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Synthesis, characterization and application of uranyl ion imprinted polymers of aniline and 8-hydroxy quinoline functionalized aniline

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In this work we report a simple method for the synthesis of uranyl ion imprinted and non imprinted polyaniline (IPAN and NIPAN) and a copolymer of 8-hydroxyquinoline functionalized aniline (ANHQ) and aniline (IFPAN and NIFPAN) using potassium dichromate and ammonium persulphate as the initiators. The structural characterization of the synthesized materials were done by FTIR and UV-Visible spectroscopy, morphology by SEM, thermal properties by TG and electrochemical properties by cyclic voltammetry. Application of the synthesized materials in removal of uranyl ion was studied using solid phase extraction (SPE). Various parameters were optimized to get quantitative removal from aqueous sample buffered to neutral pH using ammonium acetate. Selectivity and reusability studies were carried out to demonstrate the possible application in real sample analysis.

Introduction

Imprinting can be defined as the molding of complimentary binding sites for target molecules into synthetic polymers, with memory of their shape, size and functional group, formed by polymerization in presence of the target molecules. Their removal leaves recognition cavities which can selectively rebind them from a mixture of closely related compounds.^{1,2} Generally, widely accepted systems for preparation of imprinted polymers are free radical vinyl polymerization and sol gel process. Polymerization of aromatic monomers like pyrrole, o-phenylenediamine, oaminophenol, o-aminothiophenols and aniline by both chemical and electrochemical methods comprises another system.^{2,3} But imprinting by chemical polymerization of aromatic monomers for recognition and removal of ions still remains less explored area. There are only three reports on metal ion extraction by imprinted polyanilines, one by Cui et al.4 in which aromatic monomers with various functional groups were utilized in horseradish peroxidase-catalyzed polymerisation reactions with metal ions Cu(II), Ni(II), and Fe(III) as imprinting templates, another by Homayon et al.⁴ and by Kalal et al.⁶ which describes synthesis of anilineformaldehyde polymers in presence of extra aniline as crosslinker for selective adsorption of Ni(II) and Sr(II) respectively.

We have chosen uranium as the target metal ion. Uranium is an important nuclear fuel. Though only weakly radioactive, U(VI) exerts chemical toxicity due to its solubility and mobility.^{7,8} In the wake of recent events

regarding the contamination by nuclear hazards, it is worthwhile to explore new materials that can remove hazardous wastes selectively and efficiently from environment. Imprinted polymers can serve the purpose as they have the advantage of predetermined selectivity and excellent stability⁹ and the removal can be effected by solid phase extraction. Rao et al. and recently Branger et al. have given a detailed review on the use of imprinted polymers for removal of metal ions using SPE.¹⁰⁻¹² Aniline and functionalized aniline were used as the aromatic monomers. Aniline as a monomer in imprinting has the advantage of simple polymerization method possible in aqueous media, which considerably reduces the consumption of toxic organic solvents and vinylated compounds. To enhance the selectivity and removal efficiency, aniline was functionalized with 8hydroxyquinoline before imprinting. Polyaniline has been utilized for removal of uranyl ions, one by redox active polyaniline resin doped with polystyrene sulfonate in which binding of the cations is controlled electrochemically,¹³ another one where uranyl ion is converted to its anion by use of suitable complexing agents to facilitate the uptake by polyaniline at $pH=5.5^{14}$ and by polyaniline grafted graphene oxide nanosheets used for sorption of uranyl ions at pH=3.0.¹⁵

Here, we have synthesized ion imprinted polymer in both polyaniline and functionalized polyaniline matrix that can selectively remove uranyl ion from aqueous samples at neutral pH. We have characterized the prepared material, carried out optimization studies to get maximum removal and has done the selectivity studies so that it can be used in decontamination of real environmental samples.

EXPERIMENTAL

Materials

Aniline (99.5%, Merck) was distilled under reduced pressure. Uranyl nitrate hexahydrate (99%, Spectrochem), ammonium per sulphate (98% Sigma Aldrich), potassium dichromate (99% Merck) and arsenazo III (analytical grade purity, Fluka) were used as received. All other chemicals used in this work are of reagent grade and were used as received. The solutions were prepared in distilled water.

Extraction of uranyl ion from imprinted polymers (Leaching)

Uranyl ion was leached from the imprinted polymer by stirring the polymer in 1M HCL for the required period of time. Non imprinted polymers were also leached, although they do not contain uranyl ion, to maintain the same environment during SPE studies. The leached polymers are indicated by the notation (L).

Solid Phase Extraction Studies

In SPE studies, preconcentration was done with appropriate amount of the polymer from 100 mL of aqueous phase volume having 100 μ g of uranyl ion, adjusted to pH=7.0 using 10^{-3} M ammonium acetate buffer. Preconcentrated uranium was eluted from the polymer using 1M HCl and determined by spectrophotometry.

Method for determination of uranyl ion.

To the filtrate obtained after solid phase extraction was added 5 mL of 1:1 hydrochloric acid, 2 mL of 0.1% arsenazo III solution in a 25 mL standard flask and made upto the mark with distilled water. The absorbance of uranium–arsenazo III complex was measured at 656 nm.¹⁶

Synthesis of imprinted polyanilne (IPAN-1) with potassium dichromate

The method for synthesis with potassium dichromate was modified from the report of Chowdhary et al.¹⁷ The ratio of aniline to oxidant was taken as [An]/[OX]=2.0, [HCl]=2.4 M and [K₂Cr₂O₇]=0.11 M. Briefly, 5 mL of concentrated HCl, 0.5 mL of aniline and 0.05 g of UO2(NO3)2.6H2O were stirred for 30 minutes to form the pre-polymerization mixture. The polymerization was initiated by addition of K2Cr2O7, with vigorous stirring, when a green precipitate starts to form. Then total volume of the reaction mixture was made to 25 mL by adding distilled water and reaction was continued for 4 h. The synthesis was done with and without purging of nitrogen gas. The precipitated polymer was filtered and washed with distilled water until the filtrate was colorless. The polymer was then dried in an oven at 50 °C. The corresponding non imprinted polyaniline (NIPAN-1) (Yield-73%) was prepared by the same procedure without the uranyl ion.

Synthesis of imprinted polyanilne (IPAN-2) with ammonium persulphate

The same procedure was followed with ammonium persulphate as the initiator maintaining a 1:1 ratio of monomer to initiator. The corresponding non imprinted polymer was prepared by the same procedure without the uranyl ion (NIPAN-2)(Yield-77%). Synthesis of imprinted polyanilne with increased amount of uranyl ion with PDC (IPAN-3) and APS (IPAN-4)

The same procedure was used but with increased amount of uranyl ion [0.066 M] to see whether this would increase the binding sites inside the polymer and hence the percentage of removal. The ratio of aniline to uranyl ion was taken as 4:1.

Synthesis of N-[5-(8-hydroxyquinoline)methyl]aniline (ANHQ)

For functionalisation of aniline, 8-hydroxyquinoline was chloromethylated following the method of Burckhalter,¹⁸ which

was then treated with aniline in presence of triethylamine in DMF to get N-[5-(8-hydroxyquinoline)methyl]aniline (ANHQ).^{19,20}

Synthesis of imprinted homopolymer (IPANHQ)

Briefly, 5 mL of concentrated HCl, 0.5 g of ANHQ and 0.5 g of $UO_2(NO_3)_2.6H_2O$ were stirred for 30 minutes to form the prepolymerization mixture. The ratio of ANHQ to uranyl ion was taken as 1:2. The polymerization was initiated by addition of ammonium persulphate (1:1 ratio with the monomer) dissolved in distilled water, with vigorous stirring, when a green precipitate starts to form. Then total volume of the reaction mixture was made to 25 mL by adding distilled water and reaction was continued for 4 h. The precipitated polymer was filtered and washed with distilled water until the washings were colorless. The polymer was then dried in an oven at 50 $^{\circ}C$. The corresponding non imprinted polymer was prepared by the same procedure in the absence of uranyl ion (NIPANHQ).

Synthesis of imprinted copolymer (IFPAN)

Imprinted copolymer of ANHQ with aniline (IFPAN) was synthesized by the following procedure. Briefly, 5 mL of concentrated HCl, 0.5 mL of aniline, 0.15 g of ANHQ and 0.15 g of UO₂(NO₃)₂.6H₂O were stirred for 30 minutes to form the pre-polymerization mixture. The ratio of ANHQ to uranyl ion was taken as 1:2. The polymerization was initiated by addition of ammonium persulphate dissolved in distilled water, with vigorous stirring, when a green precipitate starts to form. Then total volume of the reaction mixture was made to 25 mL by adding distilled water and reaction was continued for 4 h. The precipitated polymer was filtered and washed with distilled water until the washings were colorless. The polymer was then dried in an oven at 50 °C. The corresponding non imprinted polymer was prepared by the same procedure in the absence of uranyl ion (NIFPAN) (Yield-69%). The scheme for the reaction is given in Fig. 1.



Fig. 1: Schematic diagram for synthesis of IFPAN CHARACTERISATION

A Shimadzu computer controlled double beam UV-Vis spectrophotometer UV-2401PC (Shimadzu, Kyoto, Japan), was used for measuring absorbance. pH of all the sample solutions were adjusted using a digital pH meter LI-120 (ELICO, Hyderabad, India) with accuracy of 0.01 pH unit. The FTIR spectra were recorded on Bruker FT-IR spectrometer. SEM images were taken using a Carl Zeiss EVO Edn: 18 Cryo Environmental SEM Instrument. Thermogravimetric analysis were done using a TG/DTA-6200 (SII Nano Technology Inc., Japan)

RESULTS AND DISCUSSION

We have synthesized different imprinted polymers for the removal of uanyl ion. Initially imprinting was done in aniline matrix using both potassium dichromate (PDC) (IPAN 1) and ammonium persulphate (APS) (IPAN 2) as initiators. A fairly good uptake and an imprinting effect of 2.0 (the ratio of removal by IPAN to that by NIPAN) was observed during SPE studies at neutral pH with 10⁻³M ammonium acetate as buffer. This prompted us to further investigate on the possibilities of

Journal Name

obtaining quantitative recovery using the imprinted polymers and the results are compiled in Table 1. From the data we can see that IPAN 1 showed only 73% removal even after increasing

Table 1: Solid phase extraction studies with imprinted
polymers synthesized by different methods

Material	Initiator	Amount for SPE (mg)	Removal (%)
		20	48.0
IPAN 1	PDC	50	55.8
		100	72.6
IPAN 2	APS	50	56.0
	PDC	50	56.0
IPAN 3			
	APS	50	56.0
IPAN 4			
IFPAN	APS	40	>99.0

the amount to 100 mg. IPAN 2 also gave same results. Then we went on to increase the amount of template in IPAN 3 AND IPAN 4, hoping that this would increase the binding sites inside the polymer, but removal percentage remained the same. In order to improve the percentage removal, aniline was functionalized with a specific ligand like 8-hydroxyquinoline to obtain a polyaniline matrix with 8-hydroxyquinoline as pendent ligands and as expected 40mg of the IFPAN gave quantitative removal of uranyl ion. Since the initiators potassium dichromate and ammonium persulphate and synthesis of the polymer with and without purging (data not shown), gave almost same percentage of removal, further studies were carried out by polymers prepared with ammonium persulphate as the initiator without purging. Homopolymer of functionalized aniline was prepared to confirm that ANHQ can be polymerized under identical conditions used for synthesis of IPAN. The yield of non imprinted polymers (NIPAN and NIFPAN) is given, but not for ion imprinted polymers as the exact amount of uranyl ion, which can contribute to the weight of the polymer, inside the matrix was not determined.

Characterisation

UV-Visible Spectroscopy

The interaction of uranyl ion with aniline and ANHO can be understood from the UV-visible spectrum given in Fig. 2a. After polymerization, the spectra were recorded both in DMSO and NMP. Though in solid state they are green in color (emeraldine salt), in NMP they turn blue (emeraldine base) and in DMSO they retain their green color. This could be due to the weak basic property of the solvent NMP causing dedoping of the polymer.²¹ Fig. 2b and 2c shows the spectra of IPAN, NIPAN, IFPAN and NIFPAN in DMSO and NMP respectively, where two peaks appear at ~325 nm and at ~631 nm, corresponding to π - π * transition in benzenoid rings and chargetransfer-exciton transition formed in a benzenoid ring with its adjacent quinoid ring, typical for emeraldine base.²²⁻²⁴ But in DMSO, an additional peak appears at around ~450nm, due to polaron- π^* transition, characteristic of emeraldine salt.^{22,25} The leached samples (Fig. 2d) also exhibit similar behavior in DMSO and NMP (data not shown).



Figure 2: UV-Visible spectra of a) Aniline, 1:4 ratio of aniline and uranylion, N8HQ,1:2 ratio of N8HQ and uranyl ion in methanol. b) IPAN, NIPAN, IFPAN and NIFPAN in DMSO c) IPAN, NIPAN, IFPAN and NIFPAN in NMP d) IPAN, NIPAN, IFPAN and NIFPAN leached with 1MHCl in DMSO e)IPAN, NIPAN, IFPAN and NIFPAN after solid phase extraction in DMSO f) Homopolymer of IPANHQ and NIPANHQ in NMP and DMSO.

Fig. 2e is the spectra for imprinted polymers after solid phase extraction. In this case materials exhibited only emeraldine base behavior in both DMSO and NMP (data not shown) because in SPE, samples were first treated with ammonium acetate at neutral pH. Probably this cause dedoping of the polymer and helps in the uptake of uranyl ion as the nitrogens in the polymer backbone are free to coordinate with the metal ion. From the spectra it can be observed that imprinted polymers of functionalized aniline also show similar behavior as that of imprinted polyaniline. Therefore the data was compared with the homopolymer of functionalized aniline given in Fig. 2f, from which it is clear that homopolymer also exhibit similar characteristics. Hence uv-visible spectra cannot be used to distinguish between IPAN and IFPAN in the measured wavelength range.

FTIR

FTIR spectra of all the polymers exhibit peaks characteristic for polyaniline (Fig. 3). The bands at 502 and 826 cm⁻¹ confirm the para-coupling structure of the polymer as they correspond to the out of plane vibration in 1,4-disubstituted benzene ring. The peak at 1141 cm⁻¹ is due to (-N-H⁺=) vibration or asymmetric stretching vibration of sulphonate group. The peak at 1240 cm⁻¹ is associated with the 'C–N⁺ and C–N^{+•} stretching vibration in a polaron structure, and corresponds to π electron delocalization induced in the polymer by protonation. Peaks in the range 1296-1298 cm⁻¹ corresponds to C-N stretching of secondary aromatic amine. The 1488-1495 cm⁻¹ bands are assigned to the B-NH-B vibration (where B denotes benzenoid ring). The 1558-1560 cm⁻¹ bands are assigned to -N=Q=N- structure (where Q denotes quinone).²⁶⁻³² For comparison FTIR of IPANHQ were taken. The absorption band at 1667 cm⁻¹ is assigned to C-N stretching vibrations of the quinoline rings,19 but this band due to its low intensity is not detectable in the copolymer of aniline and ANHQ. Comparison of the absorption intensity of the bands at 1580 and 1495 cm⁻¹ by taking their ratio (I_{1580}/I_{1495}) gives an indication of extent of oxidation of the polymer. The values were found to be less than 1.0 (around 0.8), which shows the predominance of reduced phase with more benzene units within the polymer.³² From the ratio it can also be concluded that there will be approximately one quinoimine structure after seven benzenoid monomer units.³⁴



Fig. 3: FTIR spectra of IPAN(a), NIPAN(b), IFPAN(c), NIFPAN(d) and IPANHQ(e)

Electrochemical Characterisation

Cyclic voltammetry was done by dispersing the sample in acetone followed by drop casting onto glassy carbon electrode. After drying in air, the samples were pre-equilibrated for 20 cycles between -0.10 V and +0.40 V with silver/silver chloride as the reference electrode, before running full scan. All the redox potentials are given in Table 2.

In the voltammogram, two redox peaks appears for all the polymers (Fig. 4). The first one at ~ 0.320 V is due to the formation of radical cations (polaronic emeraldine) and the



Page 4 of 8



Fig. 4: Cyclic voltammograms of polymers

second one at ~0.728 V is due to formation of diradical dications by oxidation of PAN. In the case of functionalized aniline, there is a shift in the second redox potential to more positive values. This shift increases with increase in bulky substituents, due to induced non planar conformation in the polymer back bone, reducing the conjugation and thus increasing the oxidation potential. From the voltammogram it can also be concluded that the coupling occurs in a linear method as any ortho or meta coupling would have produced another peak in the centre.^{24,35-37}

Table 2: Redox potentials of the synthesized polymers

Material	First redox peak (V)		Second redox peak (V)	
	E _{pa}	E _{pc}	E_{pa}	E_{pc}
IPAN	0.320	0.169	0.728	0.557
NIPAN	0.369	0.164	0.728	0.584
IFPAN	0.300	0.112	0.813	0.667
NIFPAN	0.305	0.142	0.782	0.623

Morphology by SEM



Fig. 5: SEM images of IFPAN(a), IFPAN_L(b) and NIFPAN(c), NIFPAN_L(d)

The SEM images of imprinted and non imprinted polymer, both leached and un-leached are shown in Fig. 5. From the images it can be seen that the material has an aggregated spherical structure, with each sphere having size of approximately 100 nm. Addition of uranyl ion and leaching in 1M HCl has no effect on the morphology of the material.



Weight (%) 60

100

80

40

20

0

200

Table 3: Optimization of solid phase extraction parameters for IFPAN Parameters IPAN IFPAN PANHQ

Parameters	Uranium Removal
	(%)*
Weight Variation	
30	85.8
40	>99
50	>99
Preconcentration Time	
(min)	
10	79.6
20	87.1
30	> 99
Elution Time(min)	
10	65.1
20	69.8
30	> 99
Nature of Eluent	
1M HNO ₃	78.5
1M HCl	> 99
1M Na ₂ CO ₃	73.7
Amount of uranium (µg)	
50	> 99
100	> 99
200	51.2
500	20.0

Fig. 6: TG curves of IPAN, IFPAN and PANHQ Thermal stability of the imprinted polymers was measured

400

using TG (Fig. 6). In IPAN, the first weight loss observed 100 °C is due to desorption of water. The second weight los process at about 200-325 °C could be due to the exclusion doped acids and the third weight loss from 500 ⁰C is due to the disintegration of polymer back bone. In case of IFPAN an PN8HO, a two step weight loss can be observed, first step 100 °C due to loss of water and second step, due decomposition of the polymer.15,20

600 Temperature °C 800

1000

Optimization of Parameters in SPE studies

Various SPE parameters were optimized for the materi IFPAN to get quantitative removal and the values we compared with that for NIFPAN in pH variation studies. Effe of pH (5.0-8.0), weight of polymer particles (30, 40 and 5 mg), time of stirring (10, 20 and 30 min) during the preconcentration and elution of uranium and nature of eluent (1M HCl/ 1M HNO₃/ 1M Na₂CO₃) were optimized by checking the removal efficiency of 100 µg of uranyl ion present in 100 mL of aqueous solutions using the polymer. Quantitative removal was obtained at pH 7.0 as shown in Fig. 7. From the figure, it can also be seen that there is a significant imprinting effect. Weight variation studies shows that 40mg of the material is enough for removal. Pre-concentration time and elution time was fixed as 30 min and 1M HCl was found to be the best for leaching uranyl ions from the imprinted polymers. Quantitative removal of 50-100 µg of uranyl ion from 100 mL of aqueous solution adjusted to pH 7 with 10⁻³ M ammonium acetate was demonstrated. The results are compiled in Table 3. At optimized conditions, IFPAN exhibited an imprinting effect of 1.3.



Fig. 7: Effect of pH on removal of uranyl ion

*Average of duplicate measurements

Reusability Studies

Reusability studies were carried out for five cycles under the optimized conditions. 40 mg of IFPAN at pH 7.0 was used. After the first cycle, since uranyl ion is eluted with 1M HCl, IFPAN was stirred for 30 min in pH 7.0 ammonium acetate buffer for neutralisation and was repeated for the remaining cycles. Even after 5 cycles quantitative recovery >99% was obtained which shows the capability of the material in repeated removal of uranium from aqueous samples.

Retention Capacity Studies

The maximum amount of pre-concentrated uranyl ion per gram of the imprinted material (retention/binding capacity of IFPAN) was calculated by saturating 40 mg of polymer particles with 10 mgL⁻¹ of uranyl ion under optimal conditions. The maximum amount of uranyl ion pre-concentrated was eluted with 1.0 M HCl and determined by using arsenazo III procedure. The material gives a retention capacity of 83 μ molg⁻¹ and 49 μ molg⁻¹ at 10 mgL⁻¹ for IFPAN and NIFPAN respectively. This shows that the material has high retention capacity which can be utilized for removal of uranium.

Selectivity Studies

To evaluate the selectivity of IFPAN and NIFPAN for uranyl ion over other inorganic ions, 40 mg of the material was equilibrated with 100 µg of uranyl ion and 100 µg of each individual inorganic ion, likely to coexist in real samples, present in 100 mL of de ionized water under the optimized conditions.

The selectivity coefficient $S_{UO_2^{2+}/M^{n+}}$ is defined as,³⁸

$$S_{UO_22^+/M^{n+}} = \frac{D_{UO_22^+}}{D_{M^{n+}}}$$
(1)

Where ${}^{D_{UO_22+}}$ and ${}^{D_{M^{n+}}}$ are the distribution ratios of the uranyl ion and other inorganic species, respectively, with polymer materials. These distribution ratios were calculated using the formula

$$\mathbf{D} = \mathbf{A}_2 / \mathbf{A}_1 \tag{2}$$

where A_2 is the amount of uranyl ion or metal ion enriched on sorbent and A_1 is the amount of uranyl ion or metal ion in aqueous phase at equilibrium.

Imprinting coefficient (K') =
$$S_{IIP}/S_{NIP}$$
 (3)

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

$$\% E = A_2 / A_T x \ 100 \tag{4}$$

where A_T is the total amount of uranyl ion or other metal ions utilized in extraction.

The concentration of uranyl ion was then determined by spectrophotometry, 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 given in Table 4. The selectivity coefficients of IFPAN for uranium are greater by $10^2 - 10^3$ fold as compared to other ions. Furthermore the imprinting coefficients for various co-existing species lie in the range 69.4 (Cu²⁺) to 648.6 (Na⁺). These findings can be explained on the basis of imprinting effect. Based on the results it is clear that uranyl ion can be removed selectively from several inorganic species present in dilute aqueous solutions.

Table 4: Selectivity data of IFPAN and NIFPAN

Metal	Distribution		Selectivity		Imprinting
ions	Ratio (D)		Coefficient (S)		coefficient
	NIFPAN	IFFPAN	NIFFPAN	IFFPAN	(K')
UO_2^{2+}	3.2	99	-	-	-
Na ⁺	0.45	.0204	7.4	$4.8 ext{ x10}^3$	648.6
Ca ²⁺	0.76	.101	4.2	9.8×10^2	233.3
Mg ²⁺	0.78	.111	4.1	8.9×10^2	217.1
Cu ²⁺	0.82	0.45	3.9	$2.2x10^{2}$	69.4
Zn ²⁺	0.56	0.08	5.7	1.1×10^{3}	197.6
Mn ²⁺	0.72	0.16	4.4	6.1×10^2	138.3
Fe ³⁺	0.67	0.16	4.8	6.1×10^2	126.7
Co ²⁺	0.82	0.22	3.9	4.6×10^2	117.3
Ni ²⁺	0.72	0.19	4.4	5.2×10^2	118.2

Conclusions

We have synthesized ion imprinted polymers with aromatic monomers aniline and 8-hydroxyquinoline functionalized aniline for successful removal of uranyl ion from aqueous samples by solid phase extraction. The method for preparation of imprinted polymer by this approach is simpler as it requires only mild reaction conditions, like aqueous media and room temperature and can be completed within 4h. The characterization of the imprinted polymer shows that addition of uranyl ion does not alter the characteristic properties of polyaniline. The material has good selectivity and retention capacity and reusability which makes it suitable for possible use in removal of uranyl ion from real samples. We are also exploring the possibility of using the material as electrochemical sensor for uranyl ion as the material can provide a conductive matrix suitable for sensing applications.

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Synthesis, characterization and application of uranyl ion imprinted polymers of aniline and 8-hydroxy quinoline functionalized aniline.



Imprinted homopolymer of uranyl ion with aniline (IPAN) and imprinted copolymer with aniline and 8-hydroxyquinoline functionalized aniline (IFPAN) were synthesized. These polymers upon leaching, (IPAN_L and IFPAN_L), gives materials suitable for rebinding of uranyl ion selectively from aqueous samples.