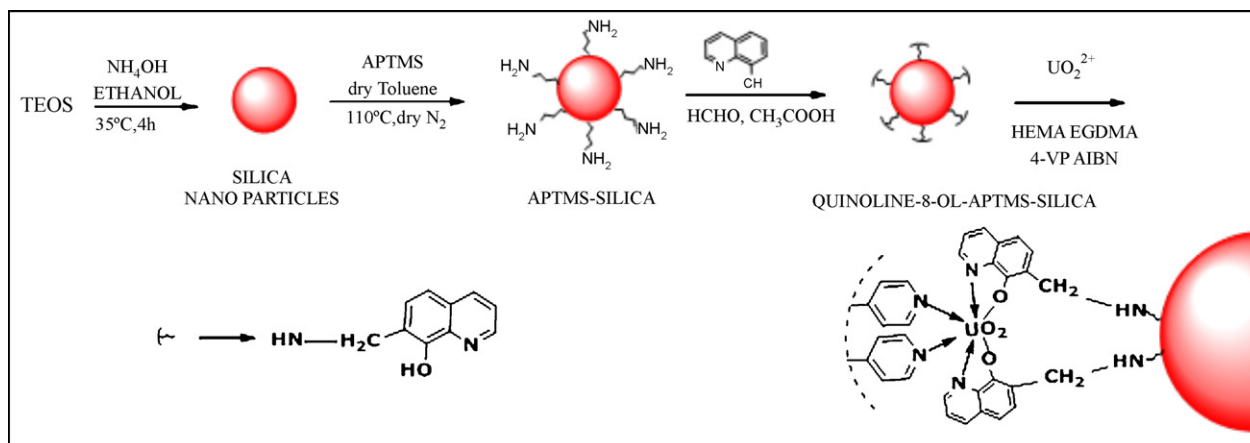
Fig. 1. Schematic representation of uranyl ion nanosurface imprinting.

2.5. Optimization of parameters

The effect of pH (4.5–7.5), weight of polymer particles (0.01, 0.015, 0.02 and 0.025 g), time of stirring (20 and 30 min) during the pre-concentration and elution of uranium, nature of eluent (1 M HCl/1 M HNO$_3$/1 M Na$_2$CO$_3$), eluent concentration (0.1–1.0 M HCl), and eluent volume (5–15 mL) were studied by checking the removal efficiency of 100 μg of uranyl ion present in 100 mL of aqueous solutions using NIP/IIP materials.

2.6. Retention capacity studies

The maximum amount of pre-concentrated uranyl ion/g of the imprinted material (retention/binding capacity of IIP) was calculated by saturating 0.02 g of polymer particles with 10 mg L^{-1} of uranyl ion under optimal conditions. The maximum amount of uranyl ion pre-concentrated was eluted with 1.0 M HCl and determined spectrophotometrically by using the arsenazo III procedure.

2.7. Selectivity studies

To evaluate the selectivity of uranyl IIP and NIP particles for uranium over other inorganic ions, 0.02 g of the material was stirred with 100 μg of each individual inorganic ion present in 100 mL of de-ionized water under identical conditions. The selectivity coefficient $S_{UO_2^{2+}M^{n+}}$ is defined as in [14]

$$S_{UO_2^{2+}M^{n+}} = \frac{D_{UO_2^{2+}}}{D_{M^{n+}}} \quad (1)$$

where $D_{UO_2^{2+}}$ and $D_{M^{n+}}$ are the distribution ratios of the uranyl ion and other inorganic species respectively with polymer particles (NIP or IIP). These distribution ratios were calculated using the formula

$$D_{M^{n+}} = \frac{C^i - C^f}{C^f} \times \frac{v}{m} \quad (2)$$

where $C^i M^{n+}$ and $C^f M^{n+}$ are the concentrations of inorganic ions in 'mg L^{-1}' in aqueous phase before and after extraction, v is the volume of the solution in 'mL', and m is the mass of the polymer in 'g'.

$$\text{Imprinting coefficient } (K') = \frac{S_{IIP}}{S_{NIP}} \quad (3)$$

The percent extraction (%E) of inorganic ion is defined as

$$\%E = \frac{C^i - C^f}{C^i} \times 100 \quad (4)$$

2.8. Uranium decontamination

To demonstrate the application of the surface imprinted nanospheres in decontamination, synthetic samples of ground and Sambhar salt lake water (Thar Desert, Rajasthan) were prepared based on the composition described elsewhere [20,21]. Removal of uranium from ground water and Sambhar salt lake water (increases from 8 μg L^{-1} in monsoon to 1400 μg L^{-1} in summer) was done by equilibration with 0.02 g of leached IIP particles in batch mode, after adjusting the pH to 6.5.

3. Results and discussion

3.1. Synthesis of IIP

Precipitation polymerization is the most popular strategy used for the synthesis of MIP nanoparticles. We have used a modified precipitation polymerization method for the synthesis of imprinted nanospheres. From the methods for synthesis given in Table 1, it is clear that difference between recipe for nanosphere IIP and others lies in the amount of porogen used and also the amount of pre-polymerization mixture. 0.33 mmol of uranium was used for PP1–PP4 and 0.1 mmol for PP5, correspondingly the amount of monomers and cross linkers will decrease. In PP5 we have used only 4.5 mL of porogen thereby decreasing the polymer matrix. We assume that only a thin layer of polymer is formed around functionalized silica as the size remains in 50–80 nm range like that of quinoline-8-ol functionalized silica. Temperature does not have any role in changing the morphology of IIP as both PP2 and PP3 gave micrometer sized particles. Only PP5 gave nanospheres and therefore further studies were done with that material. Removal efficiency of IIP (PP5) increased from 95.0% to 99.0% on addition of 4-VP as it helps in making rigid configuration inside the polymer matrix. The morphology remained same even after addition of 4-VP.

3.2. Characterization studies

3.2.1. FTIR and elemental analysis

The bands in IR spectra at 1099 cm^{-1} and 960 cm^{-1} for Si–O–Si and Si–OH respectively confirms the presence of silica matrix. The IR vibrations of NH$_2$ at around 1492 cm^{-1} and the C–H stretching modes at around 2900 cm^{-1} present in APTMS modified silica indicates that the silane moieties were anchored onto the silica after the silanization reaction [23]. IR of quinoline-8-ol modified silica was taken by making a pellet without the binder KBr [24]. In the spectra, bands for C=C and C=N stretching can be observed in the fre-
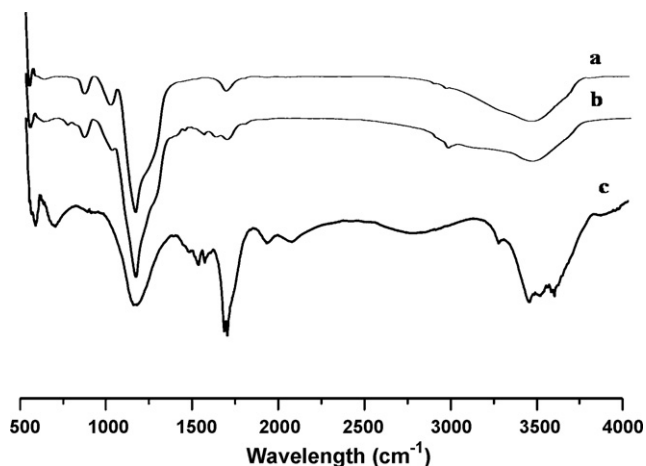
Fig. 2. FTIR spectra of (a) silica, (b) APTMS-SI and (c) quinoline-8-ol-APTMS-SI.

quency range 1300–1700 cm^{-1} for the modified silica nanoparticles at 1461 cm^{-1}, 1510 and 1617 cm^{-1}, but none for the unmodified silica [19]. Hence the functionalization of quinoline-8-ol on aminopropyl silica can be confirmed. Fig. 2 shows the IR spectra of bare silica (a), APTMS-SI (b) and HQ-APTMS-SI (c) respectively. The elemental (CHN) analysis data for APTMS-SI and HQ-APTMS-SI are 0.96 and 1.25 (%N), 3.56 and 5.46(%C) and 2.00 and 2.15 (%H) respectively.

3.2.2. Morphology (TEM and SEM)

TEM images show the particle size of quinoline-8-ol functionalized silica and the IIP (PP5) to be in the range of 50–80 nm. SEM image of polymers prepared by other methods gave bigger particles with size in micrometer range. The samples were prepared by dispersing in ethanol followed by coating on a copper grid. Agglomeration was observed when dispersed in acetone for quinoline-8-ol and a network like structure for IIP (PP2). Fig. 3 shows the TEM and
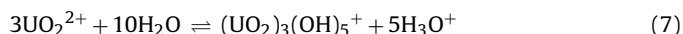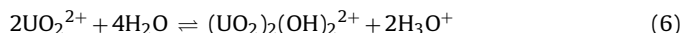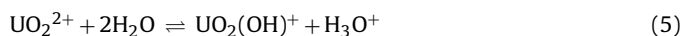
SEM images of modified silica and polymers prepared by different methods.

3.2.3. Surface area and pore size analysis

BET surface area and BJH adsorption average pore diameter of IIP and NIP were found to be 134.69 and 188.87 m^2/g and 47.39 and 51.89 Å respectively. It was observed that leached NIP showed higher surface area compared to that of leached IIP. However significant imprinting effect was observed for the material. Quantitative recovery was obtained with 20 mg of the material where as other works with materials having larger surface area requires higher amount for the same. It can be concluded that binding and selectivity in imprinted polymers is independent of porosity [25–27].

3.3. Optimization studies

Quantitative recovery of Uranium was obtained in the pH range of 5.0–7.0 as shown in Fig. 4. For the functional group quinoline-8-ol, the optimum pH range for extraction of UO_2^{2+} is 4.7–8 [28]. Uranyl chemistry is complicated due to hydrolysis phenomenon. When pH increases from an acidic value to a neutral value, various hydrolyzed species exist in equilibrium with UO_2^{2+} as given in the Eqs. (5)–(7). Monovalent uranyl species dominates at higher pH (4.0–6.0) and UO_2^{2+} at low pH (2.0) [29,30]. As UO_2^{2+} gets complexed with quinoline-8-ol, the equilibrium gets shifted to left.

$$UO_2^{2+} + 2H_2O \rightleftharpoons UO_2(OH)^+ + H_3O^+ \tag{5}$$

$$2UO_2^{2+} + 4H_2O \rightleftharpoons (UO_2)_2(OH)_2^{2+} + 2H_3O^+ \tag{6}$$

$$3UO_2^{2+} + 10H_2O \rightleftharpoons (UO_2)_3(OH)_5^+ + 5H_3O^+ \tag{7}$$

Removal efficiency increases from 4.5 to 5 because that is the pH for the complexation of quinoline-8-ol with UO_2^{2+} and decreases from 7 to 8 due to hydrolysis of uranyl ions to form non-complexable species like $UO_2(OH)_2$ and $UO_2(OH)_3^-$.

Further studies were conducted at pH 6.0. 10^{-3} M ammonium acetate was used as buffer to adjust the pH. The optimal
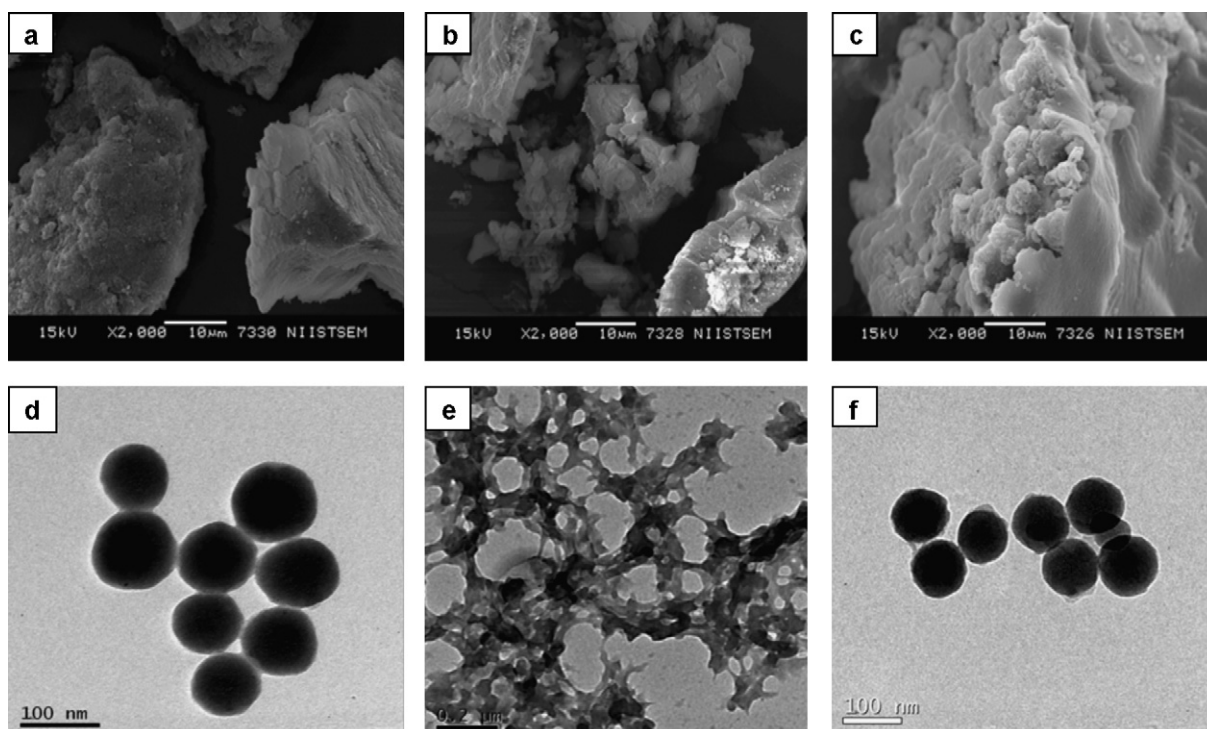

Fig. 3. SEM of IIP (a) PP2, (b) PP3, (c) PP4 and TEM of (d) quinoline-8-ol grafted silica, (e) PP2 in acetone and (f) PP5 in ethanol.
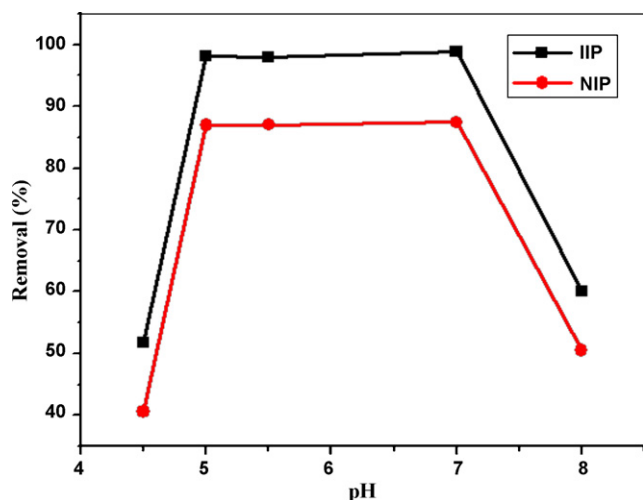
Fig. 4. Effect of pH on removal of uranium with 20 mg of IIP/NIP, 1000 μg L^{-1} U(VI) and 100 mL aqueous phase volume.
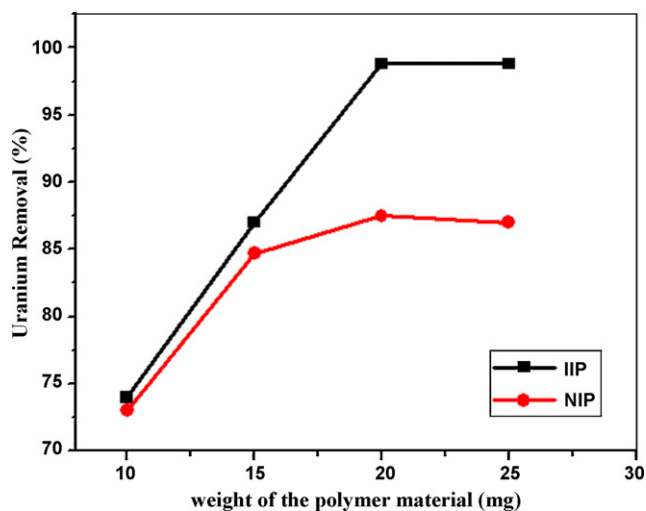

Fig. 5. Influence of weight of non-imprinted and imprinted materials on removal of uranium at pH 6, 1000 μg L^{-1} U(VI) and 100 mL aqueous phase volume.

Table 2
Optimization of solid phase extraction parameters.

Parameters	Uranium removal (%)[a]	
	NIP	IIP
Pre-concentration time (min)		
20	82.3	87.0
30	87.5	>99
Elution time (min)		
10	83.0	93.2
20	87.0	>99
30	87.0	>99
Nature of eluent		
1 M HNO$_3$	66.0	76.3
1 M HCl	87.0	>99
1 M Na$_2$CO$_3$	60.1	63.4
Eluent concentration		
0.1 M	67.4	78.2
0.5 M	73.1	85.0
1.0 M	87.0	>99
Eluent volume (ml)		
5	82.4	96.4
10	87.0	>99
15	87.0	>99

[a] Average of duplicate measurements.

Table 3
Comparison of retention capacity with other uranyl IIPs.

Chelating ligand(s)	pH range	Retention capacity[a] (μmol/g)	Reference
DCQ	4.5–7.5	55.6	[31]
VP	4.5–7.5	86.5	[31]
DCQ-VP	4.5–7.5	136.9	[31]
Catechol-VP	3.5–6.0	81.9	[32]
SALO-VP	3.0–4.0	79.4	[32]
SALO-VP	3.5–5.0	105	[14]
MAA	3.0	52	[15]
Amidoxime-VP	8.0–9.0	80	[33]
SALO-VP	3.5–6.5	80	[34]
N,N′ethylenebis (pyridoxylideneiminato)-VP	7.0	–	[35]
HQ-VP	5.0–7.0	97.1	Present work

[a] Retention capacity values are at concentration of 100 mg L^{-1} uranium for all other works and at 10 mg L^{-1} for the present work.

amount of material required was found to be 0.02 g (Fig. 5) and the time for pre-concentration and elution was fixed to be 30 and 20 min respectively. 100 mL of aqueous phase volume was used for removal studies. Among the various eluents, concentration and volume were used, 10 mL of 1 M HCl was effective in complete stripping of uranium. Under above optimal conditions, the quantitative removal of 50–1000 ppb of uranium is demonstrated from aqueous solutions. In all the above experiments comparison of imprinted with non-imprinted polymers shows significant imprinting effect. Results for optimizations are given in Table 2.

3.4. Retention capacity

Comparison of retention capacity of surface imprinted nanospheres with other uranyl ion IIPs is given in Table 3. We have given the retention capacity at 10 mg L^{-1} because there is always a chance for precipitation of uranyl ion at higher concentration at a pH of 6.0. From the table it can be observed that the material gives a retention capacity of 23.1 mg/g (97.1 μmol g^{-1}) at 10 mg L^{-1} whereas others are at a concentration of 100 mg L^{-1}. This shows that the material has high retention capacity which can be utilized for removal/harnessing of uranium.

3.5. Selectivity studies

Selectivity of the IIP and NIP was evaluated by equilibrating 0.02 g of the particles with 100 μg each of other inorganic ions likely to coexist in real samples under the optimized conditions. The concentrations of these elements in solutions were determined by spectrophotometry, flame atomic absorption spectrometry and flame photometry after elution with 10 mL of 1.0 M HCl. The distribution ratio and selectivity coefficients of uranyl ion with respect to other inorganics using NIP and IIP particles are shown in Table 4. The selectivity coefficients of IIP particles for Uranium are greater by 10^2–10^3 fold as compared to other ions. This can be explained on the basis of imprinting effect. The material is particularly selective towards Fe^{3+} which is a major constituent in high and low level nuclear industry effluents. Hence the material can find application in removing Uranium particularly from front end effluents. Based on the results shown in Table 4, it is clear that uranyl ion can be removed selectively from several inorganic species present in dilute aqueous solutions. The comparison of imprinting coefficients of nanospheres with other IIPs is given in Table 5. Imprinted materials with higher imprinting coefficients than the surface imprinted nanospheres were reported, but the recovery is not quantitative in comparison with the present material.

Table 4
Selectivity data of NIP and uranyl IIP materials[a].

Metal ions	Analysis Procedure	D		$S_{UO_2^{2+}/M^{n+}}$		Imprinting coefficient (K')
		NIP	IIP	NIP	IIP	
UO_2^{2+}	Spectrophotometry	6.7	99	–	–	
Na^+	Flame photometry	0.08	0.07	83.7	1.4×10^3	17
K^+	Flame photometry	0.08	0.07	83.7	1.4×10^3	17
Ca^{2+}	FAAS	0.75	0.7	8.9	1.4×10^2	15.7
Mg^{2+}	FAAS	0.05	0.04	1.3×10^2	2.5×10^3	19.2
Cu^{2+}	FAAS	99	5.5	0.06	18	300
Zn^{2+}	FAAS	0.72	0.59	9.2	1.7×10^2	18.4
Fe^{3+}	FAAS	0.12	0.10	55.8	9.5×10^2	17.2
Co^{2+}	FAAS	1.24	0.98	5.4	10^2	18.5
Ni^{2+}	FAAS	1.17	0.88	5.7	1.1×10^2	19.3

[a] Average of duplicate measurements.

Table 5
Comparison of imprinting coefficients with other uranyl IIPs.

Chelating ligands with UO_2^{2+}	Weight of IIP (g)	% Recovery		Imprinting coefficient (K')	Reference
		NIP	IIP		
VBA-Styrene-DVB	–	Not dealt	> 99	–	[36]
MAGA-EGDMA	0.02	Not dealt	96.0	–	[37]
Silica matrix	–	75.0	85.0	1.13	[38]
VP-Styrene-DVB	0.02	41.7	78.8	1.9	[31]
DCQ-Styrene-DVB	0.02	30.6	40.0	1.31	[31]
Catechol–VP-HEMA-EGDMA	0.02	30.1	62.9	2.1	[32]
SALO–VP HEMA-EGDMA	0.02	19.7	67.9	3.4	[32]
DCQ-VP–Styrene-DVB	0.02	71.0	> 99	1.4	[31]
Amidoxime-VP-HEMA-EGDMA	0.075	81.0	>99	1.2	[33]
HQ-APTMS-SI	0.02	87.0	> 99	1.14	Present work

Table 6
Composition of natural water samples.

Sample description	Uranium recovery (%)
Sambhar salt lake water simulant (Jhapok) U(VI): $1.4 \, mg \, L^{-1}$ Na: $146 \times 10^3 \, mg \, L^{-1}$ K: $0.9 \times 10^2 \, mg \, L^{-1}$ Ca: $2.4 \, mg \, L^{-1}$ Mg: $10 \, mg \, L^{-1}$	$70.0 \pm 3\%$
Ground water stimulant (Sambhar township) U(VI): $71.6 \, \mu g \, L^{-1}$ Na: $3.3 \times 10^3 \, mg \, L^{-1}$ K: $9.1 \, mg \, L^{-1}$ Ca: $5.4 \times 10^2 \, mg \, L^{-1}$ Mg: $1.9 \times 10^2 \, mg \, L^{-1}$	$94.0 \pm 2\%$

3.6. Application to real samples

Removal of uranium from ground and Sambhar salt lake water has been demonstrated. Simulants were prepared as per the ground water (SambharTownship) composition and Sambhar salt lake water composition (Jhapok) given in Table 6, as reported elsewhere [20,21]. Percentage of removal is $70.3 \pm 3\%$ and $94.0 \pm 2\%$ respectively. In single stage of equilibration, about 94% of Uranium could be removed from ground water simulant compared to 70% from Sambhar salt lake water (average of two determinations), as the concentration of NaCl was very high in case of latter ($146 \times 10^3 \, mg \, L^{-1}$) than in former ($3.3 \times 10^3 \, mg \, L^{-1}$). Therefore sodium ions compete with uranyl ion in complexing with quinoline-8-ol functionality thereby decreasing the removal efficiency.

4. Conclusions

Surface imprinted nanospheres were synthesized by modified precipitation polymerization method. These nanospheres, with high imprinting coefficients and retention capacity offer possible application towards removal of 50–1000 ppb of uranium from simulants of natural waters. Simple preparation procedures and significant selectivity of this material, arising out of imprinting (particularly for iron), opens up a novel method for the treatment of polluted effluents. The method can be extended for preparation of imprinted nanomaterials for other toxic metal ions and their application in pollution control processes.

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