ION IMPRINTED POLYMER NANOSTRUCTURES AND THEIR APPLICATION IN SELECTIVE REMOVAL OF URANIUM FROM AQUEOUS MEDIA BY SOLID PHASE EXTRACTION

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By

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2014

DECLARATION

I hereby declare that the Ph. D thesis entitled "**ION IMPRINTED POLYMER NANOSTRUCTURES AND THEIR APPLICATION IN SELECTIVE REMOVAL OF URANIUM FROM AQUEOUS MEDIA BY SOLID PHASE EXTRACTION**" is an independent work carried out by me at the Chemical Sciences and Technology Division, National Institute for Interdisciplinary Science and Technology (NIIST), CSIR, Trivandrum, under the supervision of Dr. T. Prasada Rao and the same has not been submitted elsewhere for any other degree, diploma or title.

In keeping with the general practice of reporting the scientific observations, due acknowledgements has been made wherever the work described is based on the findings of other investigators.

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CERTIFICATE

This is to certify that the work embodied in the thesis entitled "**ION IMPRINTED POLYMER NANOSTRUCTURES AND THEIR APPLICATION IN SELECTIVE REMOVAL OF URANIUM FROM AQUEOUS MEDIA BY SOLID PHASE EXTRACTION**" has been carried out by Ms. Milja T. Elias, under my supervision and guidance at the Chemical Sciences and Technology Division, National Institute for Interdisciplinary Science and Technology (NIIST), CSIR, Trivandrum and the same has not been submitted elsewhere for a degree.

Dr. T. PRASADA RAO

(Thesis Supervisor)

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LIST OF ABBREVIATIONS

aapts	3-(2-aminoethylamino)-propyltrimethoxysilane
AIBN	2, 2’-azobisisobutyronitrile
ANHQ	N-[5-(8-hydroxyquinoline)methyl]aniline
APS	Ammonium persulphate
CTAB	Cetyltrimethylammonium bromide
CV	Cyclic voltammetry
DDA	Dodecylamine
DMF	N,N-dimethylformamide
DMSO	Dimethyl sulphoxide
DVB	Divinylbenzene
ECH	Epichlorohydrin
EGDMA	Ethylene glycol dimethacrylate
FTIR	Fourier transform infrared spectroscopy
HEMA	2-hydroxyethyl methacrylate
HRTEM	High resolution transmission electron microscopy
HQ	8-hydroxyquinoline
IFPAN	Imprinted copolymer of functionalised aniline and aniline
IIP	Ion imprinted polymers
IPAFC	Imprinted aniline-formaldehyde copolymer
IPAFC-C	Imprinted aniline-formaldehyde copolymer with CTAB
IPAFC-S	Imprinted aniline-formaldehyde copolymer with SDS
IPAFC-T	Imprinted aniline-formaldehyde copolymer with Triton X 100
IPAN	Imprinted polyaniline
IPAN-C	Imprinted polyaniline with CTAB
IPANHQ	Imprinted polymer of N-[5-(8-hydroxyquinoline)methyl]aniline
IPAN-S	Imprinted polyaniline with SDS
IPAN-T	Imprinted polyaniline with TX 100
MAA	Methacrylic acid
MAGA	N-methacryloyl-(L)-glutamic acid
MIP	Molecular imprinted polymer

MWCNT	Multi-walled carbon nanotube
NIP	Non-imprinted polymer
NIPAN	Non-imprinted polyaniline
NIFPAN	Non-imprinted copolymer of functionalised aniline and aniline
NIPAFC	Non-imprinted aniline-formaldehyde copolymer
NIPAFC-C	Non-imprinted aniline-formaldehyde copolymer with CTAB
NIPAFC-S	Non-imprinted aniline-formaldehyde copolymer with SDS
NIPAFC-T	Non-imprinted aniline-formaldehyde copolymer with Triton X 100
NIPAN	Non-imprinted polyaniline
NIPAN-C	Non-imprinted polyaniline with CTAB
NIPAN-S	Non-imprinted polyaniline with SDS
NIPAN-T	Non-imprinted polyaniline with TX-100
NMP	N-Methyl-2-pyrrolidone
PAN	Polyacrylonitrile
PDC	Potassium dichromate
PEI	Polyethyleneimine
PMA	Polymethacrylic acid
PMMA	Polymethyl methacrylate
ppb	Parts per billion
ppm	Parts per million
PS	Polystyrene
PVC	Polyvinyl chloride
SDS	Sodium dodecyl sulphate
SEM	Scanning electron microscopy
SPE	Solid phase extraction
TEMED	N,N,N’,N’-tetramethylenediamine
TEOS	Tetraethoxysilane
THF	Tetrahydrofuran
TX-100	Triton X -100
UV	Ultraviolet
4-VP	4-vinylpyridine
WHO	World health organization

PREFACE

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 molecules. Ion imprinted polymers are synthesized using the same strategy with metal ions as the targets. Removal of toxic metal ions from polluted waters is of utmost importance in maintaining cleaner and safer environment. Imprinted polymers can serve the purpose as they have the advantage of predetermined selectivity and excellent stability and the removal can be effected by solid phase extraction. We have focused on synthesis of imprinted polymers for removal of uranium from neutral aqueous media. Uranium, an important nuclear fuel is also an emerging pollutant. Though only weakly radioactive, U(VI) exerts chemical toxicity due to its solubility and mobility. Recent reports on nuclear hazards make it worthwhile to explore new materials for the removal of hazardous wastes selectively and efficiently from environment. A general introduction to the technique of imprinting and the different polymers prepared so far for uranium removal has been described in chapter 1.

Chapter 2 describes the synthesis of surface imprinted nanospheres for selective removal of uranium from simulants of Sambhar salt lake and ground waters. Bulk polymerization is the most commonly used imprinting technique which produces highly irregular particles with 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. Uranyl ion was complexed on to 8-hydroxyquinoline functionalized 3-aminopropyltrimethoxysilane modified silica nano particle. Surface imprinting was done with 4-VP (4-vinyl pyridine) and 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 without uranyl ion. The material offers high retention capacity of 97.1 μmol/g for 10 mgL^{-1} of uranium, do not require tedious grinding and sieving steps, is water compatible and works in the pH range of 5 to 7, making it ideal for possible use in decontamination of polluted natural water samples or front end effluents of nuclear power reactors.

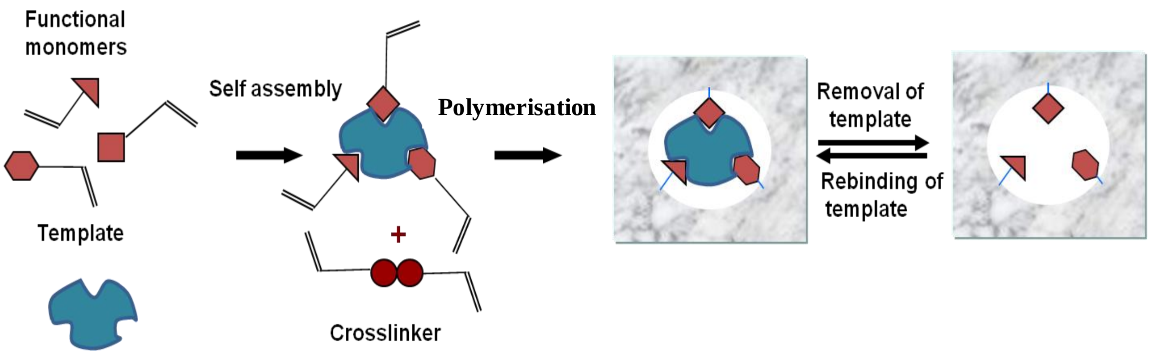
Synthesis, characterization and application of uranyl ion imprinted polymers of aniline and 8-hydroxyquinoline modified aniline using potassium dichromate and ammonium persulphate as the initiators is discussed in chapter 3. This is based on polymerization of aromatic monomers by chemical method which still remains less explored area. It also addresses the challenge of aqueous phase imprinting and removal of toxic species. 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. Ion imprinted polymer-solid phase extraction (IIP-SPE) has been utilised for removal of uranium. Various parameters were optimized to get quantitative removal from aqueous samples buffered to neutral pH using ammonium acetate. Selectivity and reusability studies were carried out to demonstrate the possible application in real sample analysis.

Chapter 4 highlights the synthesis of hierarchically double imprinted polymers with uranium and surfactants as templates and aniline and aniline-formaldehyde as the polymer matrix. Here surfactants and uranium act as templates which on removal by acid and ethanol mixture, gives different sized imprints each with a specific function. The removal of the metal ion from the complex leaves cavities that exhibit ionic recognition and that of the surfactants results in the formation of relatively large pores that give the polymer an overall porosity which improves metal ion transport kinetics. Comparison of the properties of the imprinted polymers, synthesized using anionic SDS, cationic CTAB and neutral Triton X-100, in terms of removal efficiency of uranium by IIP-SPE has been provided. The synthesized polymers were characterized by UV-Visible, FTIR, SEM and cyclic voltammetry.

The conclusions of all the results described above and suggestions for future work are presented in the last part of the thesis.

Chapter 1

Imprinted polymers and their application in removal of uranium



1.1 Molecular imprinting-origin

The concept of imprinting was introduced by Polyakov as early as in 1931, in silica matrices. But he failed to effectively explain selectivity exhibited by silica towards the corresponding additives used during drying stage and his studies went largely unnoticed. At the same time theories were formulated to explain selectivity exhibited by antibodies. In 1940's Pauling and Campbell, following the instructional theory tried to explain the phenomenon and that procedure is considered as the first example of bio imprinting. They precipitated globulins under denaturing conditions in the presence of an antigen, which acts as a template, and then removal and redissolution of the globulins resulted in specificity towards the antigen. This was followed by works from his student Dickey involving silica gels prepared analogous to the formation of antibodies leading to development of imprinting in silica. Though extensive research was carried out in this area, there was a decline due to instability of the material and limitations in reproducibility. However, revival of research in this field occurred with the introduction of organic polymers as matrices reported by Wulff in 1972.

Imprinting was then defined as the molding of complimentary binding sites for target molecules into synthetic polymers, with memory of their shape, size and functional group [Sellergren, 2003; Alexander *et al.*, 2006]. They can be synthesized by copolymerisation of the functional monomers and cross-linkers in the presence of template molecules. The functional monomers initially forms a complex with the imprint molecule and these are held in position by highly cross linked polymeric structure. Removal of the template molecules thus leaves recognition cavities complementary to the template molecule in shape, size and chemical functionality which can selectively rebind it from a mixture of closely related compounds. In other words, a molecular memory is introduced into the polymer, which is capable of binding the template with very high specificity [Haupt and Mosbach, 2000; Chen *et al.*, 2011]. The whole procedure for imprinting can be schematically represented as given in Figure 1.1.

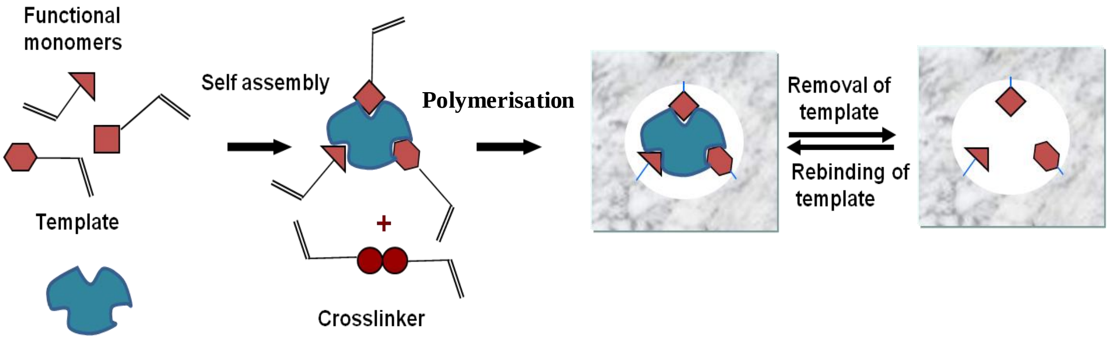


Figure 1.1: Schematic representation of imprinting

1.2 Strategies of imprinting

Based on the interactions between templates and functional monomers, there are three main strategies for imprinting namely, covalent, non-covalent and semi-covalent.

1.2.1 Covalent imprinting

Wulff and Sarhan developed covalent imprinting relying on the formation of reversible covalent bonds [Wulff and Sarhan, 1972]. The template, after imprinting, is removed by breaking the covalent bond and rebinding occurs via reformation of the bond. Their first report was on the interaction between D-glyceric acid as the template with the monomers 4-vinylphenylboronic acid and 4-vinylaniline. D-glyceric acid is covalently attached to vinyl aniline as amide and to boronic acid as diboronate (Figure 1.2a). Rebinding studies revealed that the acid is bound with a boronic ester linkage and an electrostatic interaction as shown in Figure 1.2b.

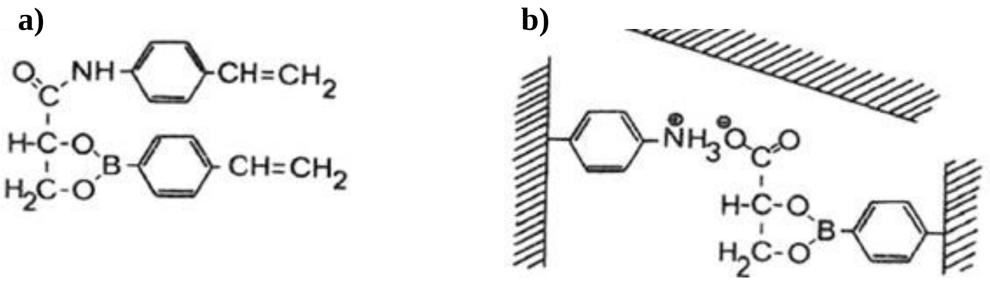


Figure 1.2: a) Covalent bond formation between D-glyceric acid, 4-vinylaniline and 4-vinylphenylboronic acid b) Rebinding of D-glyceric acid [Wulff and Sarhan, 1972]

Though covalent imprinting has the advantage of homogeneous binding sites as all the functional groups are present inside the imprint cavities providing precise spatial arrangement for rebinding, they have the drawback of limited range of monomers able to form labile covalent bonds with the template and also the rebinding kinetics are extremely slow.

1.2.2 Non-covalent imprinting

Mosbach proposed non-covalent imprinting taking advantage of various interactions such as hydrogen bonding, ionic interactions, van der Waals forces, π - π interactions etc. In this case, removal and rebinding occurs via the same non-covalent interactions as shown in Figure 1.3. They used rhodanile blue and safronine O as the templates with acrylic acid based monomers for providing complimentary binding sites [Arshady and Mosbach, 1981].

Majority of imprinted polymers utilizes the non-covalent imprinting strategy due to simplicity of the method which can be applied to imprint large number of compounds and due to faster kinetics as it does not require synthesis steps. But the method produces inhomogeneous binding sites resulting in less specificity and requires excess monomers since the binding constants are low.

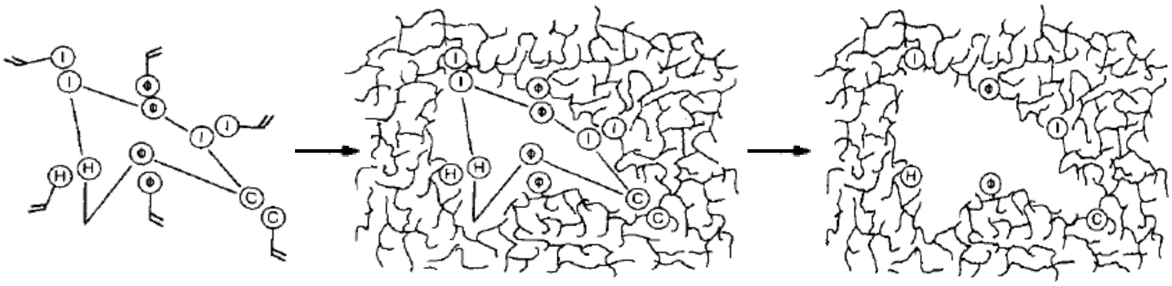


Figure 1.3: Non covalent imprinting. Interactions: 11**,** ionic; ϕϕ, hydrophobic; HH, hydrogen bond; CC**,** charge transfer [Arshady and Mosbach, 1981]

1.2.3 Semi-covalent imprinting

An approach combining the above two methods forms the basis for semi-covalent imprinting, in which imprinting is done using covalent linkage but rebinding through non-covalent interactions. Semi-covalent imprinting can be done by two methods,

i) by direct connection of template and monomer by an ester or amide linkage

ii) using a spacer between the template and polymerisable recognition element in the imprinting step [Yan and Ramstrom, 2005]

The second method also known as sacrificial spacer method was introduced by Whitcombe, in which cholesterol was covalently bound to 4-vinylphenol to give cholesteryl-4-vinylphenyl carbonate as the template monomer. After imprinting, cholesterol can be hydrolytically cleaved with the loss of carbonyl group as CO_2. The phenolic hydroxyl group left behind acts as the non-covalent recognition site capable of binding to cholesterol through hydrogen bonding. Here carbonyl group leaves sufficient space between functional groups to establish bonding and hence called the sacrificial spacer [Whitcombe *et al.*, 1995]. The scheme for the entire process is given in Figure 1.4. This method was claimed to have the virtues of covalent imprinting, like formation of homogeneous binding sites and not the vices like slow rebinding kinetics as it does not require formation of covalent bond upon rebinding. But this method also has the limitation of applicability to narrow range of functional monomers.

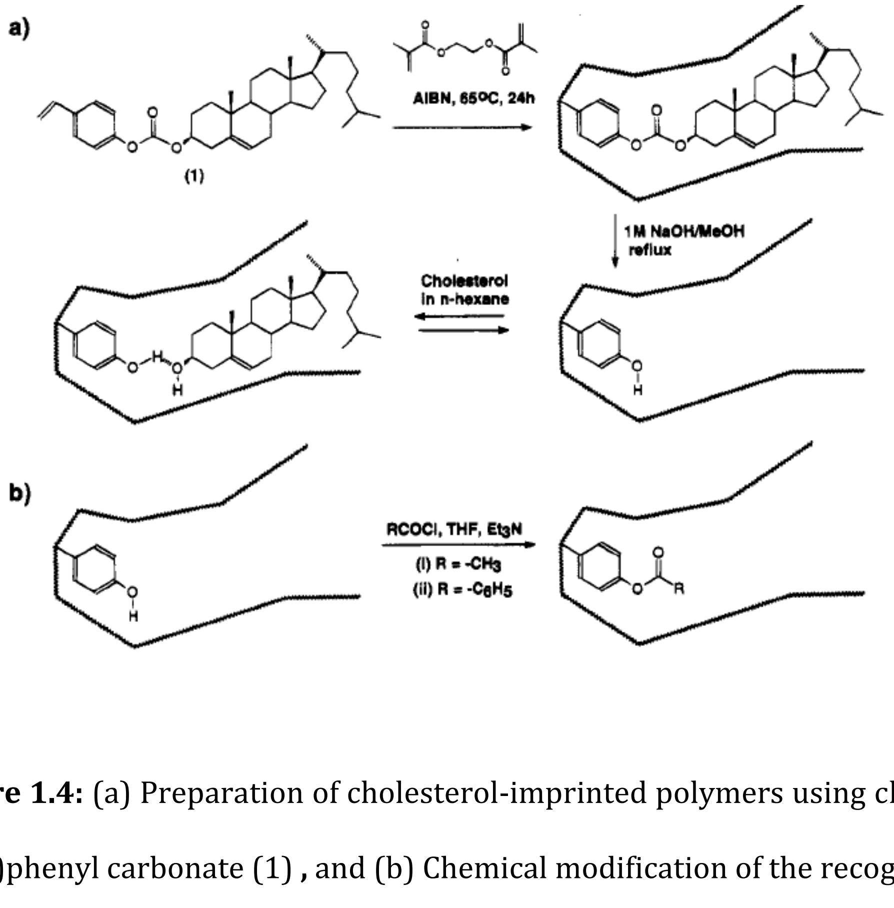


Figure 1.4: (a) Preparation of cholesterol-imprinted polymers using cholesteryl (4-vinyl)phenyl carbonate (1) , and (b) Chemical modification of the recognition site by acylation [Whitcombe *et al.*, 1995]

In addition to above strategies, metal co ordination imprinting and metal ion imprinting is also in use as depicted in Figure 1.5.

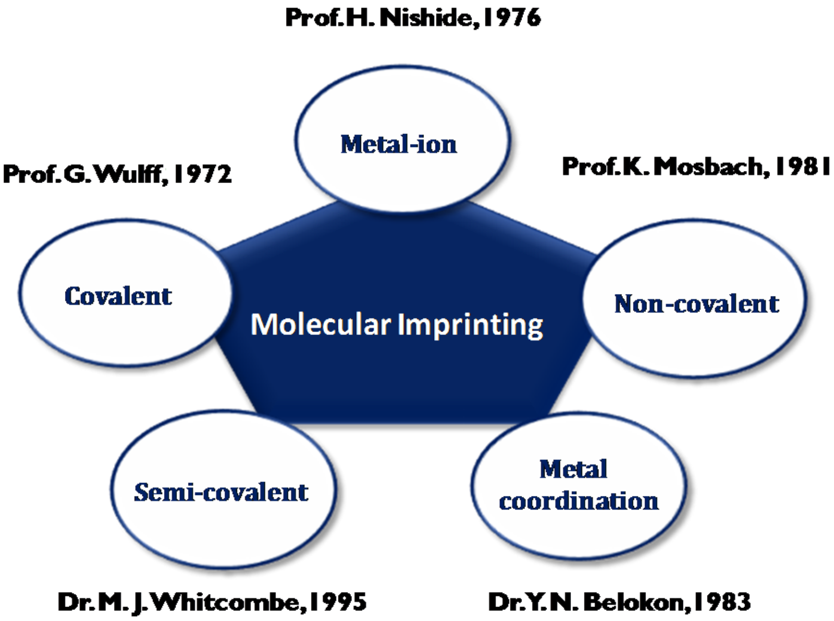


Figure 1.5: Scheme for classification of imprinting

1.2.4 Metal Coordination imprinting

The concept was put forward by Belokon [Sellergren, 2001]. This method explores the ability of metal ions to bind to a wide range of ligands through donation of electrons from the ligand to the unfilled orbitals of metal ions. Polymerisable ligands are used to complex metal ions which in turn forms coordination bond to the template. The first report was copolymerisation of potassium Λ and Δ-bis[*N*-(5-methacryloylamino) salicylidene-(*S*)-norvalinato]-cobaltate(III) with acrylamide and *N,N′*-methylene diacrylamide to give crosslinked gels. Deuterium exchange studies with the material shows retention of configuration of aminoacid suggesting initial conformation of the complex was retained in the polymer matrix [Belokon *et al.*, 1983]. The group of Fujii used the concept to imprint aminoacid [Fujii *et al.*, 1985]. Co(III)-Schiff base complex was used to discriminate stereoisomers of N-benzyl-D-valine as given in Figure 1.6.

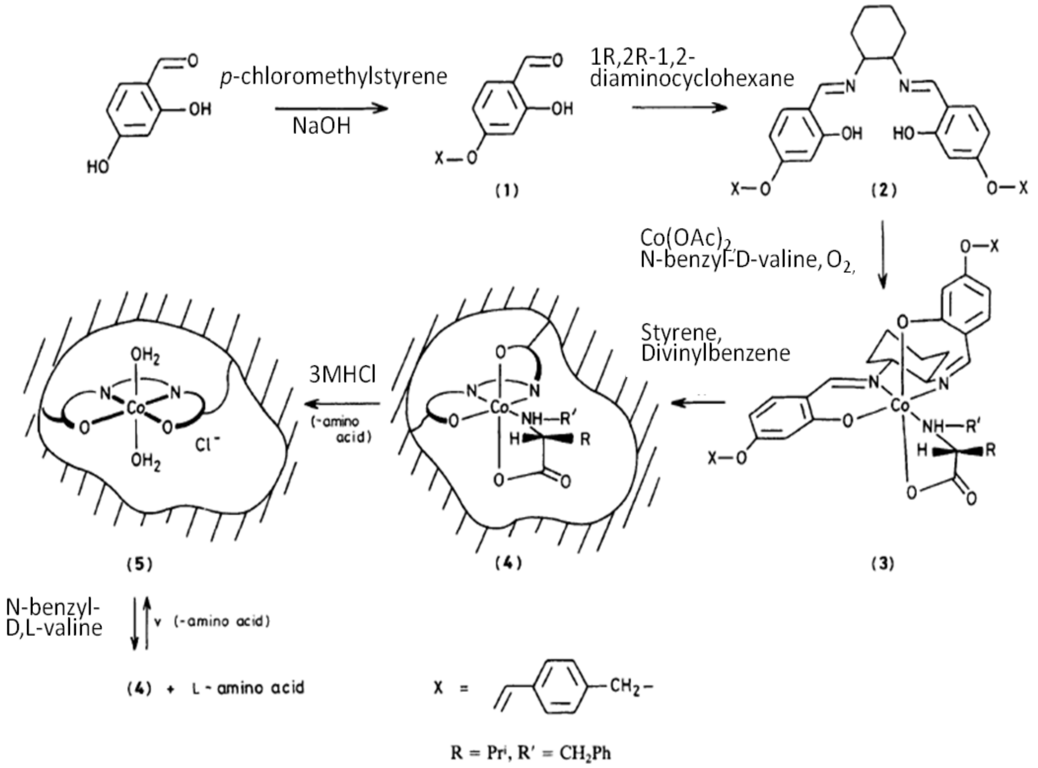


Figure 1.6: Scheme for imprinting of N-benzyl-valine [Fuji *et al.*, 1985]

1.2.5 Metal ion imprinting

Ion imprinted polymers (IIP) are formed when a metal ion is used as template instead of a molecule in molecular imprinting technique. Nishide, the pioneer in this field, imprinted metal ions-Cu(II), Co(II), Zn(II), Ni(II), Hg(II) and Cd(II) with poly(4-vinylpyridine) in presence of 1,4-dibromobutane as the cross linker [Nishide *et al.*, 1976]. This resin could selectively adsorb the corresponding metal ion from weakly acidic solutions. This was followed by a report by Kabanov who cross-linked a copolymer of diethyl vinylphosphonate and acrylic acid with N,N’-methylenediacrylamide in the presence of metal ions [Kabanov *et al.*, 1979].

Yet another approach for metal ion imprinting using polymerisable ligands was put forward by Kato *et al*., [1981]. Here 1-vinylimidazole was used to complex the metal ion and copolymerized and crosslinked with 1-vinyl-2-pyrrolidone and divinylbenzene (DVB).

Kuchen and Schram [1988] for the first time isolated the complex of metal ion and polymerisable ligand before imprinting. Cu(II)-methacrylic acid complex was separated and polymerized with water, 4-vinyl pyridine and ethylene glycol dimethacrylate (EGDMA). All these methods results in the formation of bulk imprinted polymers which has the disadvantage of binding sites situated deep inside the polymer matrix, requires grinding and sieving steps leading to partial destruction of imprinted structures and the existence of residual guests inside the polymer.

As a solution to this problem, the group of Takagi introduced the concept of surface imprinting using aqueous organic interface i.e. oil in water emulsion. A seed microsphere emulsion was prepared consisting of linear chain polymers carrying functional groups which can interact with the template. This was followed by addition of divinyl type monomers so that emulsion becomes swollen. Introduction of template allows interaction with the functional groups and the structure thus obtained was immobilized by polymerisation of divinyl monomers [Yu *et al.*, 1992]. Surface imprinting can also be done using water in oil emulsion [Uezu *et al.*, 1994].

Another novel concept in metal ion imprinting was put forward by Dai using both surfactants and metal ion as template for imprinting copper in inorganic silica matrix. The removal of the metal ion from the complex leaves cavities that exhibit ionic recognition. Removal of surfactants results in the formation of relatively large pores that imparts an overall porosity to the polymer, which improves metal ion transport kinetics. The method is called as hierarchical double imprinting since two templates are used at different length scales [Dai *et al.*, 2000].

The concept of trapping in metal ion imprinting was brought in by the group of Rao, in which both vinylated and non-vinylated ligands are used. Vinylated ligands remain chemically bound to the polymer whereas non-vinylated ligand gets trapped inside. Palladium ion was imprinted using dimethylglyoxime as non-vinylated ligand and 4-vinylpyridine as the vinylated ligand, in presence of styrene as monomer and divinylbenzene as crosslinker [Sobhi *et al.*, 2003]. Therefore the synthesis of imprinted polymers can be generalized into five methods as given in the Figures [1.7-1.12] below.

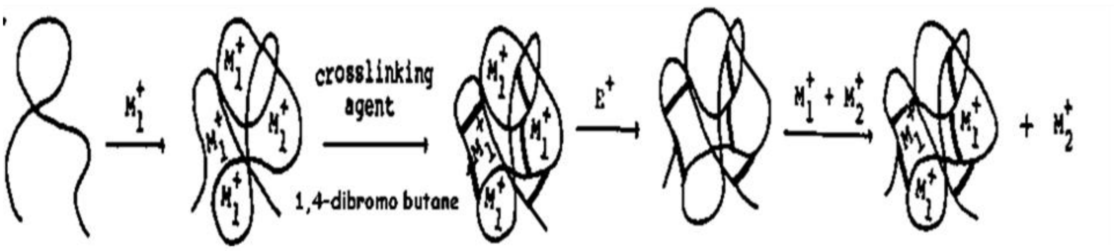


Figure 1.7: Method 1 - Linear chain polymers carrying metal-binding groups cross linked with a bifunctional reagent in presence of metal-ions [Nishide *et al.*, 1976]

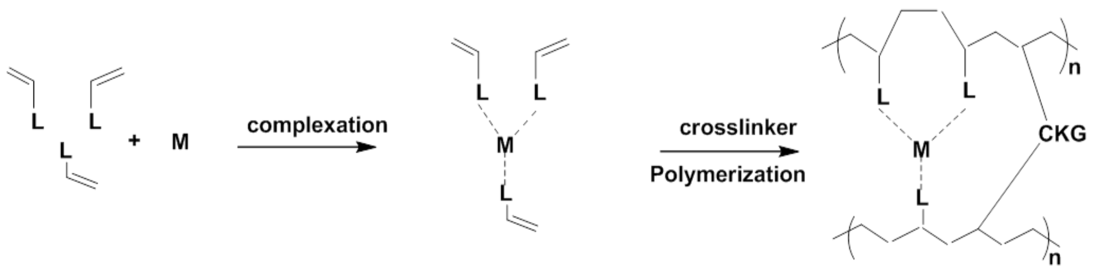


Figure 1.8: Method 2 - Metal-ion complexing monomers (metal-ion complexing ligand with vinyl group) [Nishide *et al.*, 1981]

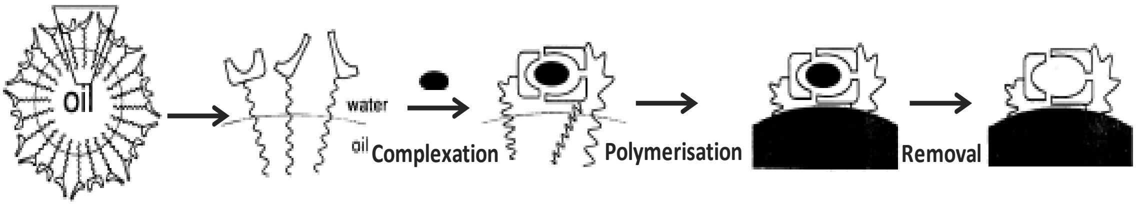


Figure 1.9: Method 3a - Surface imprinting – oil in water emulsion [Yu *et al.*, 1992]

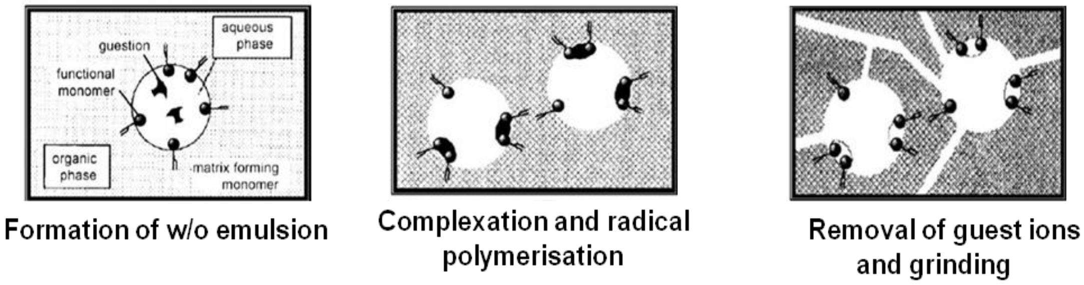


Figure 1.10: Method 3b - Surface imprinting – water in oil emulsion [Uezu *et al.*, 1994]

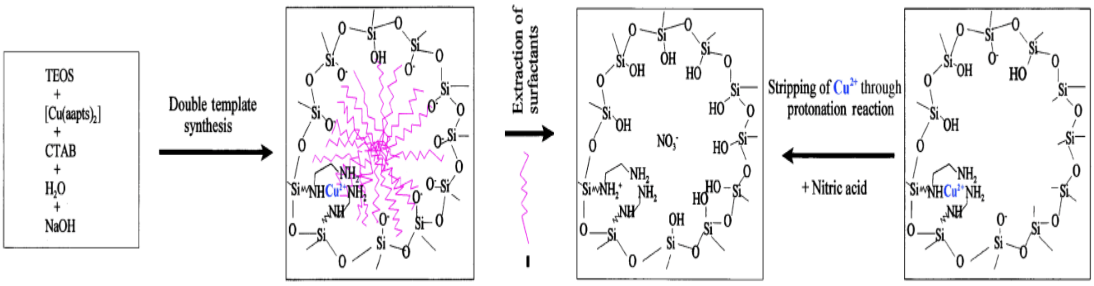


Figure 1.11: Method 4 - Hierarchical or double template synthesis [Dai *et al.*, 2000]

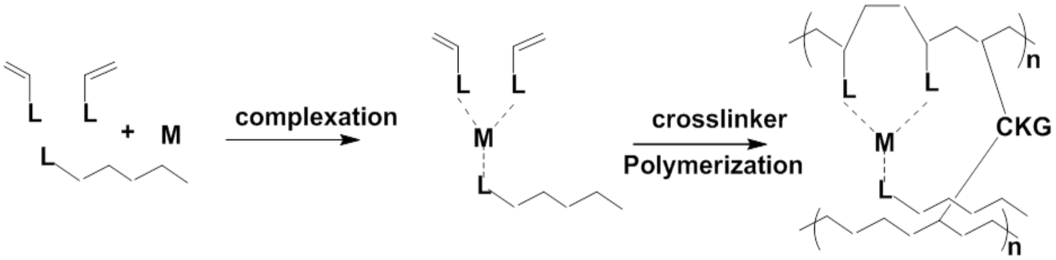


Figure 1.12: Method 5 - Trapping of non-vinylated ligand [Sobhi *et al.*, 2003]

IIP's prepared by these methods have the advantage of predetermined selectivity and excellent stability in harsh environments like high temperature and pressure.

The selectivity depends mainly on i) the specificity of interaction of ligand with the metal ion ii) pH iii) the coordination geometry and coordination number iv) charge and size of the metal ion and v) metal-ligand binding constant [Rao *et al.*, 2004]. The ability of the imprinted polymers for the selective readsorption of metal ion also depends on the binding sites formed inside the polymer, which is determined by the components used in preparing the polymer matrix.

1.3 Components in imprinting

General method for synthesis of ion imprinted polymers includes the use of the following components, ligand, functional monomers, crosslinker, porogen and an initiator.

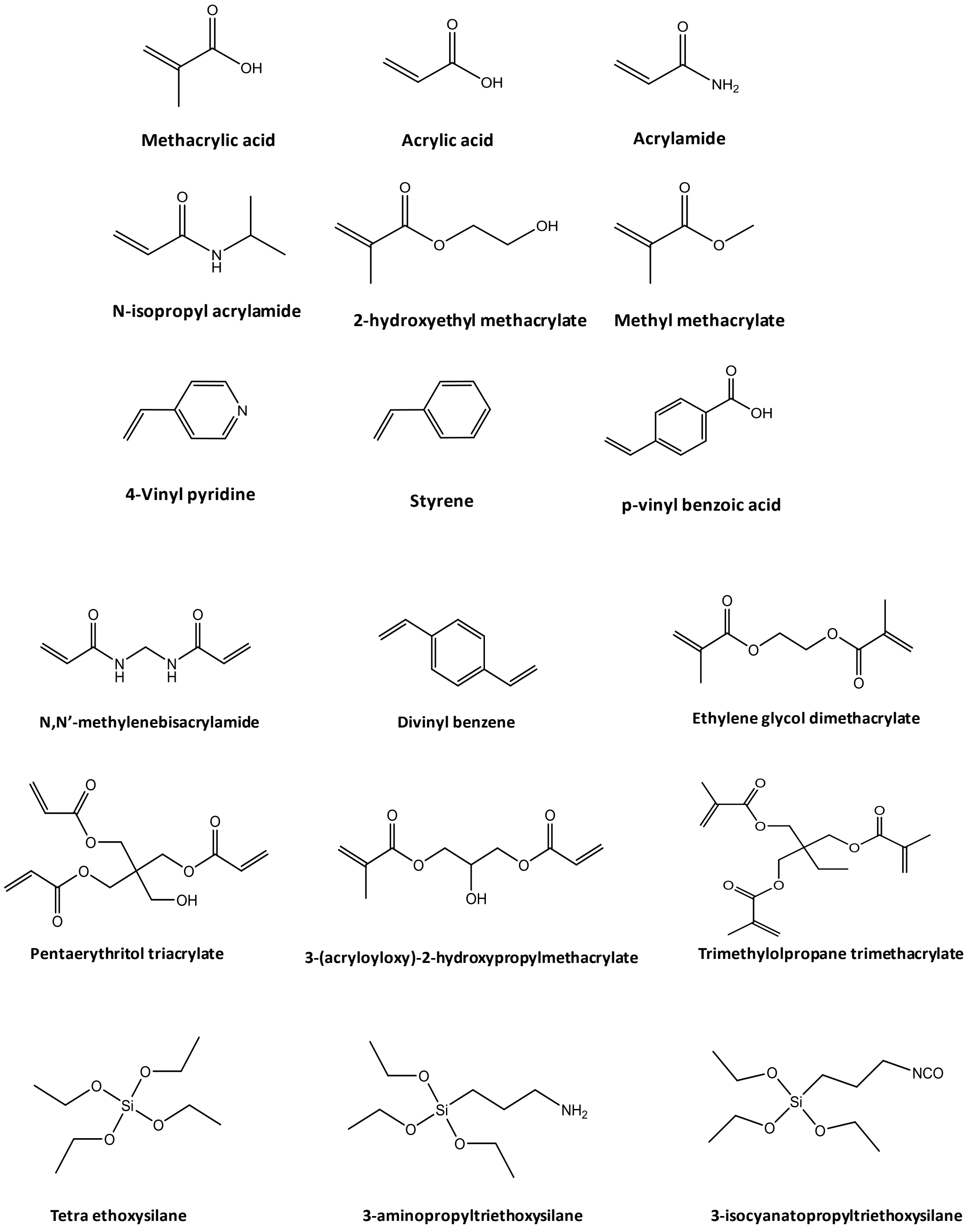
1.3.1 Ligand and functional monomer

In ion imprinted polymers, metal-ligand interaction plays a crucial role in maintaining the selectivity and specificity. Metal-ligand bonding involves donation of electrons from hetero atoms in the functional group of ligand to unfilled orbitals of metal ions. In the method of trapping, non-vinylated ligands are used. Some of them are 8-hydroxyquinoline and its di-halo derivatives [Gladis and Rao, 2003], formamidoxime [James *et al.*, 2009], dithizone [Saraji and Yousefi, 2009] and thiosemi- carbazide [Zambrzycka, *et al.*, 2011].

Functional monomers are mono vinylated and sometime serve the dual purpose of a ligand and a polymer. It coordinates to a metal ion as a ligand and gets itself fixed in position in the matrix through vinyl group as a polymer. Structures of some common monomers are given in Figure 1.13. Among these, 4-vinylpyridine (4-VP) is one of the frequently used functional monomer. To add better specificity in imprinted polymers towards metal ions, vinylated ligands are synthesized. Some examples are 5-vinyl-8-hydroxyquinoline [Otero-Romani *et al.*, 2009], 4-vinyl-phenylazo-2-naphthol [James *et al.*, 2008], 1-hydroxy-2-(prop-2'-enyl)-9,10-anthraquinone [Fasihi *et al.*, 2011] and benzo-15-crown-5-acrylamide [Wu *et al.*, 2011]. Usually a ligand and a functional monomer or more than one functional monomer is used for forming prepolymerisation mixture during imprinting.

1.3.2 Crosslinker

Crosslinkers contain more than one vinyl functionality which gets linked to the matrix at multiple points upon polymerisation. They are added to provide porosity and rigidity to the polymer. The rigidity of the polymer helps in keeping the binding sites intact. EGDMA and DVB are the most commonly used crosslinkers. Structures of some common crosslinkers are given in Figure 1.13. Various studies have been carried out to compare the efficiency of the systems by preparing polymers with different crosslinkers and also by varying the ratio of functional monomer and crosslinker. It has been observed that results vary according to the template-monomer systems used. In case of molecular imprinting, high selectivity was obtained with the presence of more than 50 % EGDMA [Wulff, 1995] and in case of metal ion imprinting, DVB gave better results in terms of preconcentration rates [Sadeghi and Mofrad, 2007] and selectivity [Kala *et al.*, 2005].



Methacrylic acid
Acrylic acid
Acrylamide
N-isopropyl acrylamide
2-hydroxyethyl methacrylate
Methyl methacrylate
4-Vinyl pyridine
Styrene
p-vinyl benzoic acid
N,N'-methylenebisacrylamide
Divinyl benzene
Ethylene glycol dimethacrylate
Pentaerythritol triacrylate
3-(acryloyloxy)-2-hydroxypropylmethacrylate
Trimethylolpropane trimethacrylate
Tetra ethoxysilane
3-aminopropyltriethoxysilane
3-isocyanatopropyltriethoxysilane

Figure 1.13: Structures of some common functional monomers and crosslinkers

1.3.3 Porogen

Solvents used during imprinting are called porogens due to its pore forming properties. Porosity is an important factor in making the binding sites accessible for the metal ion which in turn can affect the rebinding kinetics. The effect of various porogens 2-methoxyethanol, methanol, tetrahydrofuran (THF), acetic acid, dichloroethane, N,N-dimethylformamide (DMF) and toluene were studied and imprinted polymers with 2-methoxyethanol was found to give better retention capacity and selectivity [Gladis and Rao, 2004]. The solvents generally used can be classified as non polar, polar aprotic and polar protic. Toluene and chloroform are the non polar solvents. Acetonitrile and DMF and 2-methoxyethanol and methanol are frequently used polar aprotic and polar protic solvents respectively [Branger *et al.*, 2013]. Aqueous media are rarely used in metal ion imprinting.

1.3.4 Initiator

In the case of vinylated ligands, the double bonds are reactive towards free radicals resulting in polymerisation. Initiators are added to provide free radicals during imprinting. Free radical polymerisation is the popular strategy used in imprinting as they are less selective due to electrical neutrality allowing application in many systems and the polymerisation is not affected by the presence of acids, bases or polarity of solvents. Free radicals can be generated by using thermal decomposition, photolysis or ionizing radiation (γ radiation) [Sellergren, 2001]. Azo compounds like azobisisobutyronitrile (AIBN) are usually used as initiator. Other initiators are benzoyl peroxide [Walas *et al.*, 2008], H_2O_2/TEMED (N,N,N’,N’-tetramethylene-diamine) [Ozkara *et al.*, 2011], 2,2-dimethoxy-2-phenylaceto- phenone [Lopes Pinheiro *et al.*, 2012], and potassium persulphate [Demiralay *et al.*, 2010].

For imprinting in inorganic matrix like silica, condensation reactions are enough for polymerisation. Same is the case with imprinted polymers using chitosan where condensation reaction is used for crosslinking with epichlorohydrin or glutaraldehyde. Using these components imprinted polymers can be prepared in different matrices and their selection is extremely important in getting an imprinted polymer with optimum properties.

1.4 Polymer matrices in imprinting

In this section we try to classify the imprinted polymers according to the matrix used and provide a short description of the pioneering work done in each field. As already stated imprinting began with the work in silica matrix, which was followed by work in organic matrices. Matrices used for metal ion imprinting can be broadly classified as organic, inorganic, bio and hybrid systems. Metal ion imprinting began in organic polymers with the work of Nishide [1976], where the template is allowed to form a complex with functional monomer which is then polymerized with a crosslinker (to enhance the selectivity by stabilizing the active sites) and an initiator in presence of a porogen. In the field of organic molecularly imprinted materials, apart from the most commonly used vinyl polymerisation, other systems include polymerisation of aromatic monomers by both chemical and electrochemical methods. Majority of ion imprinted polymers falls under the category of organic matrices.

Polymerized aromatic monomers were used as the matrix for metal ion imprinting using the enzyme, horseradish peroxidase. Cu(II), Ni(II) and Fe(III) were imprinted with the method [Cui *et al.*, 2002]. Figure 1.14 shows the different aromatic monomers used for imprinting.

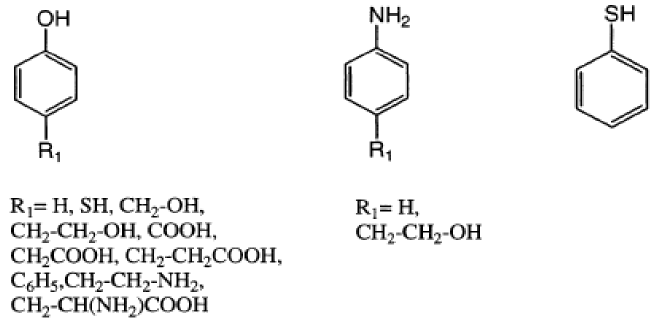


Figure 1.14: Structure of different aromatic monomers [Cui *et al.*, 2002]

Imprinting in bio matrices was done using metal complexed chitosan crosslinked with chloromethyl oxirane. Amino groups in chitosan is allowed to form complex with metal ions Cu(II), Cd(II), Zn(II), Ni(II) and Fe(III) before cross-linking [Ohga *et al.*, 1987].

Hybrid systems involve the use of two systems, inorganic-organic hybrid of silica matrix and organic matrix as demonstrated in the work where poly (4-vinylpyridine) was sorbed onto silica gel having high surface area with Cu(II) as template and crosslinked with 1,4-dibromobutane. Selectivity studies carried out in presence of nickel, cobalt, zinc and uranyl ion. The imprinted material was found to be selective towards copper in presence of nickel and also exhibited an order of magnitude increase in rate of sorption [Chanda and Rempel, 1992].

In another report, tris aminopropyl sites were introduced on silica gel which was functionalised with pyridyl and bipyridyl groups to complex Fe(II) and Cu(II) [Hwang *et al.*, 1995].

Cu(II) was imprinted in a histidine containing tripeptide matrix, Gly-Gly-His and His-Gly-Gly. The tripeptides were immobilized on aldehyde decorated silicon wafers in presence of copper ion as given in Figure 1.15. Metal ion was leached by washing with 1M HNO_3. It was found that imprinted Gly-Gly-His showed 62 % higher complexation of copper than the non-imprinted one [Bi *et al.*, 2007].

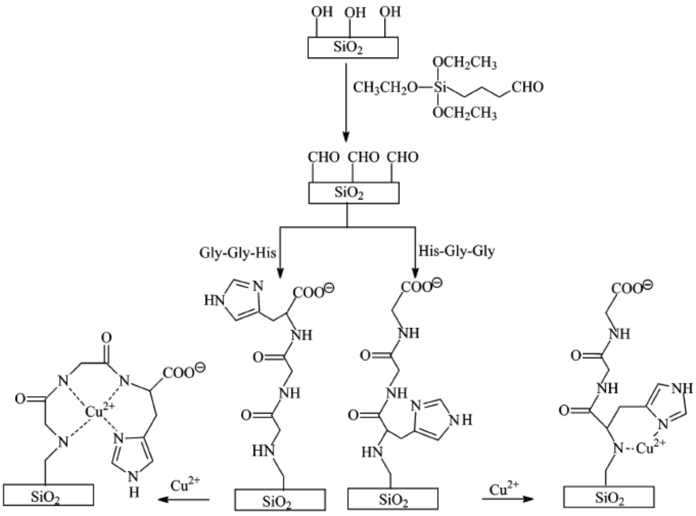


Figure 1.15: Scheme for copper imprinting in tripeptides [Bi *et al.*, 2007]

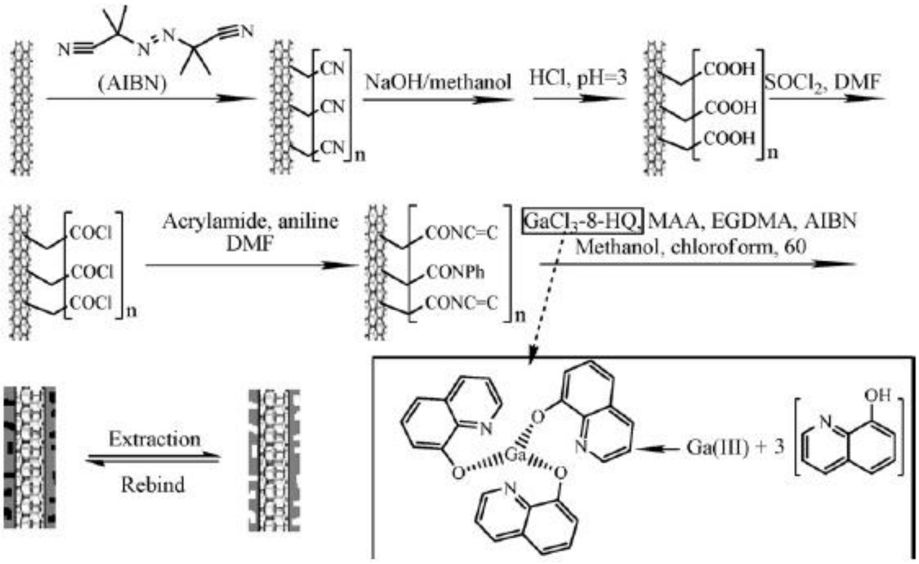


Figure 1.16: Scheme for imprinting in MWCNT-organic matrix [Zhang *et al.*, 2010]

A hybrid of MWCNT (multi-walled carbon nanotube)-organic system was used for impinting Ga(III) (Figure 1.16). Vinyl and phenyl functionalised MWCNT was synthesized and Ga(III)-8-hydroxyquinoline complex was trapped inside by thermal polymerisation with MAA (methacrylic acid), EGDMA and AIBN. The material was used for Ga(III) determination from fly ash samples [Zhang *et al.*, 2010].

A magnetic imprinted polymer for Au(III) extraction was synthesized using inorganic-organic system. Vinylated Fe_3O_4 was used as the support for imprinting Au(III)-vinylated bipyridylamine complex (Figure 1.17). The method was validated by preconcentration of Au from four certified reference materials [Ebrahimzadeh *et al.*, 2012].

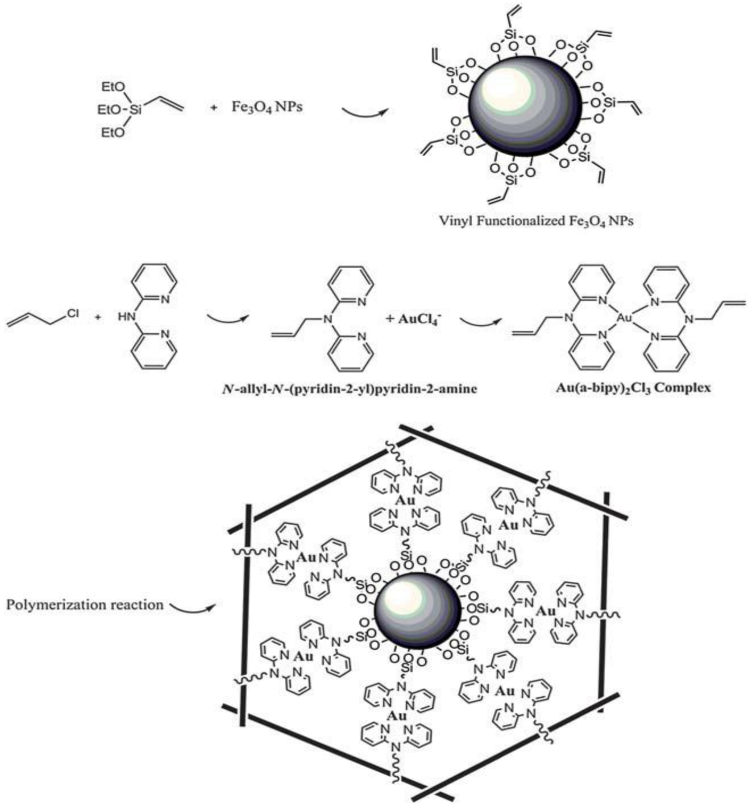


Figure 1.17: Scheme for synthesis of magnetic imprinted polymer for Au(III) extraction [Ebrahimzadeh *et al.*, 2012]

Imprinting in inorganic matrix includes formation of silica gel in presence of metal ions. First report was given for imprinting uranyl ions in sol gel glass [Dai *et al.*, 1997].

Zeolite was used as the matrix to prepare imprinted polymers (Figure 1.18). A complex of Cu(II) with the bifunctional ligand 3-(2-aminoethylamino) propyltrimethoxysilane was employed as the template. This method helps in functionalising inner surfaces of zeolites through ion imprinting [Zhang *et al.*, 2001]. Ion imprinted polymers thus synthesized can be used for different applications in various fields.

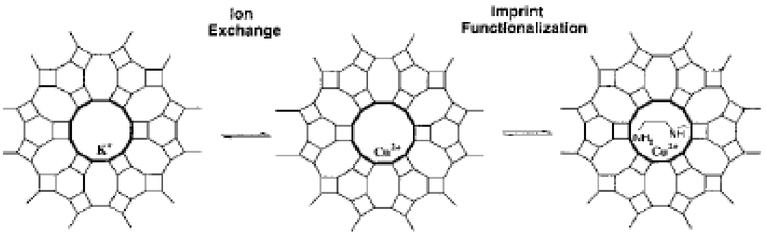


Figure 1.18: Schematic representation of imprinting in zeolite [Zhang *et al.*, 2001]

1.5 Applications

A glimpse into the recent literature shows that research in imprinting is an ever growing field as they find applications in many areas owing to their selectivity, stability and simple methods of synthesis. Some of the important applications are given in Figure 1.19. Among the various applications, ion imprinted polymers are widely used in membrane separations, as sensors and for solid phase extraction (SPE).

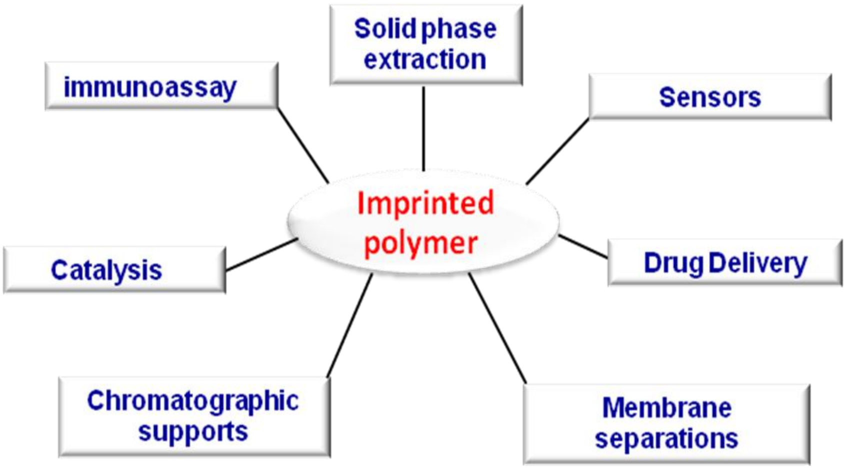


Figure 1.19: Applications of imprinted polymers

1.5.1 Membrane separations

Imprinted membranes for uranyl ion via bulk polymerisation of uranyl -vinyl benzoate and styrene/DVB was reported by Kimaro *et al.,* [2001]. Zn(II) ion-selective membrane was synthesized by surface molecular imprinting technique utilizing water-in-oil (w/o) emulsion polymerisation in combination with acetonitrile–butadiene rubber and hydrophilized poly(tetrafluoroethylene) membranes [Araki *et al.*, 2005]. A patent was filed describing an MIP (molecular imprinted polymer)-based membrane for the removal of phosphate, nitrate and ferric ions by copolymerizing a matrix monomer, cross-linking agent, ion-imprinting complex, permeability agent and polymerisation initiator [Murray, G. M., 2004].

Another report describes the use of imprinted polymer for removal of Fe(III) from human plasma. N-methacryloyl-(L)-glutamic acid (MAGA)-poly (2-hydroxyethyl methacrylate) (HEMA) – Fe(III) membranes were prepared by UV-initiated photo-polymerisation in the presence of benzoyl peroxide as initiator. The membranes were also found to be reusable [Yavuz *et al.*, 2006]. Silver ion imprinted membranes were prepared using a blend of chitosan-polyvinyl alcohol with glutaraldehyde as crosslinker. This was applied for removal of Ag (I) from aqueous solutions and can be reused for 5 cycles but with 15 % loss in removal capacity [Shawky, 2009]. Membrane adsorbents for Cr(III) removal from aqueous samples were synthesised using polyvinyl-sodium alginate blend with polyethylene glycol as porogen and glutaraldehyde as the cross linker [Chen *et al.*, 2010]. Ni(II) imprinted membrane was prepared by copolymerising with dithizone, MAA and EGDMA on a porous polyvinylidene porous support [Vatanpour *et al.*, 2011].

In a novel method, hydrolysed polyacrylonitrile (PAN) ultrafiltration membrane was utilised as a support for depositing polyethyleneimine (PEI) by applying a fixed flow rate of PEI. Imprinting was done in presence of Cu(II) and epichlorohydrin as crosslinker. This membrane was used for removal of copper from mixed ion solution [Deng *et al.*, 2012].

1.5.2 Sensors

Imprinted polymers were applied in the field of sensors for getting better selectivity and lower detection limit. This is due to the presence of template selective cavities and the possibility of templates getting preconcentrated on to the imprinted material respectively. Imprinted polymers acts as the recognition element and electrochemical or spectroscopic methods are used for signal transduction. First report was on fluorescence based sensing of Pb(II) using Pb(II)-methyl 3,5-divinylbenzoate as the complex for imprinting [Murray *et al.*, 1997]. A fluorescent sensor for Al(III) was designed using Al(III)-8-hydroxyquinoline sulphonic acid-HEMA-EGDMA imprinted polymer [Ng and Narayanswamy, 2006]. A fluorescent functional monomer 4-[(*E*)-2-(4′-methyl-2,2′-bipyridin-4-yl)vinyl]-phenyl methacrylate was used for imprinting and Cu(II) was determined by quenching of fluorescence [Lopes Pinheiro *et al.*, 2012]. An optode based on absorbance was reported for uranyl ion using imprinted polymer [James *et al.*, 2008].

Electrochemical sensing can be done either by incorporating imprinted polymers in PVC (polyvinyl chloride) membranes or carbon paste for use as ion selective electrodes or by electrochemical polymerisation for use in voltammetric sensing. Rosatzin *et al.*, [1991] developed the first ion selective electrode for potentiometric sensing of Ca(II) and Mg(II). Some recent reports on electrochemical sensors for toxic metal ions are carbon paste electrode for Pb(II) sensing prepared using nanosized lead imprinted polymer [Alizadeh and Amjadi, 2011]. Cd(II)-quinaldic acid-4-VP imprinted polymer incorporated CPE (carbon paste electrode) was used for voltammetric sensing of Cd(II) [Alizadeh *et al.,* 2011]. Same group reported CPE for Hg(II) sensing using imprinted polymer synthesized with 4-VP [Alizadeh *et al.,* 2011].

Another sensor for Hg(II) was reported with poly(2-mercapto-benzothiazole)- Au nanoparticle – single-wall carbon nanotube modified glassy carbon electrode [Fu *et* al., 2012]. Imprinted self assembled monolayer gold electrode was employed for Pb(II) sensing [Wang *et* al., 2012]. Ashkenani and Taher [2012] reported Cd(II) sensing with 1-(pyridylazo)-2-naphthol as the complexing agent. The same group reported a CPE for Cu(II) sensing [Ashkenani and Taher, 2012]. Differential pulse voltammetric detection of nanomolar levels of Hg(II) using glassy carbon electrode modified with imprinted polymer and MWCNT was reported.

IIP was prepared with a porphyrin derivative-MAA-EGDMA-AIBN system [Rajabi *et al.*, 2013]. Imprinted polymer (Eu(III)-VP-MAA-DVB) was incorporated in carbon paste electrode and used for indirect voltammetric detection of Eu(III) by monitoring decrease in copper signal [Alizadeh and Amjadi, 2013].

Another voltammetric sensor was reported for detection of sub-nanomolar levels of Pb(II) using imprinted polymer impregnated carbon paste electrode [Bahrami *et al.*, 2014]. A conductance based sensor for Cu(II) was reported using Cu(II)-N-vinyl pyrrolidone-EGDMA imprinted polymer with a detection limit of 0.02 mmolL^{-1} [Bajwa *et al.*, 2014]. A potentiometric sensor for As(III) by incorporating imprinted polymer (As(III)-MAA-EGDMA) in plasticized PVC matrix was reported. Nernstian slope of 20 mV for As(III) with a detection limit of 5x10^{-7} mol L^{-1} was obtained [Alizadeh and Rashedi, 2014].

1.5.3 Solid Phase Extraction (SPE)

SPE was introduced as a method for sample pretreatment in the field of analytical chemistry to separate and/or preconcentrate trace amounts of analyte from a complex sample matrix. 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 physical sorption, complex formation and other chemical reactions on or in the sorbents. This involves the partitioning between a liquid (sample matrix) and a solid phase sorbent [Liska, 1993, Rao *et al.*, 2004]. Though it is estimated that the method has been in use for over thousand years, its emergence into the field of analytical chemistry occurred after developments through different phases. The ability of granulated active carbon in concentrating organic compounds from water was checked in 1950's [Braus *et al.*, 1951] and they were able to identify some specific organic compounds. A major development was the introduction of polymer materials for extraction in 1960's. Amberlite XAD-1(crosslinked polystyrene resin) was used for separation of organic compounds from water [Riley and Taylor, 1969]. Another phase occurred with the use of bonded silica sorbents which was used for the first time to separate histamines from wine samples [Subden *et al.*, 1978]. In 1989, different formats like SPE disks and membranes were introduced which holds the sorbent between Teflon or fibre or glass fibres [Liska, 2000; Simpson, 2000]. Different types of sorbents for SPE are represented schematically in Figure 1.20.

SPE is widely used as a method for separation and enrichment owing to its flexibility, low cost and environment friendly nature. Imprinted polymers were coupled with SPE for the first time by Sellergren for the selective separation of pentaimidine in urine after preparing the material by dispersion polymerisation.

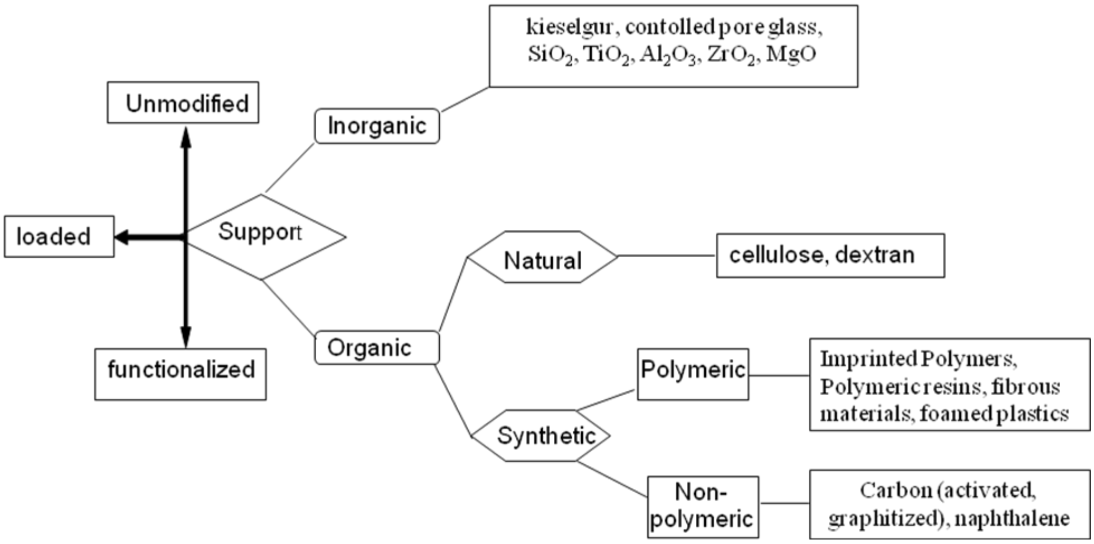


Figure 1.20: Different types of solid phase extraction sorbents

Pentaimidine was detected during desorption step, thus avoiding chromatographic separation [Sellergren, 1994]. The combination of imprinting with SPE gives additional advantage of selectivity. In this method, the polymer after leaching out the template is used as the solid phase for extraction from complex sample matrix. Different steps involved in SPE are 1) Retention, where the analyte gets distributed between the liquid phase and solid phase. This distribution can be quantified using K_d, the distribution coefficient which is the ratio of concentration of analyte in solid phase to that in liquid phase, 2) Elution in which the analyte is desorbed from the solid phase using a suitable solvent for determination by various methods, 3) Washing to remove impurities and 4) Conditioning, where the solid phase after removal of analyte is regenerated by appropriate methods making it available for reuse [Simpson, 2000]. The steps involved in IIP-SPE are shown in Figure 1.21.

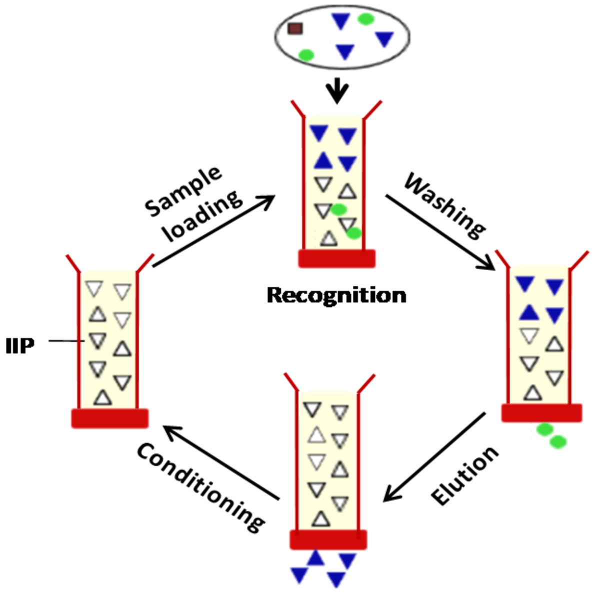


Figure 1.21: Steps involved in SPE

SPE is considered as a way to commercialise imprinted polymers as many sorbents based on imprinted polymers are available as products in the market [Whitcombe *et al*., 2014]. Ion imprinted polymers are used extensively for removal of toxic inorganic ions from environment and also for recovery of precious metals. It has been applied for removal or recovery of the following metal ions, Co(II) [Tarley et al., 2011], Rh(III) [Zheng *et al*., 2011], Pb(II) [Pan *et al*., 2006; Zhu *et al*., 2009; Jiang *et al*., 2010; Zhang *et al*., 2011], Ni(II) [Ersoz *et al*., 2004; Su *et al*., 2005; Jiang *et al*., 2006; Li *et al*., 2007; Rammika *et al*., 2011], Cd(II) [Asir *et al*., 2004; Fang *et al*., 2005; Zhai *et al*., 2007; Candan *et al*., 2009; Gawin *et al*., 2011], Cu(II) [Zhai *et al*., 2008; Ren *et al*., 2008; Hoai *et al*., 2010], Th(IV) [Lin *et al*., 2010], Hg(II) [Fan, 2006; Dakova *et al*., 2009], Ce(III) [Li *et al*., 2009], Sm(III) [Shirvani-Arani *et al*., 2008], Cr(III) [Birlik *et al*., 2007; Zhang *et al*., 2008], Dy(III) [Zhang *et al*., 2007], Pd(II) [Daniel *et al*., 2005] and Fe(III) [Owen *et al*., 2005]. We are concentrating on the removal of uranyl ion which is a recent addition to the list of toxins.

1.6 Uranium

Uranium remained an element of little curiosity for a century after its discovery in 1789 by Martin Klaproth. Early use of uranium was in giving green color to ceramics and glasses (Figure 1.22). As a metal it was also used in gas discharge tube electrodes.

Figure 1.22: Green coloration of glasses provided by uranium

Uranium came into limelight with the discovery of nuclear fission and its subsequent use in nuclear power industry and in nuclear weapons. Since then it is best known and feared for its involvement in nuclear energy. However, U^{238} is only weakly radioactive with a half-life of 4.468×10^9 years and only emits alpha particles having a low penetration depth which can be arrested by the skin [Monreal and Diaconescu, 2010]. Uranium is an electron donor, is easily oxidized and hence shows +3 to +6 oxidation states, among which +6 is the most prominent. Hence the linear dioxocation, UO_2^{2+} is the most stable form of uranium in contact with water and atmosphere [Burns *et al.*, 1997]. The reduced uranium from mineral deposits, mine tailings or nuclear wastes gets oxidized upon contact with oxygenated water. The chemical toxicity of U(VI) arises from its solubility and mobility [Fletcher *et al.*, 2010]. Uranium oxides are of physiological significance as it is soluble in bio fluids. It can react with biological molecules and exert adverse effects after entering the body [Craft *et al.*, 2004].

Uranium gets into the environment through natural and manmade activities. Natural deposits of minerals are one source of uranium in environment, the other being industrial activities like mining, nuclear wastes and the use of depleted uranium (byproduct of production of enriched uranium which contains < 0.3 % U^{235}) as counter weights in aircrafts, as radiation shields and as armor plating or armor piercing projectiles.

Exposure to uranium occurs mainly through intake by ingestion if the drinking water and food is contaminated, by inhalation which is mainly applicable to workers in uranium-mining industry or when uranium deposits in the environment gets suspended in the air due to natural disturbances or the possibility of coming to contact during aircraft crash or uranium containing munitions during war. Intake through skin contact is very low though it can happen through wounded skin.

The important target organs of uranium are kidneys and lungs. Long term exposure to uranium causes nephrotoxic effects and study on workers chronically exposed to uranium shows kidney impairment. Uranium dioxide and peroxides can cause pulmonary toxicity. Prolonged exposure to depleted uranium may cause lung cancer [Craft *et al.*, 2004].

Reproductive and developmental defects are observed in rats exposed to extremely high levels of soluble uranium [Domingo, 2001]. There are no reports suggesting uranium as the cause of skin cancer and also its effect on central nervous system. Though the presence of uranium was found in skeleton and liver of individuals exposed to uranium, adequate studies are not carried out to prove its adverse effects.

The boom in nuclear field, both energy and weapon led to increased exploitation of uranium resources causing widespread contamination. 11 % of world's total electricity is provided by nuclear power. In India it is the 4th largest source of electricity after thermal, hydroelectric and renewable sources. To avoid adverse effects inflicted by uranium contamination certain standards have been put forward. The tolerable daily intake of uranium established by WHO based on Gilman's studies is 0.6 μg/kg of body weight/day [Gillman *et al.*, 1998]. 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 [WHO, 2003] . Hence it is important to develop strategies for removal of trace amounts of uranium, which poses serious health hazards, for environmental cleanup. One way of approaching the problem is utilizing imprinted polymers in conjunction with solid phase extraction for selective removal of uranium.

1.7 Imprinted polymers for uranium

First attempt towards synthesis of uranyl ion imprinted polymer was reported in 1997 in sol gel glasses [Dai *et al.*, 1997]. The material was synthesised on the basis of interaction between hard acid and hard base. Uranyl ion which is a hard acid forms strong complex with hard base like oxygen and they have proposed a cation exchange mechanism for the adsorption by silica gel as given in equation1.

$$=\mathrm{SiOH} + \mathrm{UO_2}^{2+} \rightleftharpoons \underset{[\mathrm{UO_2}^{2+}]_s}{[=\mathrm{SiO(UO_2)}]^+ + \mathrm{H}^+} \qquad (1)$$

Comparison of uranyl uptake with non imprinted polymer and selectivity studies were carried in acetic acid sodium acetate buffer solution of pH=5.0, with an equilibration time of 24 h.

This was followed by a report of uranyl ion imprinting in organic matrix where polymerisable halogen substituted carboxylic acids like chloroacrylic acid was used as the functional monomer and EGDMA as the crosslinker. AIBN was used as the initiator. Experiments were carried out at pH 1.0 to 3.0 and the selectivity studies were carried out for both imprinted and non-imprinted polymer.

Imprinted polymers exhibited better selectivity and binding towards uranyl ion whereas non imprinted polymers showed less selectivity and binding capacity [John *et al.*, 1999, Saunders *et al.*, 2000]. The possible interaction of the ligand chloroacrylic acid with uranyl ion is as shown in Figure 1.23.

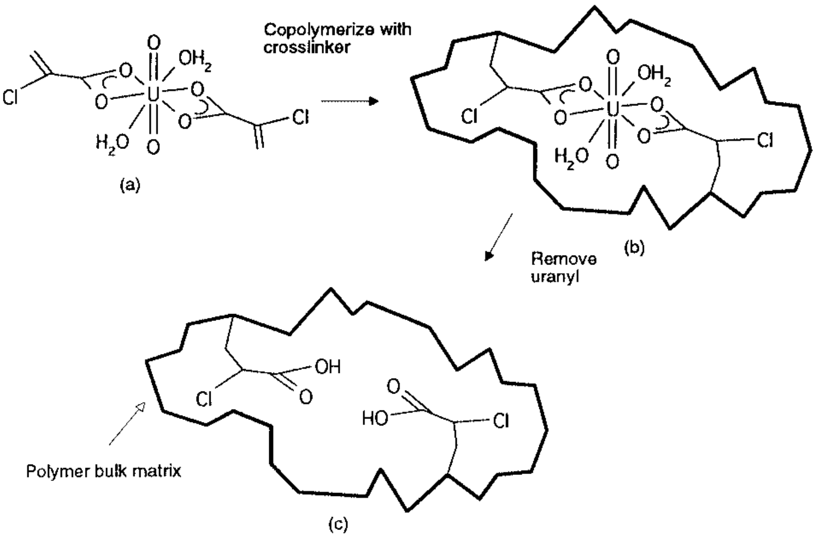


Figure 1.23: Possible interaction of uranyl ion with ligand inside the polymer matrix [Saunders *et al.*, 2000]

Imprinted polymer resins were synthesised and used for uranyl ion extraction from aqueous solutions and sea water. In this method, uranium-vinyl benzoate complex after separation was copolymerised in presence of styrene and divinyl benzene [Bae *et al.*, 1999]. Bifunctional ligands such as amines, sulphonic acids and phosphonic acids were employed for synthesising mesoporous sorbents of uranium [Dai *et al*,. 2001]. Bulk polymerisation of uranium-vinyl benzoate-styrene-divinyl benzene with addition of 2-nitrooctylphenylether and polyester was used for synthesis of uranyl ion permselective membrane. This membrane had better selectivity for uranyl ion over other competitive bivalent ions [Kimaro *et al.*, 2001]. In another report, methacryloyl amidoglutamic acid consisting of pendant carboxylic groups available for complexation with uranium was used and polymerised with ethylene glycol dimethacrylic acid for selective separation of uranyl ions from aqueous solutions [Say *et al.*, 2003].

Several imprinted polymers for uranium were reported employing the concept of trapping. The first report was from Gladis and Rao [2003]. A ternary mixed ligand complex UO_2^{2+}-(5, 7 dichloro 8-hydroxyquinoline)$_2$-(4-vinylpyridine)$_2$ was trapped inside a matrix of styrene (monomer) and divinyl benzene (DVB, cross-linker) and thermally polymerised in presence of AIBN as initiator. The leached imprinted polymers were used for determination of trace uranium from soils and sediments and its recovery from aqueous solutions and synthetic seawater. The same ternary complex was subjected to the study on effects of different porogens during polymerisation. 2-methoxyethanol was found to be best for the system in terms of better retention capacity and selectivity exhibited by the imprinted polymer for uranium over thorium [Gladis and Rao, 2004]. This was followed by a study on the enrichment of uranyl ion from dilute aqueous solutions using binary (UO_2^{2+}-DCQ or UO_2^{2+}-VP) and ternary (UO_2^{2+}-DCQ-VP) complexes [Metilda *et al.*, 2004]. The results show that only the ternary complex gave quantitative recovery with better retention capacity and selectivity. Imprinted polymer with salicylaldoxime (SALO) as the ligand was employed for removal of uranium from nuclear power reactor effluents. Here also a comparative study was carried out between binary (UO_2^{2+}-SALO or UO_2^{2+}-VP) and ternary (UO_2^{2+}-SALO-VP) complexes and the latter was found to give quantitative recovery of 5µg to 300mg of uranium form the effluents [Preetha *et al.*, 2006]. Imprinted polymers with various uranophiles like salicylaldoxime (SALO), catechol, succinicacid (SA), 5,7-dichloroquinoline-8-ol (DCQ) were synthesized with 4-vinylpyridine (VP), HEMA - (functional monomer), EGDMA -crosslinking monomer and AIBN - initiator. Ternary complex based imprinted resins UO_2^{2+}-SA-VP and UO_2^{2+} - DCQ-VP alone gave quantitative recovery of uranium from synthetic sea water solutions [Metilda *et al.*, 2007].

Shamsipur *et al.* [2007] have reported the preparation of surface imprinted polymer for uranium utilising grafting from approach on silica gel. An initiator ACPC – 4,4'-azobis (4-cyanopentanoic acid chloride) was functionalised on the surface of aminopropyl silica gel. Grafting step was carried out by polymerisation in presence of uranyl ion, MAA and EGDMA by irradiating with UV light as shown in Figure 1.24. The material was effective in absorbing 59 µmol/g of uranium at a pH of 3.0. The method was used for uranyl ion determination from tap water, Caspian sea water and ore leach liquor. The sorbent was also found to be stable as it could be repeatedly used and regenerated for 3 months.

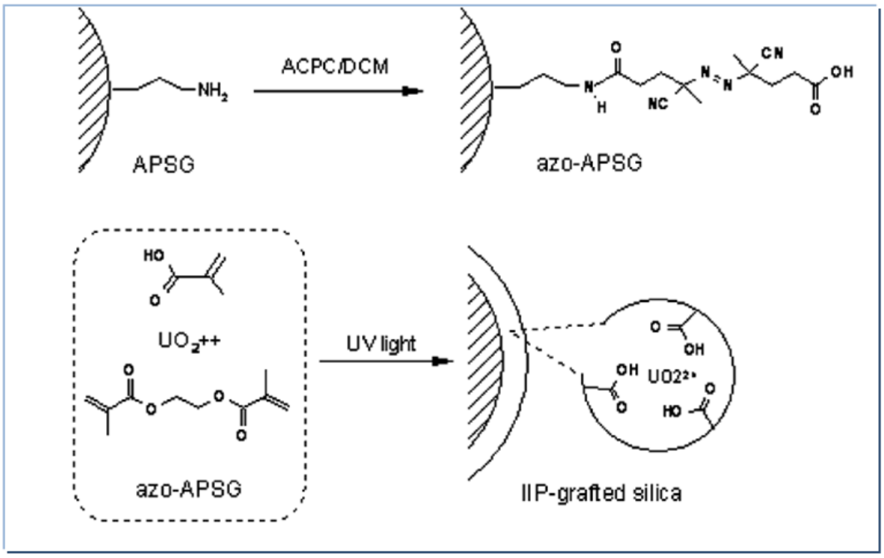


Figure 1.24: Synthesis of initiator functionalised silica and imprinted polymer by photograft polymerisation [Shamsipur *et al.,* 2007]

The concept of trapping was again used to imprint uranyl ion with piroxicam as the ligand (Figure 1.24) polymerized using the same 4-VP, styrene, DVB, EGDMA, AIBN system for preconcentration of uranium from ground and sea water [Sadeghi and Mofrad, 2007].

A new ligand 4-vinyl phenylazo-2-naphthol was synthesized and uranyl ion was imprinted by thermal copolymerisation with 4-VP, EGDMA and AIBN. The leached material was applied for both preconcentration and sensing. An optode was fabricated for sensing of uranium by spectrophotometry. The material was incorpoated in polymethyl methacrylate and was casted as thin film on a glass plate without plasticizer as shown in Figure 1.25 [James *et al.*, 2008]. The method was applied to detect uranium from real water samples in the vicinity of uranium deposits. Another polymer was reported with formamidoxime as the ligand and 4-VP-HEMA-EGDMA-AIBN as the polymerisation system [James *et al.*, 2009].

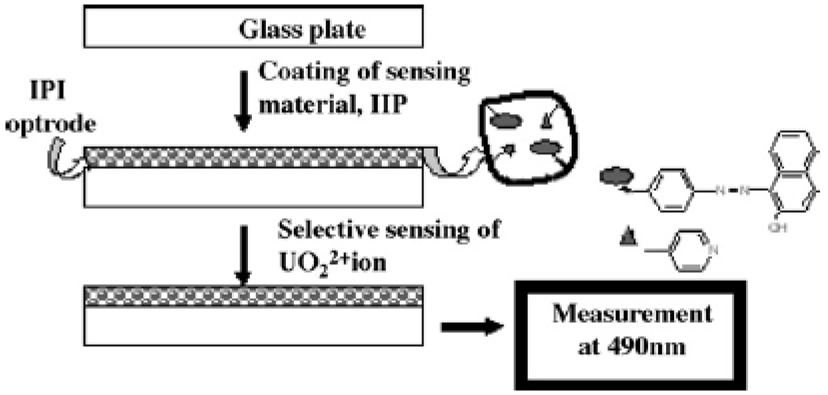


Figure 1.25: Fabrication of optode [James *et al.*, 2008]

Trapping method was utilized for the synthesis of imprinted polymer with the same system binary (UO_2^{2+}-SALO or UO_2^{2+}-VP) and ternary (UO_2^{2+}-SALO-VP) complexes using MAA-EGDMA-AIBN-polymerisation system. The material was applied to recover uranium from sea water, ground water and river water [Singh *et al.*, 2009]. The same concept was again used but with the ligand N,N-ethylenebis(pyridoxylideneiminato) and styrene-DVB-AIBN as the matrix

[Ahmadi *et al.*, 2010]. 8-hydroxyquinoline functionalised chitosan was synthesized and polymerized in presence of uranyl ion using epichlorohydrin. The method was validated with one standard reference material and used for uranium determination from contaminated soil and sediments [Liu *et al.*, 2010].

In another method, ion imprinted hydrogel was prepared. Uranyl ion was complexed on blended chitosan polyvinyl alcohol and polymerised with ethylene glycol diglycidyl ether as the crosslinker [Liu *et al.*, 2010]. The synthesized interpenetration network - ion-imprinting hydrogel exhibited significant selectivity and retention capacity and was used for uranium removal from aqueous solutions.

An imprinted polymer for separation and sensing of uranium using salophen and oligonucleotide as double receptors were reported. Salophen acts as the solid phase receptor and fluorescent labeled oligonucleotide as the sensor [Wu *et al.*, 2012]. 1-(prop-2-en-1-yl)-4-(pyridin-2-ylmethyl)piperazine-MAA-EGDMA system was used for preparing imprinted polymer for uranium removal from pit water and stream water [Pakade *et al.*, 2012]. Ion imprinted magnetic chitosan resins were utilized for uranium removal [Zhou *et al.,* 2012]. Removal of uranium from ground water and mineral water samples were effected with imprinted amino-functionalised silica coated Fe_3O_4 nanoparticles [Sadeghi and Aboobakri, 2012].

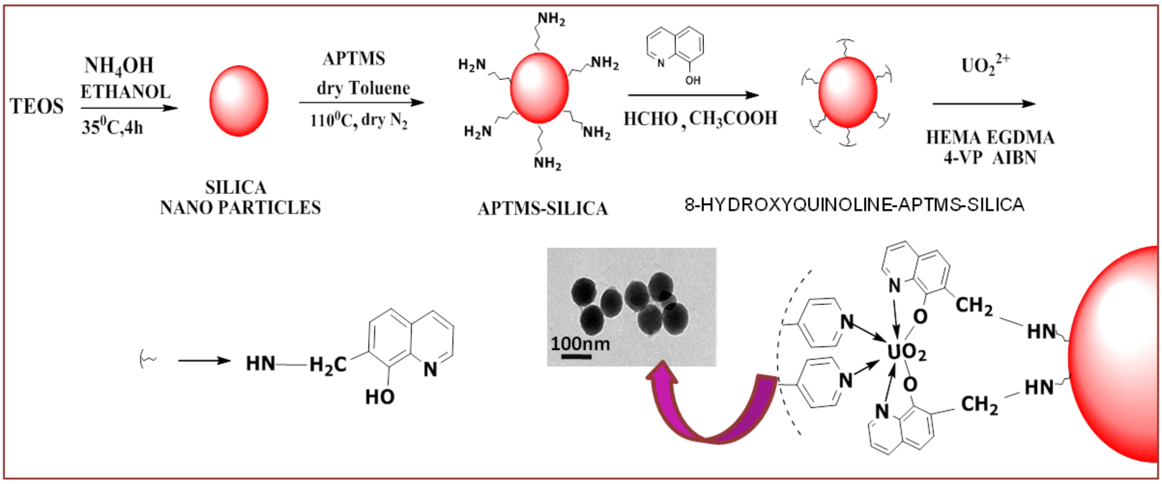
In a novel approach uranyl ion complexed cucurbit[5]uril oligomer was grafted onto palm shell powder. The two portals of cucurbit[5]uril helps in selective binding of uranium [Kushwaha and Sudhakar, 2012]. 2,4-dioxopentan-3-yl-methacrylate-EGDMA-AIBN system based imprinted polymer was synthesized to extract uranium from sea water [Zhang *et al.*, 2013].

1.8 Scope of the present work

In the wake of recent events regarding the contamination by nuclear hazards, it is worthwhile to explore new materials which can remove the hazardous wastes selectively and efficiently from environment. At the same time it is equally important to have sources for sustainable energy. This makes uranyl ion an ideal template as it is considered as an emerging pollutant and also a source for nuclear energy. Removal or recovery of uranyl ion requires materials with high selectivity, retention capacity and stability. Imprinted polymers are known to have all these virtues and hence the focus of this study is to synthesise uranyl ion templated imprinted polymers for its removal or recovery from aqueous solutions. Thus the synthesis of imprinted polymers, their characterisation, optimisation studies to get maximum removal and selectivity studies for application in detoxification of real environmental samples have been carried out. These studies and the results obtained are described in this thesis.

Chapter 2

Surface imprinted polymer nanospheres for selective removal of uranium



2.1 Abstract

Bulk polymerisation is the most commonly used imprinting technique which produces highly irregular particles with 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. Here we describe the synthesis of surface imprinted nanospheres for selective removal of uranium from simulants of Sambhar salt lake and ground waters. Uranyl ion was complexed on to 8-hydroxyquinoline functionalised 3-aminopropyltrimethoxysilane modified silica nanoparticle. Surface imprinting was done with 4-VP (4-vinyl pyridine), HEMA (2-hydroxyethyl methacrylate) and EGDMA (ethylene glycol dimethacrylate) as the functional monomers and cross linking agent respectively. AIBN (2, 2'-azo-bis-isobutyronitrile) was used as initiator and 2-methoxyethanol as the porogen. Non imprinted polymer was also prepared under similar conditions without uranyl ion. The material offers high retention capacity of 97.1 μmol g^{-1} *for 10 mg* L^{-1} *of uranium, do not require tedious grinding and sieving steps, is water compatible and works in the pH range of 5.0 to 7.0, making it ideal for possible use in decontamination of polluted natural water samples or front end effluents of nuclear power reactors.*

2.2 Introduction

Imprinting is the molding of complimentary binding sites for target molecules into synthetic polymers, which relies on the formation of a cross linked polymer in the presence of template. They are remarkably stable against mechanical stresses, high temperatures and pressures, intense radiation and a range of organic solvents and also resistant against treatment with acid or base [Greibrokk and Sellergren, 2008; Sellergren, 2010]. Bulk polymerisation is the most commonly used imprinting technique, but is not amenable to scale up and it has to be ground and sieved to generate particles of approximately 10-20 µm size. 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 or in the proximity of materials surface, providing the complete removal of templates, good accessibility to the target species, and low mass-transfer resistance [Perez-moral and Mayes, 2006; Gao *et al*., 2007; Tan *et al*., 2007]. 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.

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 [Ober *et al.*, 2009]. Removal of trace amounts of toxic uranium is essential for environmental cleanup. During removal, uranium gets preconcentrated in the polymer matrix, which can be utilized in the field of nuclear energy.

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 physical sorption, complex formation and other chemical reactions on or in the sorbents. A detailed report on the topic is given in a review by Rao *et al.*, [2004, 2006]. Preetha *et al.*, [2006] has reported uranium removal from nuclear power reactor effluent, but the material works only in weakly acidic pH.

Silica gel has been widely used in surface imprinting. High surface area, porosity, stability in acidic conditions and presence of easily functionalisable silanol groups on the surface makes silica an ideal inorganic support [Buhani *et al.*, 2010]. Surface imprinted polymer for Cd(II) was reported. After complexing Cd(II) on to chitosan, imprinting was done by condensation reactions in presence of γ-glycidoxypropyl trimethoxysiloxane and silica gel [Li *et al.*, 2007]. Aminopropyl functionalised silica gel was used for Cr(III) adsorption and determination. The method was validated by analyzing certified reference materials and by speciation of chromium in natural waters with satisfactory results [He *et al.*, 2008]. Similar methods were utilized to imprint Pd(II) [Zheng *et al.*, 2007], Fe(III) [Chang *et al.*, 2007] and Zr(IV) [Chang *et al.*, 2008]. Shamsipur have reported the preparation of surface imprinted polymer for uranium using “grafting from” method on silica [Shamsipur *et al.*, 2007]. A surface imprinted biosorbent was prepared for treatment of waste water contaminated with Ag(I) ions. *Mycelium* from waste biomass of *Penicillium chysogenum* in presence of chitosan cross-linked with ECH (epichlorohydrin) was used as the sorbent [Huo *et al.*, 2009]. In another report a functional macromolecule polyethyleneimine (PEI) was grafted onto silica gel surface by coupling grafting method. Imprinting was done in the presence of Cu(II) or Cd(II) with ECH as the cross-linker as given in Figure 2.1, [Gao *et al.*, 2007].

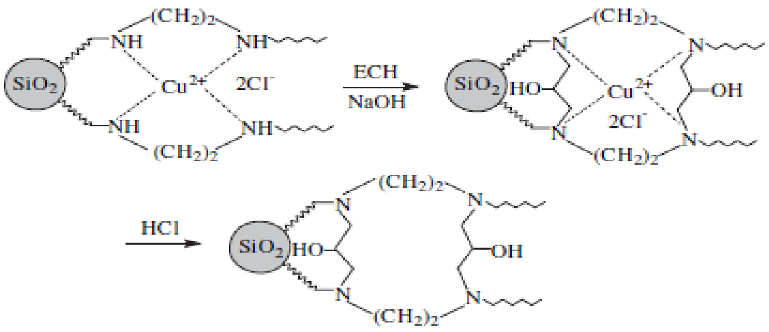


Figure 2.1: Synthesis of surface imprinted polymer in PEI/ECH [Gao *et al.*, 2007]

A core-shell surface imprinted polymer was synthesized for Cu(II) adsorption. Surface imprinting was done on an organic shell layer composed of copper methacrylate and EGDMA with polystyrene as the core. Obtained core shell microspheres had diameter in the range 2.5 to 3.2 μm [Dam and Kim, 2009].

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. Surface imprinting was done after functionalizing aminopropyl silica nanospheres with 8-hydroxyquinoline as the complexing agent for uranium. After optimizing several SPE parameters, the material was utilized for decontamination of ground and Sambhar salt lake water simulants.

2.3 Synthesis procedure

2.3.1 Synthesis and chemical modification of silica nanoparticles

Uniform silica nanoparticles were prepared by the Stober method [Stober *et al.*, 1968; Qiu *et al.*, 2007], which involves the hydrolysis of TEOS (tetraethoxysilane) with aqueous ammonia in presence of ethanol. 6.3 mL of TEOS was added to 7.5 mL of NH_4OH in 105 mL ethanol. The solution was sonicated at a temperature of 35 ^{0}C for 4 h. The resulting residue was centrifuged, washed with water and ethanol respectively and dried in an oven at 50 ^{0}C. Aminopropyl modification was done by the reported method [Philipse and Vrij, 1989; Gao *et al.*, 2007]. Appropriate amount of silica was added to 4 % v/v of 3-aminopropyl-trimethoxysilane (APTMS) 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 ^{0}C. 8-hydroxyquinoline was grafted on to the amino end group by Mannich reaction. Definite amount of APTMS-SI was added to 50 mL dry ethanol containing 0.1 mol L^{-1} 8-hydroxyquinoline, 0.1 mol L^{-1} formaldehyde and 0.2 mL glacial acetic acid. The mixture was refluxed for 4 h [Bernal *et al.*, 2000]. The resulting solid (HQ-APTMS-SI) was centrifuged, washed with ethanol, 1 mol L^{-1} HCl and distilled water respectively and dried at 50 ^{0}C.

2.3.2 Synthesis of imprinted polymer by modified precipitation method

Imprinted polymers were synthesized by different methods to get nanospheres. Both micrometer sized particles and nanosphere was obtained. The details of synthesis and the size of particles obtained are given in Table 2.1.

Imprinting of uranyl ion was done by thermal polymerisation. 4-VP, HEMA and EGDMA were used as the functional monomers and cross linking agent respectively in the ratio given in Table 2.1. AIBN was used as initiator and 2-methoxyethanol as the porogen. 0.1 mmol uranium and appropriate amount of HQ-APTMS-SI were added to required amount of porogen and sonicated for 10 min. Then the pre-polymerisation mixtures (functional monomer, cross linker and initiator) were added and soniated for 10 min, cooled to 0 ^{0}C (by keeping in a trough containing ice), purged with N_2, sealed, and thermally polymerized in an oil bath at 60 ^{0}C with stirring for 1 h. The resulting IIP material was washed with methanol and distilled water respectively and then dried. Non-imprinted polymer (NIP) was similarly prepared without the uranyl ion. Scheme for the synthesis is shown in Figure 2.2.

Table 2.1: Synthesis of uranyl ion imprinted polymers*

Precipitation polymerisation UO_2^{2+} : HEMA: EGDMA	Porogen volume (mL)	Temperature (^{0}C)	Morphology
PP1) 1 : 8 : 32	20	80	Micrometer particles (>10 µm)
PP2) 1 : 8 : 32	40	80	”
PP3) 1 : 8 : 32	40	60	”
PP4) 1 : 8 : 32	60	60	”
PP5) 1 : 4 : 20	4.5	60	nanospheres (50-80 nm)

* All polymerisations were done with AIBN as initiator and 2-methoxy ethanol as porogen.

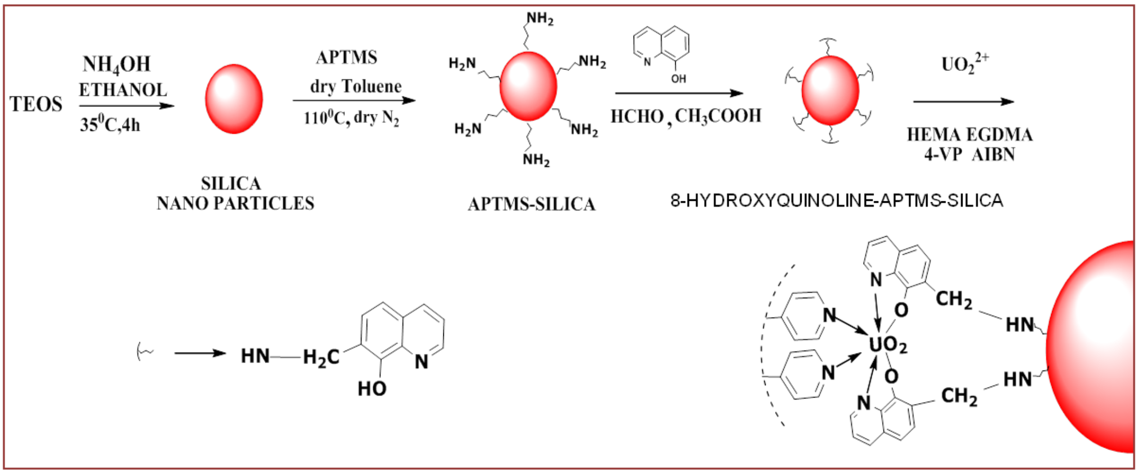


Figure 2.2: Schematic representation of uranyl ion nano surface imprinting

Precipitation polymerisation is the most popular strategy used for synthesis of nanoparticles. We have used a modified precipitation polymerisation method for the synthesis of imprinted nanospheres. From the methods for synthesis given in Table 2.1, 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-polymerisation 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 functionalised silica as the size remains in 50-80 nm range like that of 8-hydroxyquinoline functionalised 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.

2.4 Characterisation

The functionalisation of prepared materials was confirmed using FTIR and elemental analysis. Morphology studies were done using HRTEM and SEM and also surface area and pore size analysis was done.

2.4.1 FTIR

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 [Li *et al.*, 2003]. IR of 8-hydroxyquinoline modified silica was taken by making a pellet without the binder KBr [Lan and Yang, 1994].

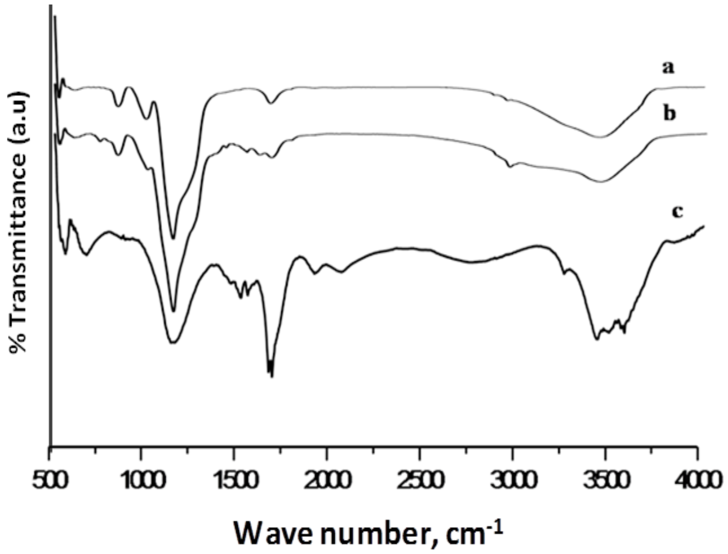


Figure 2.3: FTIR spectra of a) Silica b) APTMS-SI and c) HQ-APTMS-SI

In the spectra, bands for C = C and C = N stretching can be observed in the frequency 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 [Bernal *et al.*, 2000]. Hence the functionalisation of 8-hydroxyquinoline on aminopropyl silica can be confirmed. Figure 2.3 shows the IR spectra of bare silica (a), APTMS-SI (b) and HQ-APTMS-SI (c) respectively.

2.4.2 Elemental analysis

The elemental (CHN) analysis data for APTMS-SI and HQ-APTMS-SI are given in Table 2.2. From the data it is clear that functionalisation with 8-hydroxyquinoline increases the percentage of carbon, nitrogen and hydrogen.

Table 2.2: CHN analysis

Sample	N %	C %	H %
APTMS-Si	0.96	3.56	2.00
HQ-APTMS-Si	1.25	5.46	2.15

2.4.3 Morphology (TEM and SEM)

TEM images show the particle size of 8-hydroxyquinoline functionalised silica and the IIP (PP5) to be in the range 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.

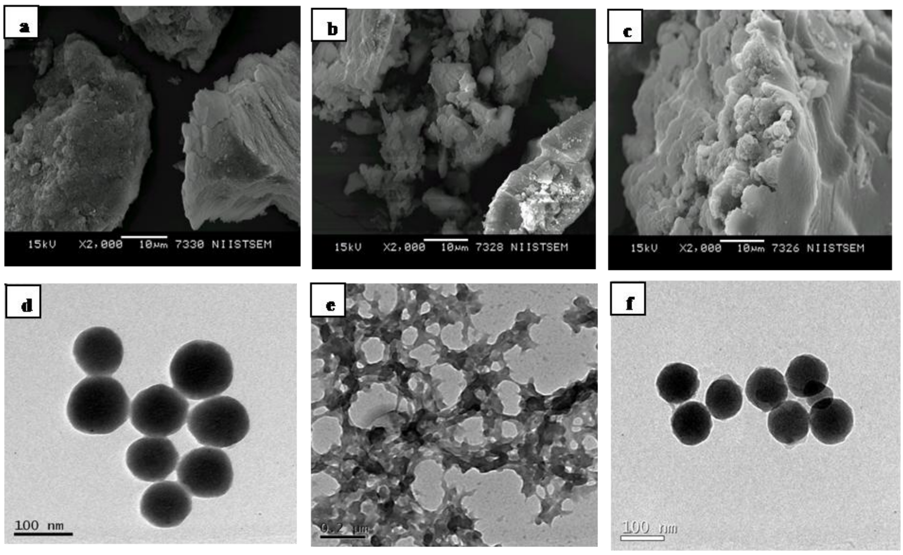


Figure 2.4: SEM of IIP a) PP2 b) PP3 c) PP4 and TEM of d) HQ-APTMS-SI e) PP2 in acetone and f) PP5 in ethanol.

Agglomeration was observed when dispersed in acetone for 8-hydroxyquinoline and a network like structure for IIP (PP2). Figure 2.4 shows the TEM and SEM images of modified silica and polymers prepared by different methods.

2.4.4 Surface area and pore size analysis

BET Surface area and BJH adsorption average pore diameter of IIP and NIP is given in Table 2.3. 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 surface area [Boonpangrak, 2006; Yan and Row, 2008; Yan and Kyung, 2006].

Table 2.3: Surface area and pore size analysis

Sample	BET surface area (m^2/g)	Average pore diameter (Å)
IIP	134.69	47.39
NIP	188.87	51.89

2.5 SPE studies

SPE studies were carried out to check the efficiency of imprinted polymers in removal of uranium. Studies were conducted with both micrometer sized particles and nanospheres.

Table 2.4: Comparison of removal efficiency of imprinted polymers

Material	Weight (mg)	Removal (%)	
		NIP	IIP
Micrometer particles			
APTMS-SI	20	54.4	74.0
HQ-APTMS-SI	20	68.6	91.0
Nanospheres			
HQ-APTMS-SI	20	84.0	95.4
HQ-APTMS-SI-VP	20	87.0	>99

From the data given in Table 2.4, it can be seen that imprinted polymers with APTMS-SI gives removal of 74.0 % only. Functionalisation with 8-hydroxyquinoline increases the removal to 91.0 % and imprinted nanospheres of 8-HQ-APTMS-SI further improves removal to 95.0 %. In order to get complete removal, 4-VP was added to the recipe of PP5 (HQ-APTMS-SI-VP). The ratio of UO_2^{2+}: 4-VP was taken as 1:2. Removal efficiency of nanospheres increased from 95.0 % to 99.0 % on addition of 4-VP as it helps in making rigid configuration inside the polymer matrix. Hence further studies were carried out with this material to obtain optimum results. Morphology remained same even after addition of 4-VP.

2.6 Optimisation of parameters

The effect of pH (4.5-7.5), weight of polymer particles (10, 15, 20 and 25 mg), time of stirring (20 and 30 min) during the preconcentration and elution of uranium, nature of eluent (1M HCl/1M HNO_3/1M Na_2CO_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.

Quantitative removal of uranium was obtained in the pH range of 5.0-7.0 as shown in Figure 2.5.]. Uranyl chemistry is complicated by a 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 equations (1)-(3). Monovalent uranyl species dominates at higher pH (4.0-6.0) and UO_2^{2+} at low pH (2.0) [Ishikawa *et al.*, 1999; Nancharaiah *et al.*, 2006]. As UO_2^{2+} gets complexed with 8-hydroxyquinoline, the equilibrium gets shifted to left.

$$UO_2^{2+} + 2H_2O \rightleftharpoons UO_2(OH)^+ + H_3O^+ \qquad (1)$$

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

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

For the functional group 8-hydroxyquinoline, the optimum pH range for extraction of UO_2^{2+} is 4.7-8.0 [Silverman *et al.*, 1953]. Hence removal efficiency increases from 4.5 to 5.0. Removal decreases from pH 7.0 to 8.0 due to hydrolysis of uranyl ions to form non-complexable species like $UO_2(OH)_2$ and $UO_2(OH)_3^-$.

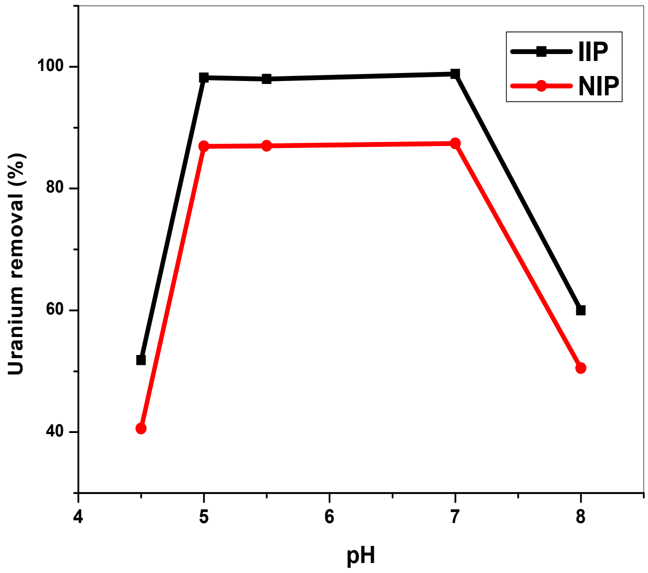


Figure 2.5: Effect of pH on removal of uranium

Further studies were conducted at pH 6.0. Ammonium acetate buffer (10^{-3} M) was used to adjust the pH. Weight variation studies shows that uranium removal increases upto 20 mg of the material and remains constant thereafter as given in Figure 2.6. Hence the optimal amount of material required was fixed to be 20 mg.

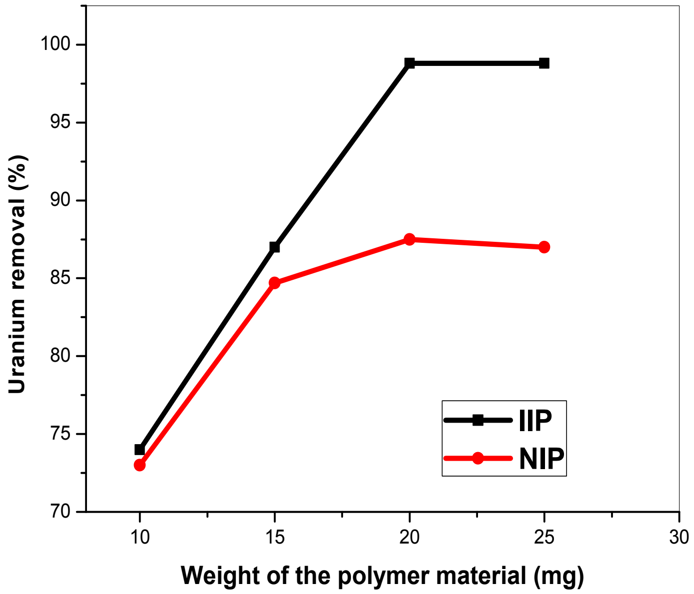


Figure 2.6: Influence of weight on removal of uranium

The time for preconcentration and elution was fixed as 30 and 20 minutes respectively. 100 mL of aqueous phase volume was used for removal studies. Among the various eluents, concentration and volume used, 10 mL of 1M HCl was effective in complete stripping of uranium. Results for optimisations are given in Table 2.5. Under above optimal conditions, the quantitative removal of 50 to 1000 ppb of uranium from aqueous solutions is demonstrated and the data is given in Table 2.6. In all the above experiments comparison of imprinted with non- imprinted polymers shows significant imprinting effect.

Table 2.5: Optimisation of solid phase extraction parameters

Parameters	Uranium removal (%)*	
	NIP	IIP
Preconcentration Time		
20	82.3	87.0
30	87.5	> 99
Elution Time		
10	83.0	93.2
20	87.0	> 99
30	87.0	> 99
Nature of Eluent		
1M HNO_3	66.0	76.3
1M HCl	87.0	> 99
1M Na_2CO_3	60.1	63.4
Eluent Concentration		
0.1M	67.4	78.2
0.5M	73.1	85.0
1.0M	87.0	> 99
Eluent Volume		
5	82.4	96.4
10	87.0	> 99
15	87.0	> 99

* Average of duplicate measurements

Table 2.6: Removal of uranium from aqueous solutions

Concentration (ppb)	Removal (%)
50	>99
100	>99
200	>99
500	>99
1000	>99
2000	55.5

2.7 Retention capacity studies

The maximum amount of preconcentrated uranyl ion/g of the imprinted material (retention/binding capacity of IIP) was calculated by saturating 20 mg 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. We have given the retention capacity at 10 mg L^{-1} because there is always a chance for precipitation of uranyl ion at higher concentrations at a pH of 6.0. From the Table 2.7, it can be observed that the material gives a retention capacity of 23.1 mg g^{-1} (97.1 μmol g^{-1}) at 10 mg L^{-1} whereas others are at a concentration of 100 mg L^{-1}. Non-imprinted polymer gave retention of 14.8 mg g^{-1} (62.5 μmol g^{-1}) only. This shows that the material has high retention capacity which can be utilised for removal/ harnessing of uranium.

Table 2.7: Comparison of retention capacity with reported literature

Chelating ligand(s)	pH range	Retention capacity* (μmol/g)	Reference
DCQ	4.5-7.5	55.6	Metilda *et al.*, 2004
VP	4.5-7.5	86.5	Metilda *et al.*, 2004
DCQ-VP	4.5-7.5	136.9	Metilda *et al.*, 2004
Catechol-VP	3.5-6.0	81.9	Metilda *et al.*, 2007
SALO-VP	3.0-4.0	79.4	Metilda *et al.*, 2007
SALO- VP	3.5-5.0	105	Preetha *et al.*, 2006
MAA	3.0	52	Shamsipur *et al.*, 2007
Amidoxime-VP	8.0-9.0	80	James *et al.*, 2009
SALO-VP	3.5-6.5	80	Singh *et al.*, 2009
N,N'Ethylenebis (pyridoxylideneiminato)-VP	7.0	-	Ahmadi *et al.*, 2010
HQ-APTMS-SI-VP	5.0-7.0	97.1	Present Work

2.8 Selectivity studies

To evaluate the selectivity of uranyl IIP and NIP particles for uranium over other inorganic ions, 20 mg of the material was stirred with 100 μg of each individual inorganic ion present in 100 mL of deionized water under identical conditions. The selectivity coefficient is defined as,

$$S_{UO_2 2+/M^{n+}} = \frac{D_{UO_2 2+}}{D_{M^{n+}}} \quad (4)$$

where $D_{UO_2^{2+}}$ 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

$$D = A_2/A_1 \quad (5)$$

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} (6)

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

$$\% E = A_2/A_T \times 100 \quad (7)$$

where A_T is the total amount of uranyl ion or other metal ions utilized in extraction [Biju *et al.*, 2003].

After elution with 10 mL of 1.0 M HCl the concentrations of these elements in solutions were determined by spectrophotometry, flame atomic absorption spectrometry and flame photometry. The distribution ratio and selectivity coefficients of uranyl ion with respect to other inorganics using NIP and IIP particles are shown in Table 2.8.

Table 2.8: Selectivity data of non imprinted and imprinted materials

Metal ions	Analysis Procedure	Distribution Ratio (D)		Selectivity Coefficient (S)		Imprinting coefficient (K’)
		NIP	IIP	NIP	IIP	
UO_2^{2+}	Spectrophotometry	6.7	99	-	-	-
Na^+	Flame photometry	0.08	0.07	83.7	$1.4x10^3$	17
K^+	Flame photometry	0.08	0.07	83.7	$1.4x10^3$	17
Ca^{2+}	FAAS	0.75	0.7	8.9	$1.4x10^2$	15.7
Mg^{2+}	FAAS	0.05	0.04	$1.3x10^2$	$2.5x10^3$	19.2
Cu^{2+}	FAAS	99	5.5	0.06	$1.8\ x10^1$	300
Zn^{2+}	FAAS	0.72	0.59	9.2	$1.7x10^2$	18.4
Fe^{3+}	FAAS	0.12	0.10	55.8	$9.5x10^2$	17.2
Co^{2+}	FAAS	1.24	0.98	5.4	$1.0x10^2$	18.5
Ni^{2+}	FAAS	1.17	0.88	5.7	$1.1x10^2$	19.3

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 2.8, it is clear that uranyl ion can be removed selectively from several inorganic species present in dilute aqueous solutions.

Table 2.9: Comparison of removal efficiency and imprinting coefficient

Polymer matrix	Weight of IIP (g)	% Recovery NIP	% Recovery IIP	Imprinting co-efficient (K’)	Reference
VBA-Styrene-DVB	-	-	> 99	-	Bae *et al.*, 1999
MAGA- EGDMA	0.02	-	96.0	-	Say *et al.*, 2003
Silica matrix	-	75.0	85.0	1.13	Dai *et al.*, 2001
VP- Styrene-DVB	0.02	41.7	78.8	1.9	Metilda *et al.*, 2004
DCQ- Styrene-DVB	0.02	30.6	40.0	1.31	Metilda *et al.*, 2004
Catechol–VP-HEMA-EGDMA	0.02	30.1	62.9	2.1	Metilda *et al.*, 2007
SALO–VP HEMA-EGDMA	0.02	19.7	67.9	3.4	Metilda *et al.*, 2007
DCQ-VP –Styrene-DVB	0.02	71.0	> 99	1.4	Metilda *et al.*, 2004
Amidoxime -VP-HEMA-EGDMA	0.075	81.0	>99	1.2	James *et al.*, 2009
HQ-APTMS-SI-VP	0.02	87.0	> 99	1.14	Present work

Comparison of imprinting coefficients of nanospheres with other IIPs is given in Table 2.9. 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.

2.9 Application to real samples

Application of the material was demonstrated by conducting uranium decontamination studies from stimulants of ground and Sambhar salt lake water (Thar Desert, Rajasthan).

Table 2.10: Application to real samples

Sample description	Uranium removal (%)
Sambhar salt lake water simulant (Jhapok) [SL # 79 (May 93)] U(VI) : 1.4 mg L^{-1} Na : 146×10^{3} mg L^{-1} K : 0.9×10^{2} mg L^{-1} Ca : 2.4 mg L^{-1} Mg : 10 mg L^{-1}	70.0 ±3
Ground water stimulant (Sambhar township) [SL # 17 (Feb 92)] U(VI): 71.6 µg L^{-1} Na : 3.3×10^{3} mg L^{-1} K : 9.1 mg L^{-1} Ca : 5.4×10^{2} mg L^{-1} Mg : 1.9×10^{2} mg L^{-1}	94.0±2

The stimulants were prepared based on the composition described elsewhere [Yadav *et al.*, 2009; Yadav *et al.*, 2007]. The concentration of uranium increases from 8 μg L^{-1} in monsoon to 1,400 μg L^{-1} in summer. Removal was done by equilibration with 20 mg of leached IIP particles in batch mode, after adjusting the pH to 6.5. Percentage of removal obtained is 70.3 ±3 % & 94.0 ±2 % for lake water and ground water respectively. In single stage of equilibration, about 94.0 % of uranium could be removed from ground water simulant compared to 70.0 % from Sambhar salt lake water, as the concentration of NaCl was very high in case of latter (146×10^3 mg L^{-1}) than in former (3.3×10^3 mg L^{-1}). This is because sodium ions compete with uranyl ion in complexing with 8-hydroxyquinoline functionality thereby decreasing the removal efficiency.

2.10 Experimental

2.10.1 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. FT-IR 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 a FEI, TECNAI 30G2 S-TWIN microscope with an accelerating voltage of 100 kV. Elemental studies were carried out with CHN Elementar Vario EL III. Surface area and pore size analysis was done using a BET surface area analyzer (Gemini 2360, Micromeritics, Norcross, USA).

2.10.2 Chemicals

Tetraethoxysilane (TEOS), 2-hydroxy ethyl methacrylate (HEMA), ethylene glycol dimethacrylate (EGDMA) 4-vinylpyridine (VP), 2-methoxyethanol, 3-aminopropyltrimethoxysilane (APTMS), and arsenazo III were purchased from Aldrich and used as received. 2, 2'-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 U(VI) was prepared by dissolving appropriate amount of $UO_2(NO_3)_2.6H2O$ (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 $molL^{-1}$ ammonium acetate was used as the buffer.

2.10.3 Extraction of uranium

Based on our earlier experience with uranyl IIP materials, uranyl ion was extracted after stirring 1 g of the material with 100 mL of 1M HCl for 3 h. This leaching procedure enabled reproducible blank as determined by arsenazo III procedure.

2.10.4 Determination of uranium by arsenazo III method

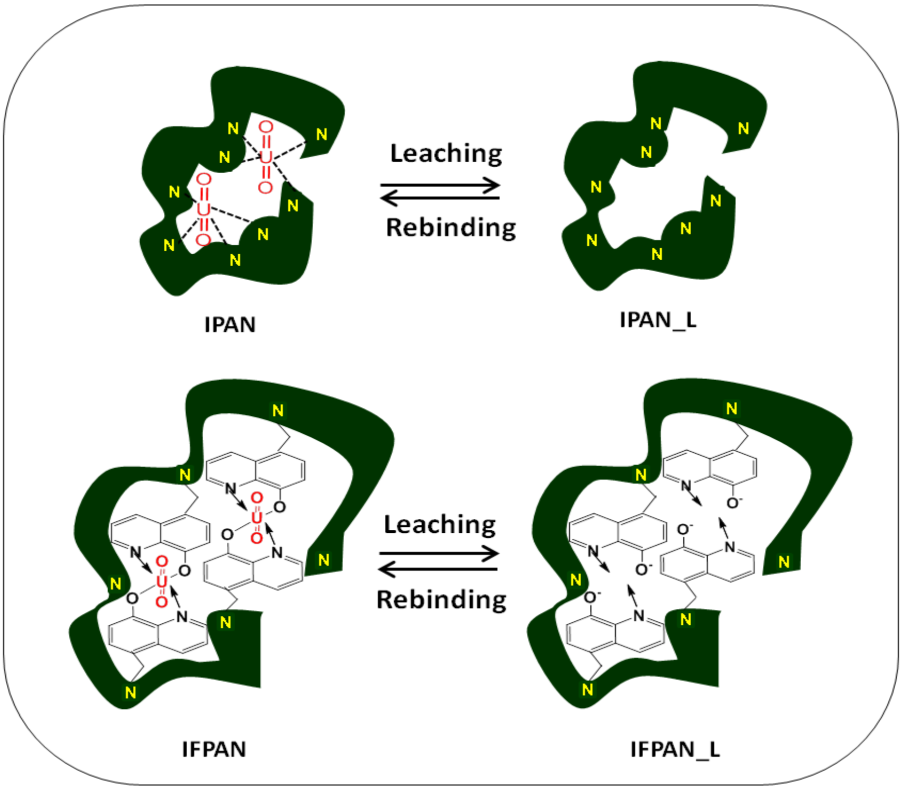
To the filtrate obtained after solid phase extraction was added 5 mL of 1:1 hydrochloric acid, 2 mL of 0.1 % arsenazo III solution and diluted to 25 mL with distilled water. The absorbance of uranium–arsenazo III complex was measured at 656 nm [Snell, 1978].

2.11 Conclusions

Surface imprinted nanospheres were synthesized by modified precipitation polymerisation method. These nanospheres, with high imprinting coefficients and retention capacity offer possible application towards removal of 50 to 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 imprinted nanomaterials for other toxic metal ions and their application in pollution control processes.

Chapter 3

Uranyl ion imprinted polymers of aniline and 8-hydroxyquinoline functionalised aniline



3.1 Abstract

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 functionalised aniline (ANHQ) and aniline (IFPAN and NIFPAN) using potassium dichromate and ammonium persulphate as the initiators. The structural characterisation 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 optimised 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.

3.2 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 polymerisation in presence of the target molecules. Their removal leaves recognition cavities which can selectively rebind them from a mixture of closely related compounds [Greibrokk and Sellergren, 2008, Chen *et al*., 2011]. Generally, widely accepted systems for preparation of imprinted polymers are free radical vinyl polymerisation and sol gel process. Polymerisation of aromatic monomers like pyrrole, o-phenylenediamine, o-aminophenol, o-aminothiophenols and aniline by both chemical and electrochemical methods comprises another system [Alexander *et al*., 2006]. But imprinting by chemical polymerisation 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.,* [2002], 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. The schematic representation for polymerisation and possible interaction with metal ions are given in Figure 3.1. Another report is by Homayon *et al*., [2012] and by Sid Kalal *et al*., [2013] which describes synthesis of aniline-formaldehyde polymers in presence of extra aniline as cross-linker 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 [Monreal and Diaconescu, 2010, Fletcher *et al*., 2010]. 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 stability [Greibrokk and Sellergren, 2008] and the removal can be effected by solid phase extraction. Rao *et al*., [2004, 2006] and recently Branger *et al*., [2013] have given a detailed review on the use of imprinted polymers for removal of metal ions using SPE.

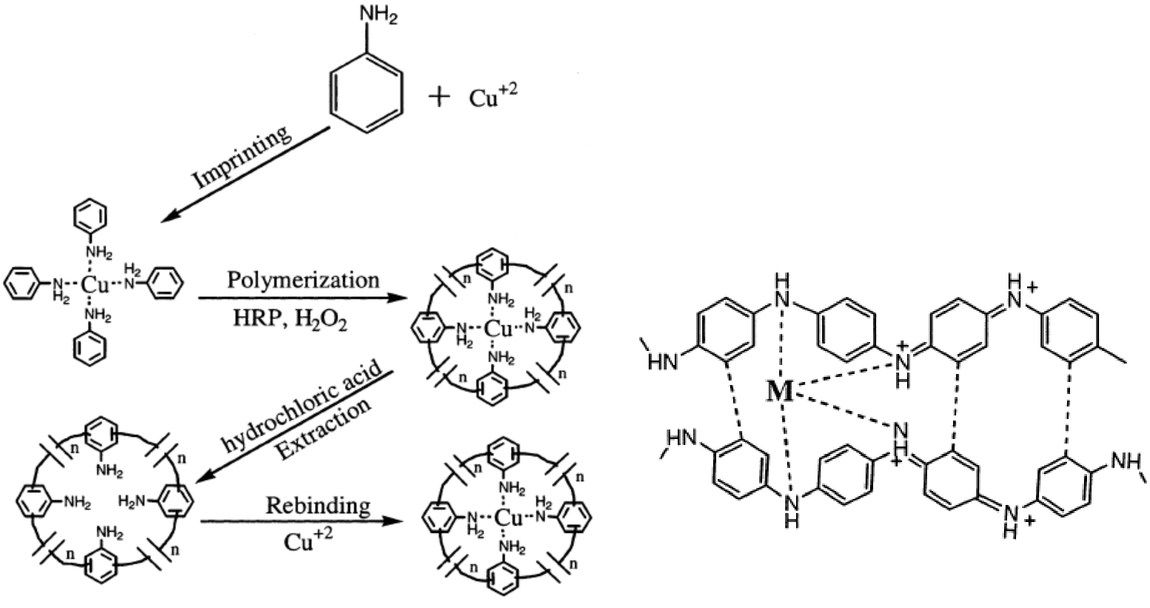


Figure 3.1: Scheme for polymerisation of aromatic monomers and the interaction of metal ions within the polymer

Aniline and functionalised aniline were used as the aromatic monomers. Aniline as a monomer in imprinting has the advantage of simple polymerisation 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 functionalised with 8-hydroxyquinoline 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 [Jerome *et al*., 2000] 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 [Ramkumar and Chandramouleeswaran, 2013] and by polyaniline grafted graphene oxide nanosheets used for sorption of uranyl ions at pH 3.0 [Sun *et al*., 2013].

3.2.1 Aniline as the monomer

The conventional method of polymerisation of aniline is by the addition of ammonium persulphate in aqueous media to an aqueous acidic solution of aniline. Neutral anilines undergo a redox reaction with ammonium persulphate to form aniline radical. Polymerisation then occurs by para-coupling in strongly acidic conditions, resulting in the formation of emeraldine salt form. Emeraldine salt form is the doped form which can be de-doped to get emeraldine base [Tang *et. al*., 2011]. The polymerisation and doping and de-doping are given in Figure 3.2. Doped polyanilines can form either polarons or bipolarons as given in Figure 3.3.

Polymerisation of aniline can be done using oxidants potassium dichromate (PDC), ferric sulphate, ferric chloride, ceric ammonium nitrate, ceric sulphate, hydrogen peroxide, potassium iodate and enzyme horseradish peroxidase. But after report of chemical oxidative polymerisation of aniline by Mac Diarmid *et al*., [1985], ammonium persulphate (APS) has been commonly used [Yasuda and Shimidzu, 1992].

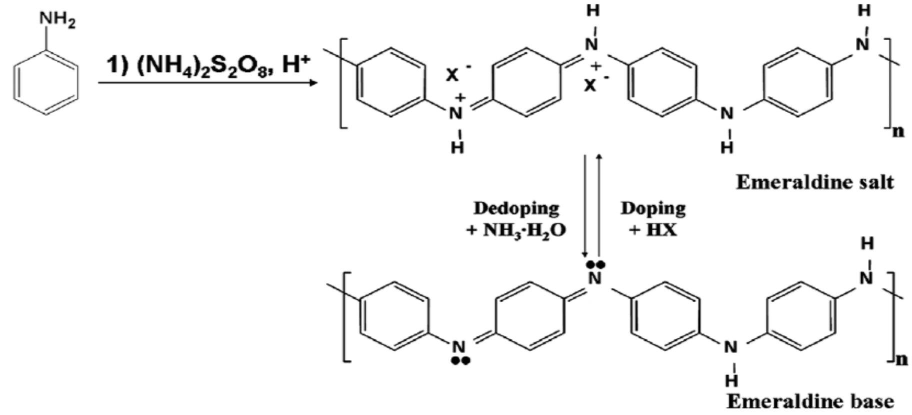


Figure 3.2: Polymerisation and doping and de-doping of aniline [Huang, 2006]

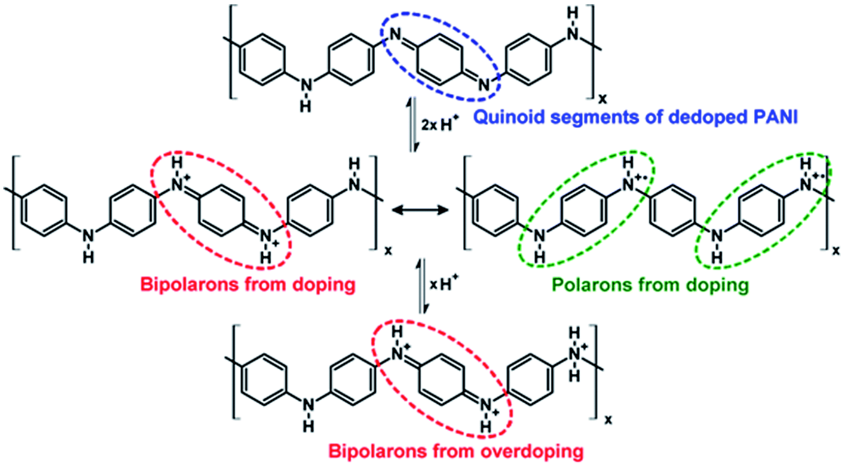


Figure 3.3: Formation of polarons and bipolarons after doping [Heeger, 2001]

Polyaniline exists in three oxidation states leucoemeraldine, emeraldine and pernigraniline. Leucoemeraldine and pernigraniline are the fully reduced (all the nitrogen atoms are amine) and the fully oxidized (all the nitrogen atoms are imine) forms respectively, and in emeraldine, the amine to imine ratio is 0.5 as given in Figure 3.4. The emeraldine salt (doped form) is the conducting material whereas the other two are insulating [Gospodinova and Terlemezyan, 1998]. The conductivity of emeraldine salt form of polyaniline is attributed to the presence of polarons or radical cations [Silva Claudio *et al*., 2014].

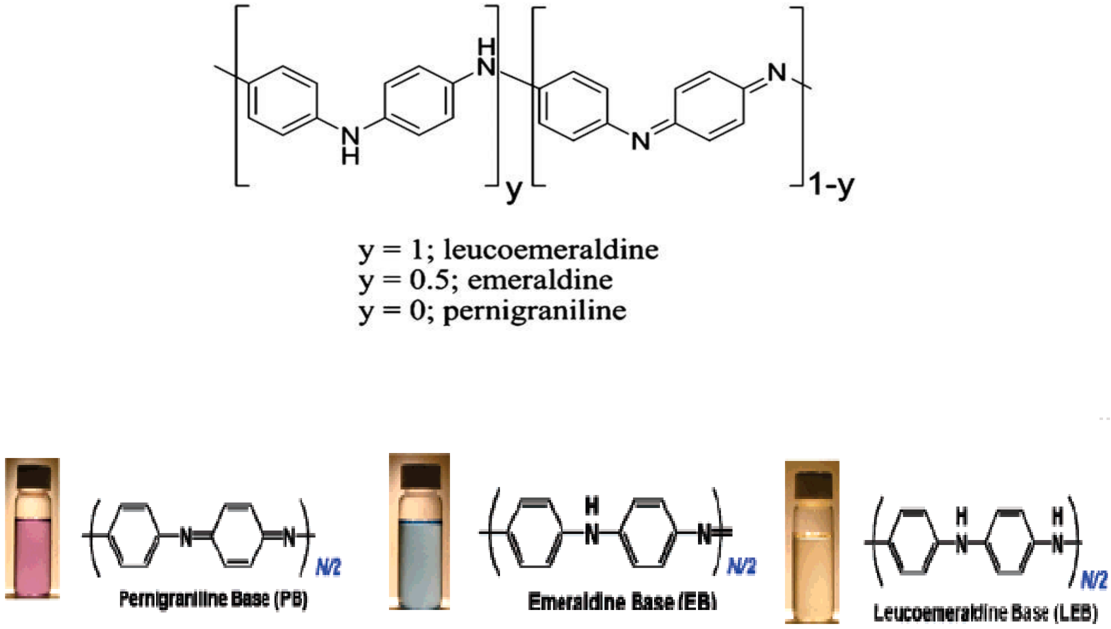


Figure 3.4: Different oxidation states of polyaniline [Kolla *et al*., 2005]

Here, we have synthesized ion imprinted polymer in both polyaniline and functionalised polyaniline matrix that can selectively remove uranyl ion from aqueous samples at neutral pH. 8-hydroxyquinoline is used as the functional group for complexing uranyl ion. We have characterized the prepared material, carried out optimisation studies to get maximum removal and has done the selectivity studies so that it can be used in decontamination of real environmental samples.

3.3 Procedure

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

The method for synthesis with potassium dichromate was modified from the report of Chowdhury *et al*., [2005]. The ratio of aniline to oxidant was taken as [An]/[OX]=2.0, [HCl]=2.4 M and [$K_2Cr_2O_7$]=0.11 M. Briefly, 5 mL of concentrated HCl, 0.5 mL of aniline and 0.05 g of $UO_2(NO_3)_2.6H_2O$ were stirred for 30 minutes to form the pre-polymerisation mixture. The polymerisation was initiated by addition of $K_2Cr_2O_7$, 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 ^{0}C. The corresponding non imprinted polyaniline (NIPAN-1) (Yield-73 %) was prepared by the same procedure without the uranyl ion.

3.3.2 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. Briefly, 5 mL of concentrated HCl, 0.5 mL of aniline and 0.05 g of $UO_2(NO_3)_2.6H_2O$ was stirred for

30 minutes to form the pre-polymerisation mixture. The polymerisation was initiated by addition of ammonium persulphate dissolved in 6 mL of 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 is continued for 4 h. The synthesis was done with and without purging of nitrogen gas. The precipitated PANI salt was filtered and washed with distilled water until the washings were colorless. The polymer was then dried in an oven at 50 ^{0}C. The corresponding non imprinted polymer was prepared by the same procedure without the uranyl ion (NIPAN-2) (Yield-77 %).

3.3.3 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.

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

For functionalisation of aniline, 8-hydroxyquinoline was chloromethylated following the method of Burckhalter and Leib [1961], which was then treated with aniline in presence of triethylamine in DMF to get N-[5-(8-hydroxy quinoline)methyl]aniline (ANHQ) [Hamaya *et al.*, 1994; Wanga *et al.*, 2009].

3.3.5 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 pre-polymerisation mixture. The ratio of ANHQ to uranyl ion was taken as 1:2. The polymerisation 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 ^{0}C. The corresponding non-imprinted polymer was prepared by the same procedure in the absence of uranyl ion (NIPANHQ).

3.3.6 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 $UO_2(NO_3)_2.6H_2O$ were stirred for 30 minutes to form the pre-polymerisation mixture. The ratio of ANHQ to uranyl ion was taken as 1:2. The polymerisation 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 ^{0}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 Figure 3.5.

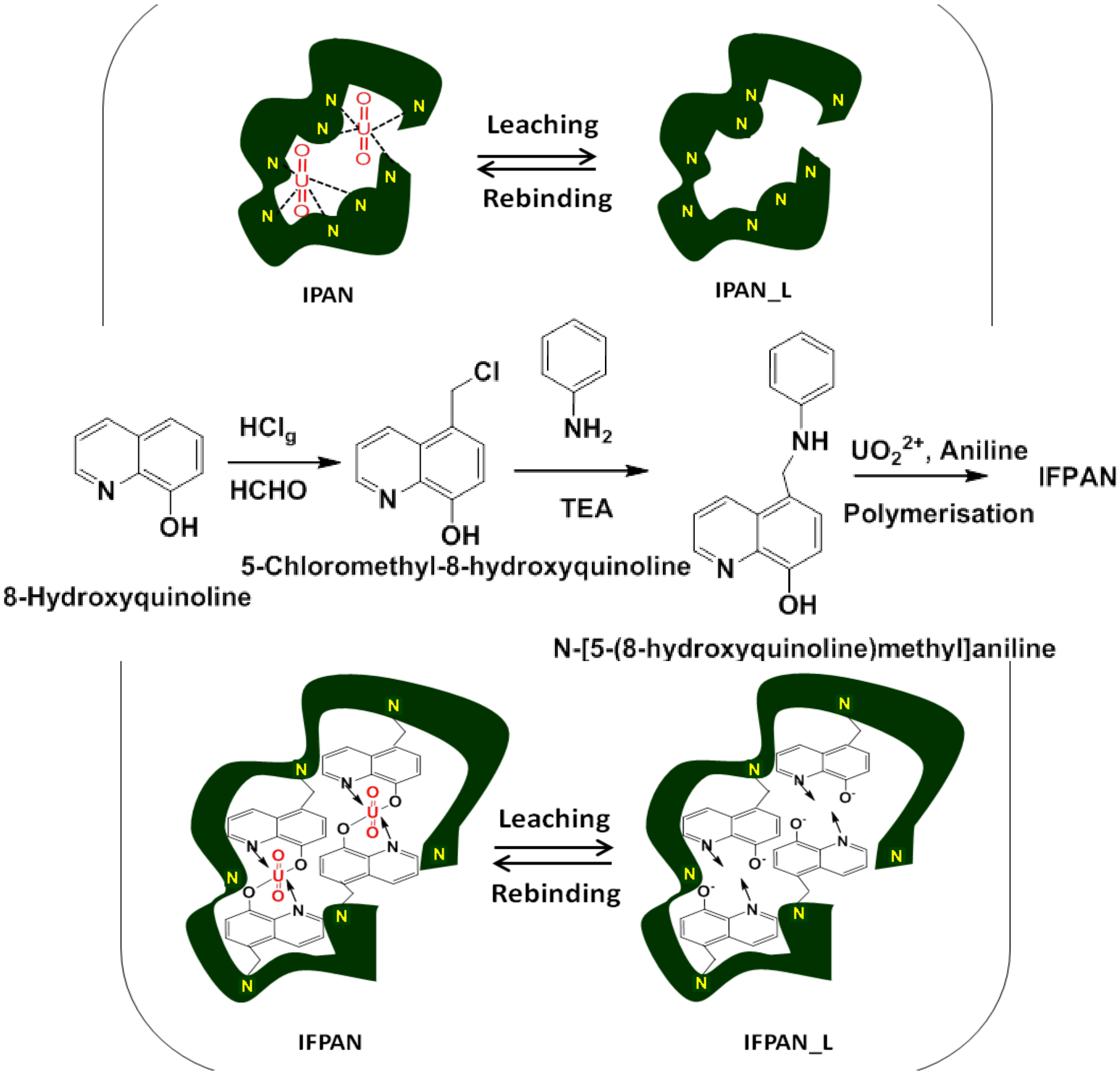


Figure 3.5: Schematic diagram for synthesis of IPAN and IFPAN

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^{-3} M ammonium acetate buffer. This prompted us to further investigate on the possibilities of obtaining quantitative recovery using the imprinted polymers and the results are compiled in Table 3.1. From the data we can see that IPAN 1 showed only 73 % removal even after increasing the amount to 100 mg.

Table 3.1: SPE studies with imprinted polymers

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

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 functionalised with a specific ligand, 8-hydroxyquinoline to obtain a polyaniline matrix with 8-hydroxyquinoline as pendent ligands and as expected 40 mg 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 functionalised aniline (PANHQ) 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.

3.4 Characterisation

3.4.1 UV-Visible spectroscopy

The interaction of uranyl ion with aniline and ANHQ can be understood from the UV-visible spectrum given in Figure 3.6a. After polymerisation, the spectra were recorded both in DMSO (Dimethyl sulphoxide) and NMP (N-Methyl-2-pyrrolidone). Though in solid state they are green in color (emeraldine salt), in NMP they turn blue (emeraldine base). But in DMSO they retain their green color.

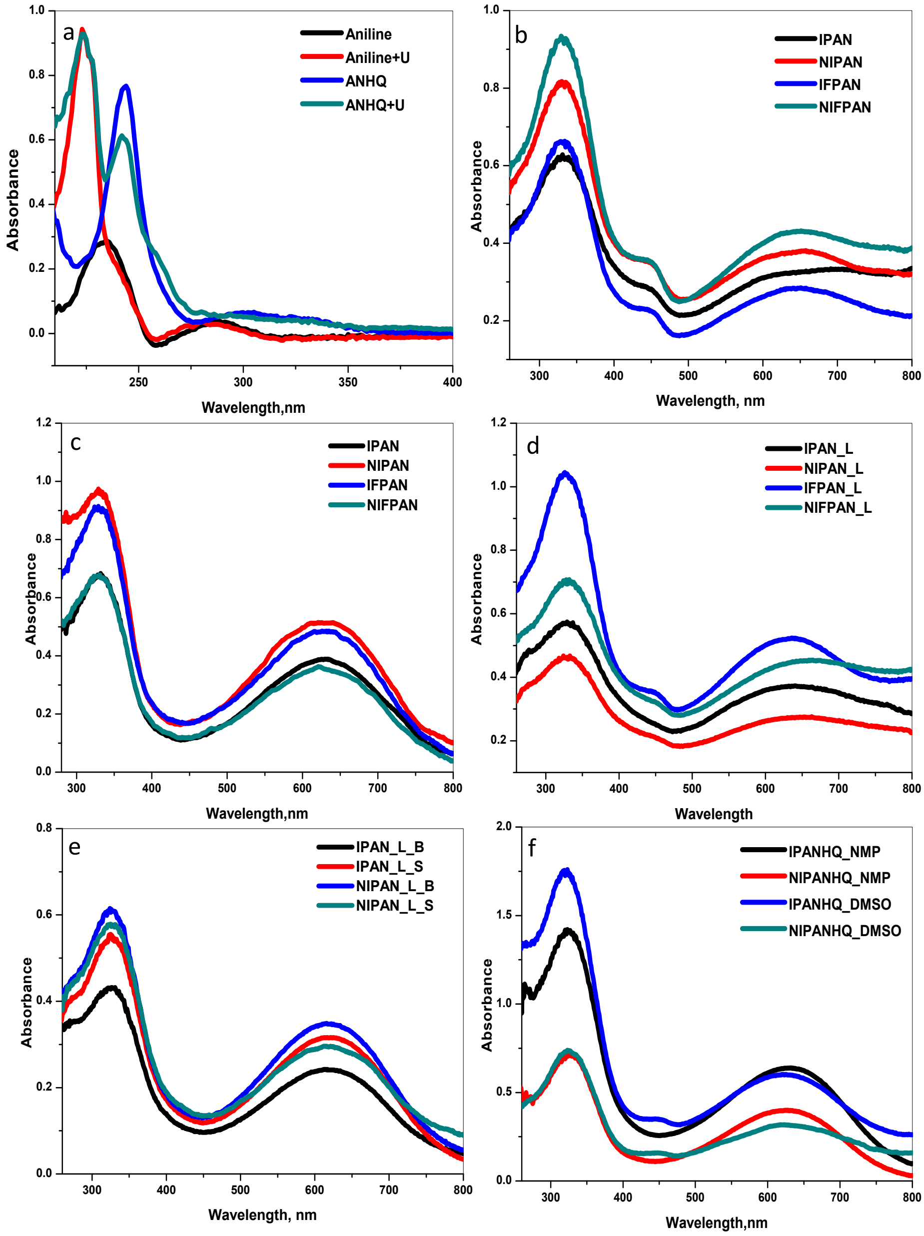


Figure 3.6: UV-Visible spectra of a) Aniline, 1:4 ratio of aniline and uranyl ion, ANHQ, 1:2 ratio of ANHQ and uranyl ion in methanol. b) IPAN, NIPAN, IFPAN and NIFPAN in DMSO c) IPAN, NIPAN, IFPAN and NIFPAN in NMP d) IPAN, NIPAN, IFPAN and NIFPAN leached with 1M HCl in DMSO e) IPAN, NIPAN, IFPAN and NIFPAN after solid phase extraction in DMSO f) Homopolymer of IPANHQ and NIPANHQ in NMP and DMSO

This could be due to the weak basic property of the solvent NMP causing de-doping of the polymer [Rannou and Nechtschein, 1997]. Figure 3.6b and 3.6c 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 charge-transfer-exciton transition formed in a benzenoid ring with its adjacent quinoid ring, typical for emeraldine base. But in DMSO, an additional peak appears at around ~450 nm, due to polaron-π* transition, characteristic of emeraldine salt [Tang *et al.*, 2011; Polk *et al.*, 2002; Kolla *et al.*, 2005; Xia *et al.*, 1995]. The leached samples (Figure 3.6d) also exhibit similar behavior in DMSO and NMP (data not shown). Figure 3.6e 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 de-doping 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 functionalised aniline also show similar behavior as that of imprinted polyaniline. Therefore the data was compared with the homopolymer of functionalised aniline given in Figure 3.6f, 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.

3.4.2 FTIR

FTIR spectra of all the polymers exhibit peaks characteristic for polyaniline (Figure 3.7). 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–$N^{+\bullet}$ 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) [Ding *et al*., 2008; Trchova *et al*., 2006; Shao *et al*., 2009; Kuczynska *et al*., 2010; Hino *et al*., 2006; Guimard *et al*., 2007; Ayad *et al*., 2009]. 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 [Hamaya *et al*., 1994], 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 [Huang *et al*., 2003]. From the ratio it can also be concluded that there will be approximately one quinoimine structure after seven benzenoid monomer units [Cataldo and Maltese, 2002].

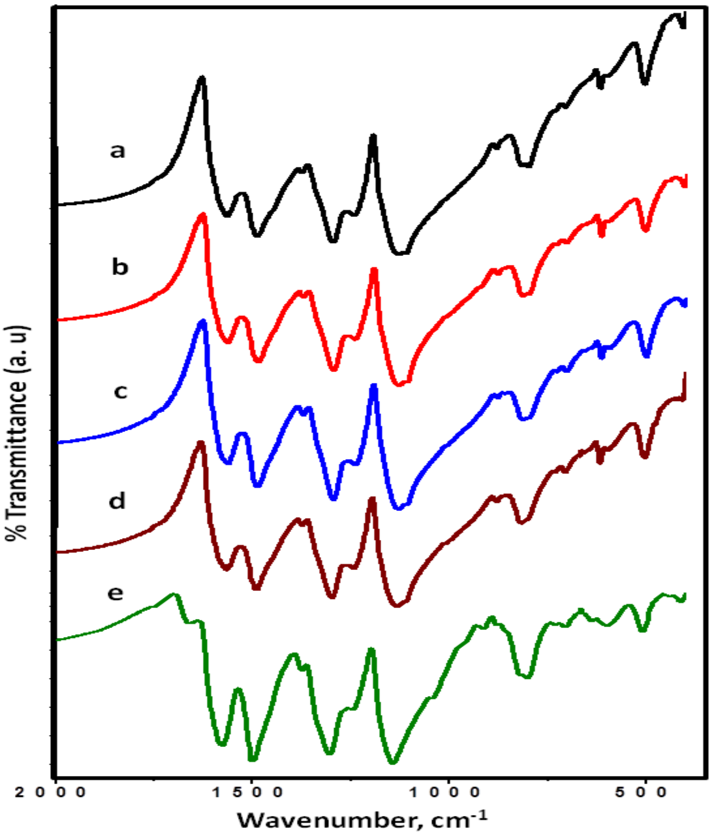


Figure 3.7: FTIR spectra of IPAN(a), NIPAN(b), IFPAN(c), NIFPAN(d) and IPANHQ(e)

3.4.3 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 3.2. In the voltammogram, two redox peaks appears for all the polymers (Figure 3.8). The first one at ~0.320 V is due to the formation of radical cations (polaronic emeraldine) and the second one at ~0.728 V is due to formation of diradical dications by oxidation of polyaniline. In the case of functionalised 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.

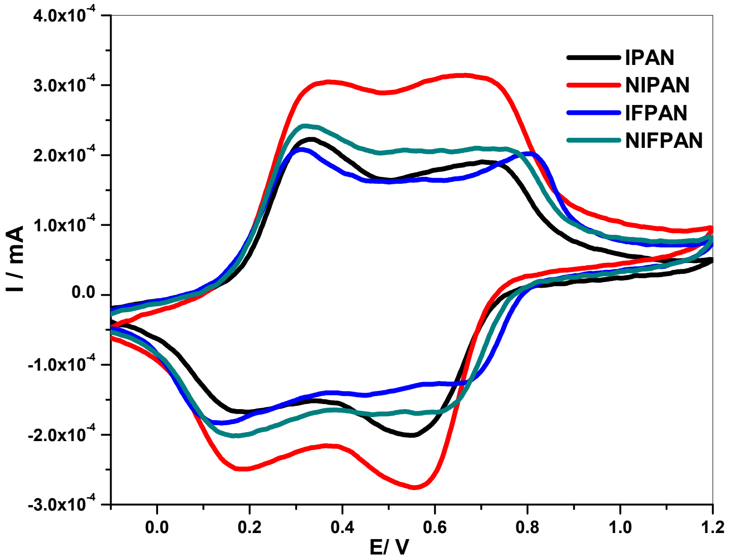


Figure 3.8: Cyclic voltammograms of polymers

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 [Kolla *et al.*, 2005; Stilwell and Park, 1988; Nabid and Entezami, 2005; Yang and Ven, 1994].

Table 3.2: 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

3.4.4 Morphology by SEM

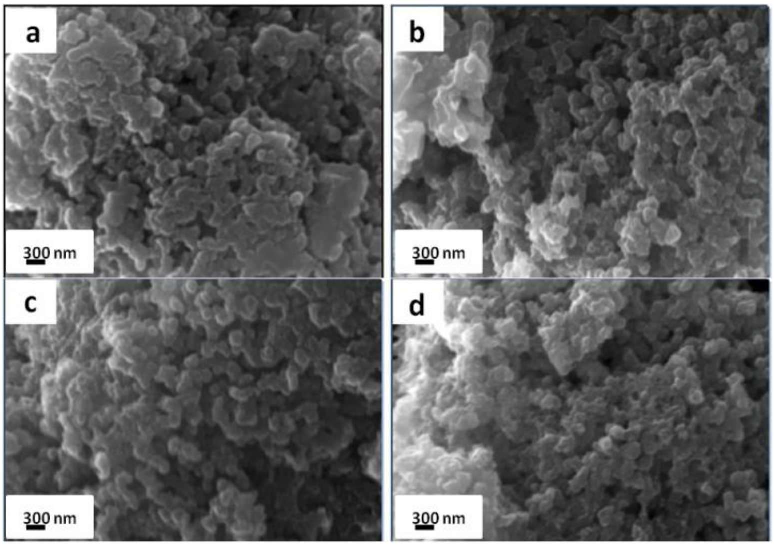


Figure 3.9: SEM images of IFPAN(a), IFPAN_L(b) and NIFPAN(c), NIFPAN_L(d)

The SEM images of imprinted and non-imprinted polymer, both leached and un-leached are shown in Figure 3.9. 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.

3.4.5 TG

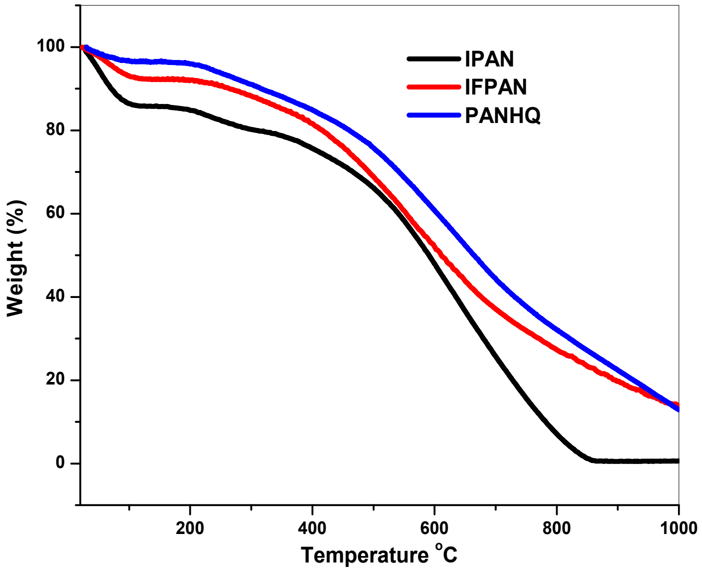


Figure 3.10: TG curves of IPAN, IFPAN and PANHQ

Thermal stability of the imprinted polymers was measured using TG (Figure 3.10). In IPAN, the first weight loss observed at 100 ^{0}C is due to desorption of water. The second weight loss process at about 200-325 ^{0}C could be due to the exclusion of doped acids and the third weight loss from 500 ^{0}C is due to the disintegration of polymer back bone. In case of IFPAN and PANHQ, a two step weight loss can be observed, first step at 100 ^{0}C due to loss of water and second step, due to decomposition of the polymer [Sun *et al*., 2013; Wanga *et al*., 2009].

3.4.6 UV-Visible spectrophotometric titration

Complexation of uranyl ions with 8-hydroxyquinoline inside the imprinted polymer can be confirmed by monitoring changes in absorbance of the polymer with the successive addition of uranyl ions. The experiment was done after dispersing leached imprinted polymers in DMSO and by successive addition of uranyl ion solution in DMSO. The corresponding spectra for IPAN (Figure 3.11a) and IFPAN (Figure 3.11b) shows the presence of single isosbestic point in case of IFPAN. In supramolecular chemistry, the presence of isosbestic point is regarded as the evidence for conversion of host into complex without presence of significant intermediate species [Steed and Atwood, 2009]. This can be extended to imprinted polymers, considering them as the host. Hence it can be concluded that complexation of uranyl ion with 8-hydroxyquinoline occurs inside the binding cavities of the imprinted polymer (IFPAN). DMSO was used as the solvent due to the better dispersion of the polymer in it. The experiment was repeated under the same conditions used for solid phase extraction studies. IFPAN was dispersed in aqueous solution buffered with ammonium acetate to neutral pH. Absorbance was measured by successive addition of 10 molL^{-1} uranium in aqueous solution. The spectrum is given in Figure 3.12 and the isosbestic point appears at 320 nm. Higher uptake of IFPAN compared to IPAN can be attributed to the presence of uranium complexing agent in the former.

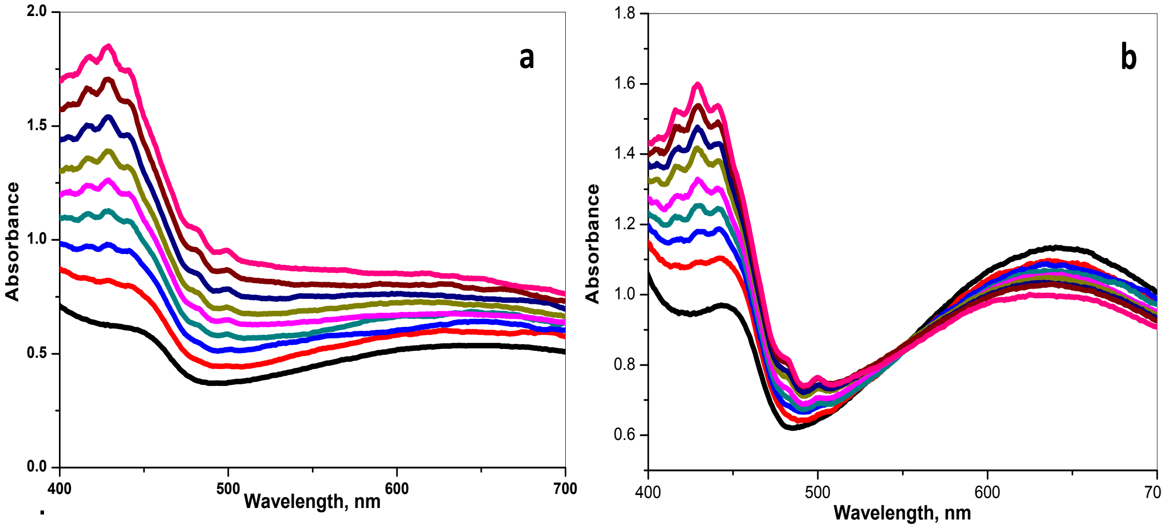


Figure 3.11: Changes in absorption spectra of IPAN a) and IFPAN b) on successive addition of 10 molL^{-1} of uranium solution in DMSO

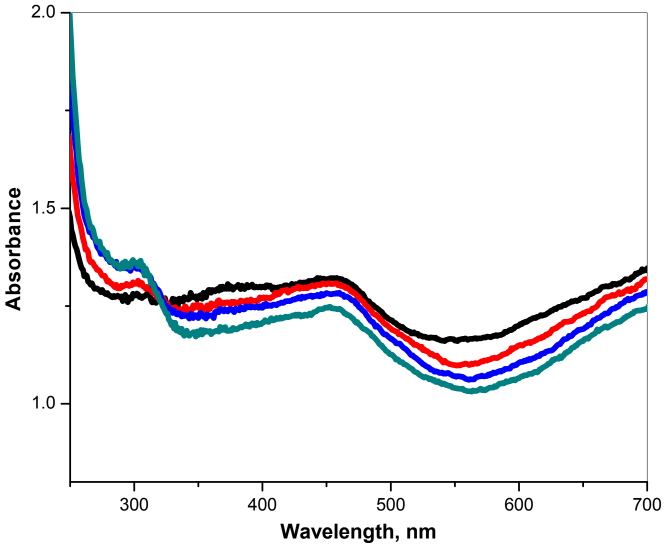


Figure 3.12: Changes in absorption spectra of IFPAN dispersed in aqueous solution of pH 7.0 upon successive addition of 10 mol L^{-1} uranium in aqueous solution

3.5 Optimisation of parameters in SPE studies

Various SPE parameters were optimised for the material IFPAN to get quantitative removal and the values were compared with that for NIFPAN in pH variation studies. Effect of pH (5.0-8.0), weight of polymer particles (30, 40 and 50 mg), time of stirring (10, 20 and 30 min) during the pre-concentration and elution of uranium and nature of eluent (1M HCl/ 1M HNO_3/ 1M Na_2CO_3) were optimised by checking the removal efficiency of 100 µg of uranyl ion present in 100 mL of aqueous solutions using the polymer. Complete removal was obtained at pH 7.0 as shown in Figure 3.13. From the figure, it can also be seen that there is a significant imprinting effect. Weight variation studies shows that 40 mg 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.

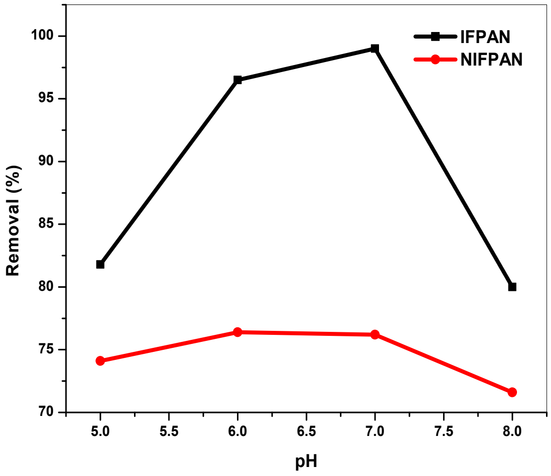


Figure 3.13: Effect of pH on removal of uranyl ion

Table 3.3: Optimisation of solid phase extraction parameters for IFPAN

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_2CO_3	73.7
Amount of uranium (µg)	
50	> 99
100	> 99
200	51.2
500	20.0

*Average of duplicate measurements

Quantitative removal of 50-100 µg of uranyl ion from 100 mL of aqueous solution adjusted to pH 7.0 with 10^{-3} M ammonium acetate was demonstrated. The results are compiled in Table 3.3. At optimised conditions, IFPAN exhibited an imprinting effect of 1.3.

3.6 Reusability studies

Reusability studies were carried out for five cycles under the optimised 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.

3.7 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 $\mathrm{mgL^{-1}}$ 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 $\mathrm{\mu molg^{-1}}$ and 49 $\mathrm{\mu molg^{-1}}$ at 10 $\mathrm{mgL^{-1}}$ for IFPAN and NIFPAN respectively. This shows that the material has high retention capacity which can be utilized for removal of uranium.

3.8 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 deionized water under the optimised conditions.

Table 3.4: Selectivity data of IFPAN and NIFPAN

Metal ions	Distribution Ratio (D)		Selectivity Coefficient (S)		Imprinting coefficient (K’)
	NIFPAN	IFPAN	NIFPAN	IFPAN	
UO_2^{2+}	3.2	99	-	-	-
Na^+	0.45	.0204	7.4	4.8×10^3	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	2.2×10^2	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

The concentration of uranyl ion was then determined by spectrophotometry, after elution with 10 mL of 1.0 M HCl. Table 3.4 gives the distribution ratio and selectivity coefficients of uranyl ion with respect to other inorganics using non-imprinted and imprinted polymers. 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 (Cu^{2+}) 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.

3.9 Experimental

3.9.1 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.

3.9.2 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)

3.9.3 Yield of the polymer

The yield of the polymer was calculated using the formula,

$$\% \text{ Yield} = \frac{W_2}{W_1} \text{ X } 100$$

where W_2 is the weight of resultant polymer and W_1 is the initial weight of the monomers.

3.9.4 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).

3.9.5 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 μg 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.

3.9.6 Method for determination of uranyl ion.

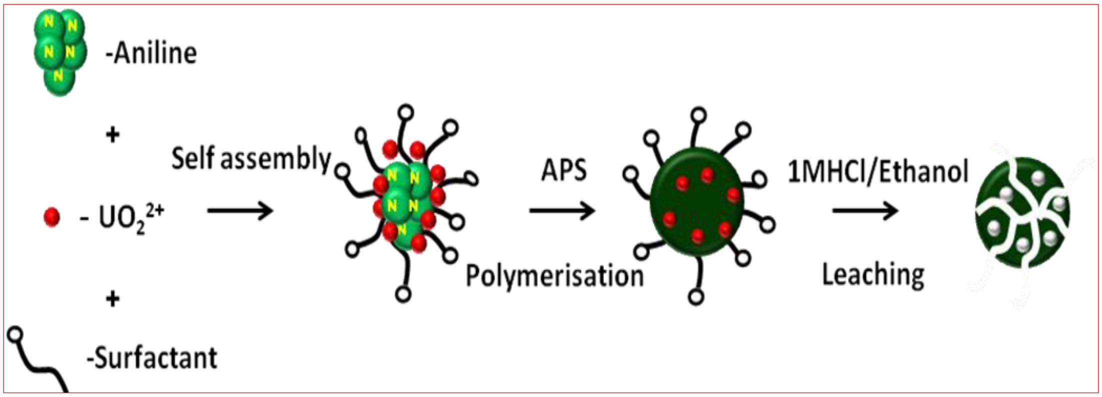
To the filtrate obtained after solid phase extraction was added 5 mL of 1:1 hydrochloric acid, 2 mL of 0.1 % arsenazo III solution in a 25 mL standard flask and made upto the mark with distilled water. The absorbance of uranium–arsenazo III complex was measured at 656 nm [Snell, 1978].

3.10 Conclusions

We have synthesized ion imprinted polymers with aromatic monomers aniline and 8-hydroxyquinoline functionalised 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 4 h. The characterisation 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.

Chapter 4

Hierarchical imprinted polymers of aniline and aniline-formaldehyde in presence of surfactants for uranium removal



4.1 Abstract

Synthesis of hierarchically double imprinted polymers with uranium in presence of various surfactants and aniline and aniline-formaldehyde as the polymer matrix is described here. The surfactant and uranium act as templates which on removal by acid and ethanol mixture, gives different sized imprints each with a specific function. Removal of the metal ion from the complex leaves cavities that exhibit ionic recognition and that of the surfactant results in the formation of relatively large pores. This gives the polymer an overall porosity which improves metal ion transport kinetics. Comparison of the properties of the imprinted polymers, synthesized using anionic (sodium dodecyl sulphate - SDS), cationic (cetyltrimethylammonium bromide - CTAB) and neutral (triton X-100 - TX-100) *surfactants, in terms of removal efficiency of uranium by IIP-SPE has been provided. The synthesized polymers were characterised by UV-Visible, FTIR, SEM, CV, TG and surface area and pore size analysis. Imprinted polymer in aniline-formaldehyde matrix with TX-100 was effective in complete removal of uranium and exhibited a retention capacity of 88 μmol g*$^{-1}$ *for 10 mg L*$^{-1}$ *of uranium. Selectivity and reusability studies carried out to demonstrate the possible application of the material for uranium removal from real samples.*

4.2 Introduction

Imprinting is a way of introducing predetermined cavities for a template inside a polymer matrix. Hierarchical imprinting involves polymerisation in presence of templates which can produce cavities at different length scales. In ion imprinting, a metal ion of interest is imprinted along with a surfactant inside a matrix. Removal of the metal ion leaves cavities that exhibit ionic recognition and that of the surfactants results in the formation of relatively large pores. These pores acts as channels providing better accessibility for the metal ion to its binding sites, thus improving overall transport kinetics.

A complex of copper and 3-(2-aminoethylamino)-propyltrimethoxysilane (aapts), $Cu(aapts)_2^{2+}$ was synthesized and doubly imprinted in presence of either cationic (CTAB), anionic (SDS) or neutral (DDA-dodecylamine), as surfactants in silica matrix. Extraction of surfactant and metal ion was carried out by refluxing in ethanol/HCl mixture. A comparison of rebinding of Cu(II) with singly imprinted material shows that doubly imprinted materials has five times better uptake capacity [Dai *et al.*, 2000]. The same method was used for imprinting Cd(II) with CTAB as surfactant. The factors affecting selectivity of the material like ratio of functional precursor silane and crosslinking silane, reaction time, temperature and ageing/drying time were also investigated. Reusability of the material was also studied [Lu and Yan 2004]. Functional silane aapts was again used for imprinting Hg(II) in presence of CTAB in silica matrix. The material was applied for separation of Hg(II) from tap water, lake water and river water [Wu *et al.*, 2007].

2-aminoethyl-3-aminobutylmethyldimethoxysilane was employed as functional monomer for imprinting Ni(II) and CTAB in silica matrix. The method was applied for determination of Ni(II) in lake water, river water and synthetic sea water samples and in a phytotherapic product [Nacano *et al.*, 2010]. Hierarchical imprinting was extended to organic and inorganic-organic hybrid by imprinting Ni(II) in polymethacrylic acid (PMA) and PMA-silica matrix In this case also CTAB was used as the surfactant [de Oliveira *et al.*, 2013]. Recently Cu(II) was imprinted in poly(acrylamide-co-ethylene glycol dimethacrylate), again with CTAB as the surfactant [Germiniano *et al.*, 2014]. Aromatic monomers like aniline have not yet been exploited for hierarchical double imprinting.

Polyaniline is a versatile material owing to its interesting optical and electrochemical properties and environmental stability. It can be synthesized by simple methods and is easily processable [Mac Diarmid, 2001; Yasuda and Shimidzu, 1993; El-Dib *et al.*, 2011]. Recent focus in research is the synthesis of nanostructured materials that exhibit better properties than their bulk counterparts [Alves *et al.*, 2013; Tran *et al.*, 2011]. Nanostructures of polyaniline can be synthesized by incorporation of hard or soft templates. Hard templates include inorganic substrates - carbon nanotubes, graphite and inorganic oxides like aluminium oxide and vanadium oxide. In this case polymerisation occurs after the adsorption of aniline monomer or aniline radical cation on the surface of the substrate. Soft templates include use of polymers or surfactants. Polyanions which can have electrostatic interaction with aniline and water soluble polymers capable of forming hydrogen bonds can act as polymer template. Surfactants forms self assembled micelles that directs the growth of the polymer [Boeva and Sergeyev, 2014, Tran *et al.*, 2011]. The interaction of aniline monomer and surfactant can be schematically represented as in Figure 4.1.

It has also been reported that apart from surfactant assemblies, surfactant molecule itself may act as mediator in controlling the morphology of polyaniline i.e. surfactants added at a concentration below critical micelle concentration can also influence the morphology of polyaniline [Han *et al.*, 2013]. Hence surfactants added to aniline during polymerisation can contribute towards nanostructured morphology as well as increase in overall porosity of the polymer.

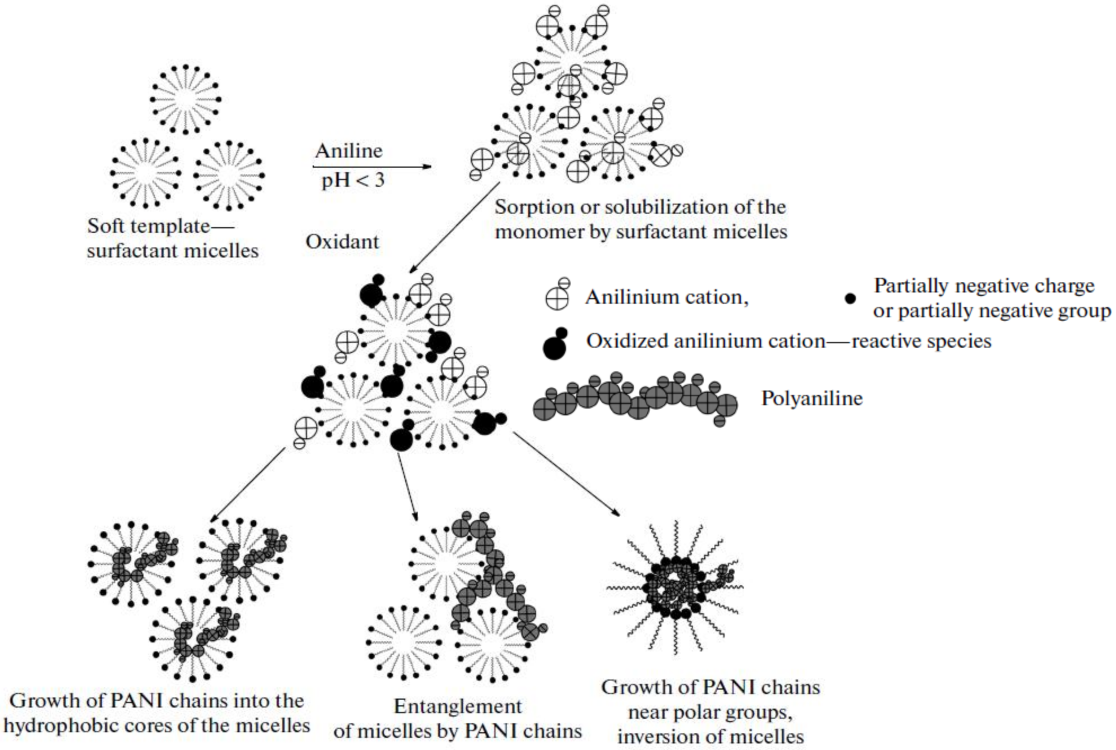
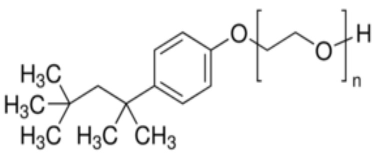


Figure 4.1: Scheme for synthesis of aniline in presence of surfactants [Boeva and Sergeyev, 2014]

Cui *et al.,* [2002] imprinted Cu(II), Ni(II), and Fe(III) in aromatic monomers with various functional groups using enzyme catalyzed polymerisation reactions. Homayon *et al.*, [2012] and by Kalal *et al.*, [2013] synthesised aniline-formaldehyde polymers in presence of extra aniline as cross-linker for selective adsorption of Ni(II) and Sr(II) respectively. Recently we reported uranyl ion imprinted polymers using aniline and 8-hydroxyquinoline functionalised aniline [Milja *et al.*, 2014]. In this work we have tried surfactant assisted synthesis of imprinted polymers with aniline and aniline formaldehyde as the matrix for removal of uranyl ion using solid phase extraction. Removal of uranium is of importance as it is a known nephrotoxin [Zamora *et al.*, 1998] with a maximum permissible limit of 30 ppb in drinking water [WHO 1998, 2003]. We have also compared the properties of the imprinted polymers synthesized using anionic (SDS), cationic (CTAB) and neutral (TX-100), in terms of removal efficiency of uranium by IIP-SPE. A possible explanation for the results observed has been provided. The structures of surfactants used are given in Figure 4.2.

Sodium dodecyl sulphate - anionic **Cetyltrimethylammonium bromide - cationic**



Triton X-100 - Neutral

Figure 4.2: Structures of various surfactants

4.3 Synthesis of imprinted polymers

The method for synthesis of imprinted polymers was modified from the report of Milja *et al.,* [2014]. The detailed procedure is given here.

4.3.1 Synthesis of imprinted polyaniline with SDS (IPAN-S)

5 mL of concentrated HCl, 0.5 mL of aniline, 0.05 g of $UO_2(NO_3)_2.6H_2O$ and 0.014 g of SDS was stirred for 30 minutes to form the pre-polymerisation mixture. The polymerisation was initiated by addition of 1.50 g of ammonium persulphate dissolved in 6 mL of 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 ^{0}C. The corresponding non-imprinted polymer (NIPAN-S) was prepared by the same procedure but without the uranyl ion.

4.3.2 Synthesis of imprinted polyaniline with CTAB (IPAN-C)

5mL of concentrated HCl, 0.5 mL of aniline, 0.05 g of $UO_2(NO_3)_2.6H_2O$ and 0.018 g of CTAB was stirred for 30 minutes to form the pre-polymerisation mixture. The polymerisation was initiated by addition of 1.50 g of ammonium persulphate dissolved in 6 mL of 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 ^{0}C. The corresponding non-imprinted polymer (NIPAN-C) was prepared by the same procedure but without the uranyl ion.

4.3.3 Synthesis of imprinted polyaniline with TX-100 (IPAN-T)

5 mL of concentrated HCl, 0.5 mL of aniline, 0.05 g of $UO_2(NO_3)_2.6H_2O$ and 0.032 g of TX-100 was stirred for 30 minutes to form the pre-polymerisation mixture. The polymerisation was initiated by addition of 1.50 g of ammonium persulphate dissolved in 6 mL of 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 ^{0}C. The corresponding non-imprinted polymer (NIPAN-T) was prepared by the same procedure but without the uranyl ion.

4.3.4 Synthesis of imprinted aniline-formaldehyde copolymer (IPAFC)

5 mL of concentrated HCl, 0.5 mL of aniline, 0.5 mL formaldehyde and 0.05 g of $UO_2(NO_3)_2.6H_2O$ was stirred for 30 minutes to form the pre-polymerisation mixture. The polymerisation was initiated by addition of 1.50 g of ammonium persulphate dissolved in 6 mL of 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 is 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 washings were colorless. The polymer was then dried in an oven at 50 ^{0}C. The corresponding non-imprinted polymer (NIPAFC) was prepared by the same procedure but without the uranyl ion.

4.3.5 Synthesis of surfactant incorporated aniline-formaldehyde polymer (IPAFC-S, IPAFC-C, IPAFC-T)

The same procedure was used as in section 4.3.1 to 4.3.3 with the addition of 0.5 mL formaldehyde.

4.4 Characterisation

The synthesised materials were characterised using UV-Visible and FTIR spectra. Electrochemical characterisation was carried out with CV and morphological characterisation with SEM. Thermal stability was checked using thermogravimetry. Surface area and pore size analysis was also done.

4.4.1 UV-Visible spectra

The spectra given in Figure 4.3 show the interaction between uranyl ion and aniline. Figure 4.4 depicts the spectra of polymers, recorded after dispersing in DMSO. In aniline matrix two peaks appear at ~325 nm and at ~631 nm, corresponding to π-π* transition in benzenoid rings and charge-transfer-exciton transition formed in a benzenoid ring with its adjacent quinoid ring.

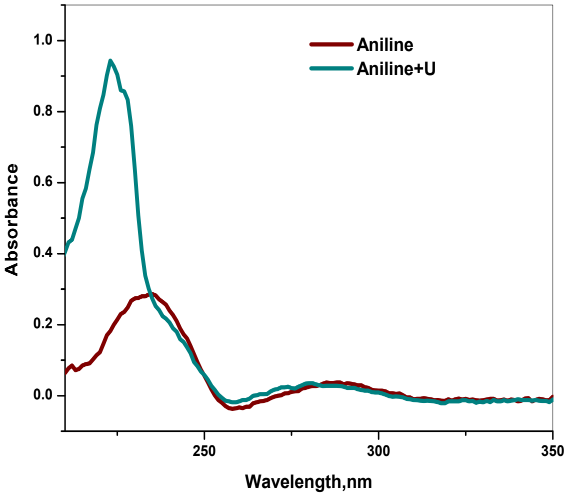


Figure 4.3: UV-Visible spectra of aniline and 1:4 ratio of aniline and uranyl ion

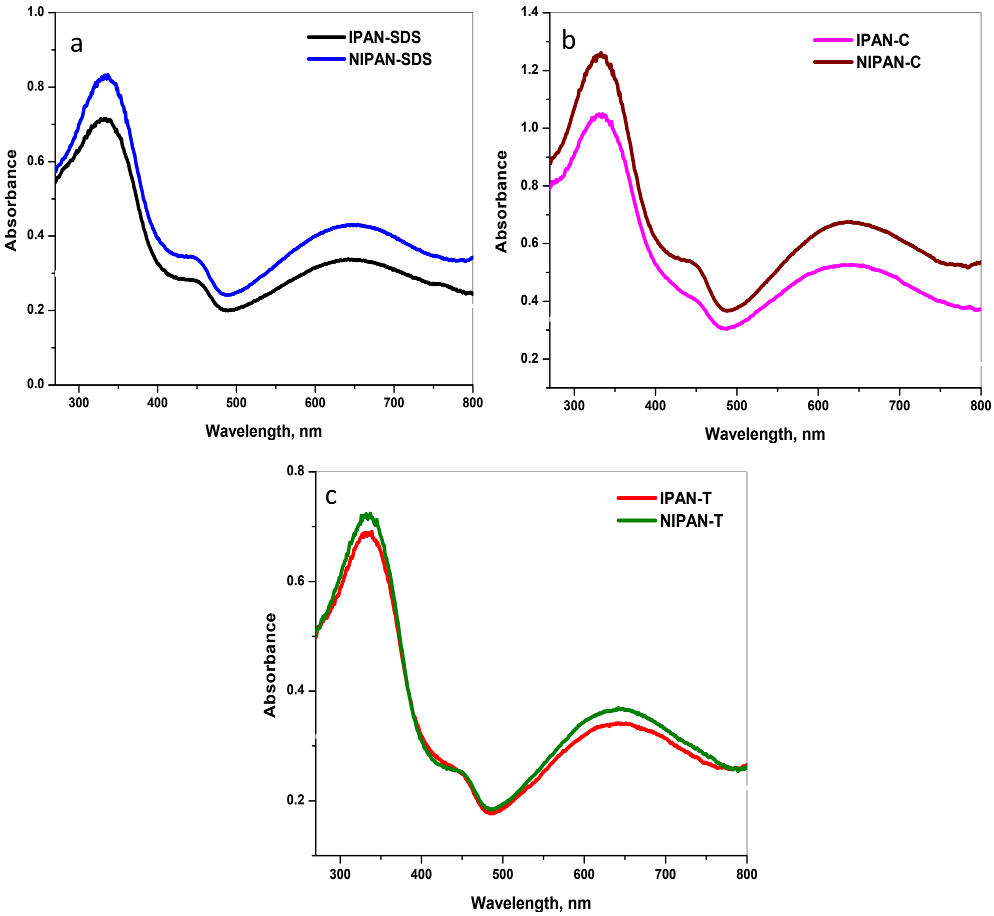


Figure 4.4: UV-Visible spectra of imprinted and non-imprinted polymers of aniline a) IPAN-S and NIPAN-S, b) IPAN-C and NIPAN-C, c) IPAN-T and NIPAN-T

The peak at ~450 nm is due to polaron-π* transition, characteristic of emeraldine salt [Tang *et al.*, 2011; Polk *et. al.*, 2002; Kolla *et al.*, 2005; Xia *et al.*, 1995]. Similar characteristics were obtained for leached polymers also.

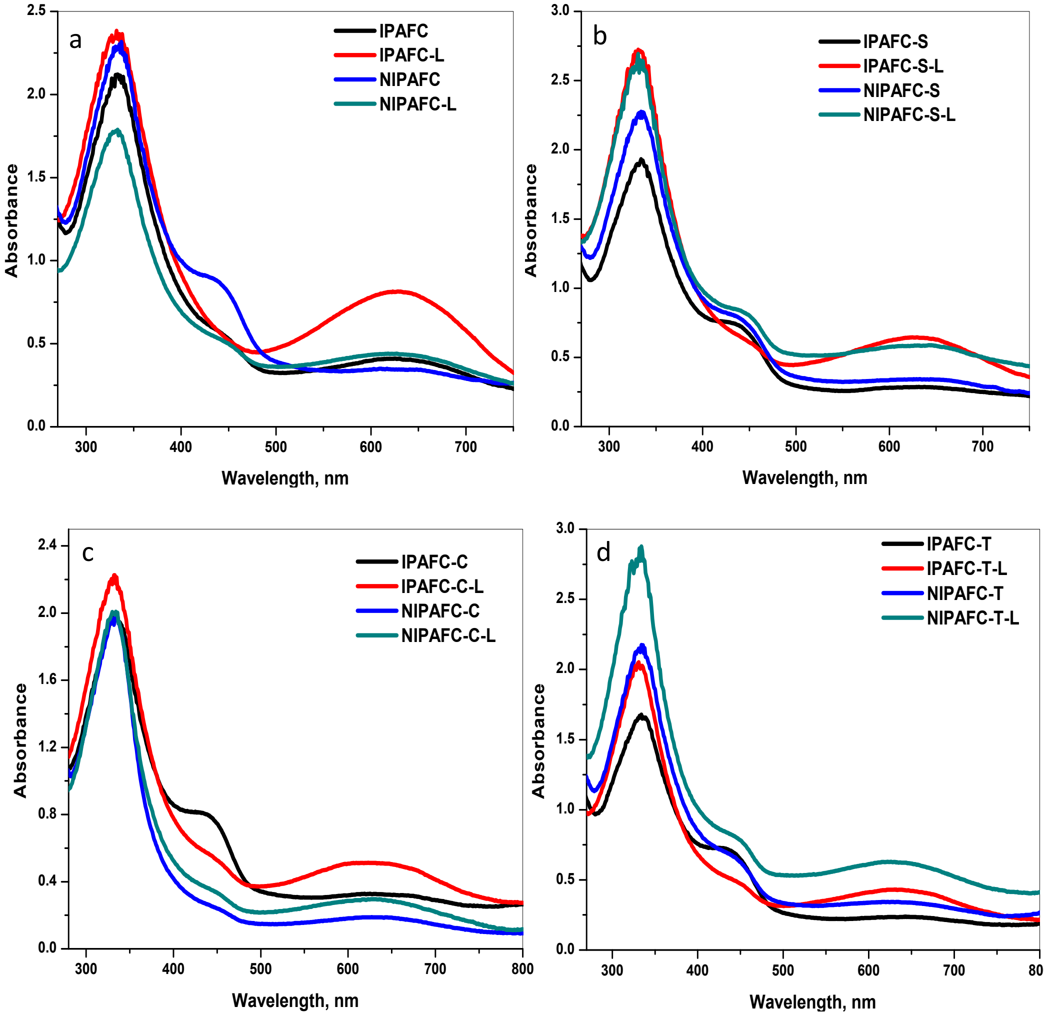


Figure 4.5: UV-Visible spectra of leached and un-leached polymers of imprinted and non-imprinted aniline-formaldehyde polymers

The spectra of aniline-formaldehyde imprinted polymers are given in Figure 4.5. From the spectra it can be seen that after incorporation of formaldehyde also spectral patterns are similar to that of imprinted polymers with aniline. Aniline polymerized in presence of aniline-formladehyde resin is reported to have similar spectra features [Liu and Freund, 1997].

4.4.2 FTIR spectra

FTIR spectra of all the imprinted polymers of aniline are given in Figure 4.6. They have peaks characteristic of polyaniline.

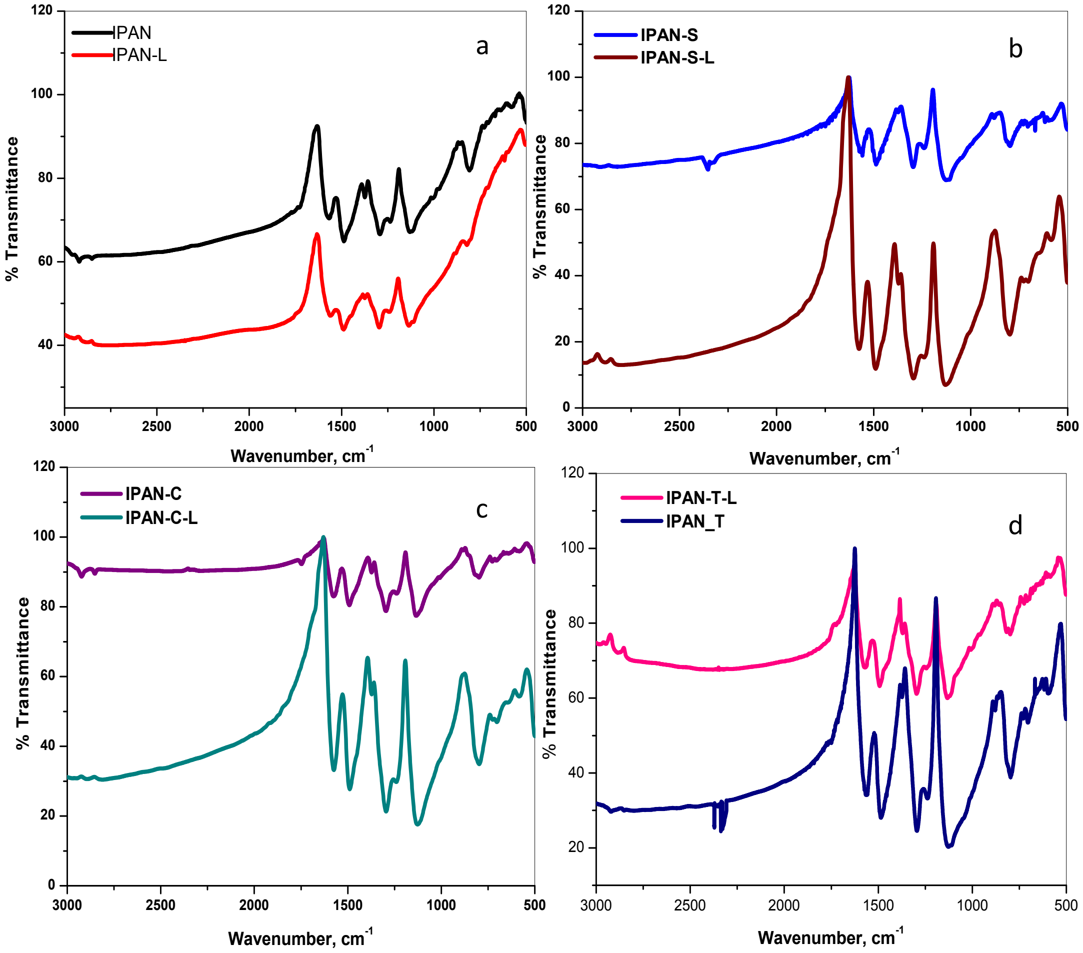


Figure 4.6: FTIR Spectra of un-leached and leached polymers of aniline a) IPAN b) IPAN-S c) IPAN-C d) IPAN-T

The out of plane vibration in 1,4-disubstituted benzene ring at 502 and 826 cm^{-1} confirm the para-coupling structure of the polymer. 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$^{+\bullet}$ stretching vibration in a polaron structure, and corresponds to π electron delocalization induced in the polymer by protonation.

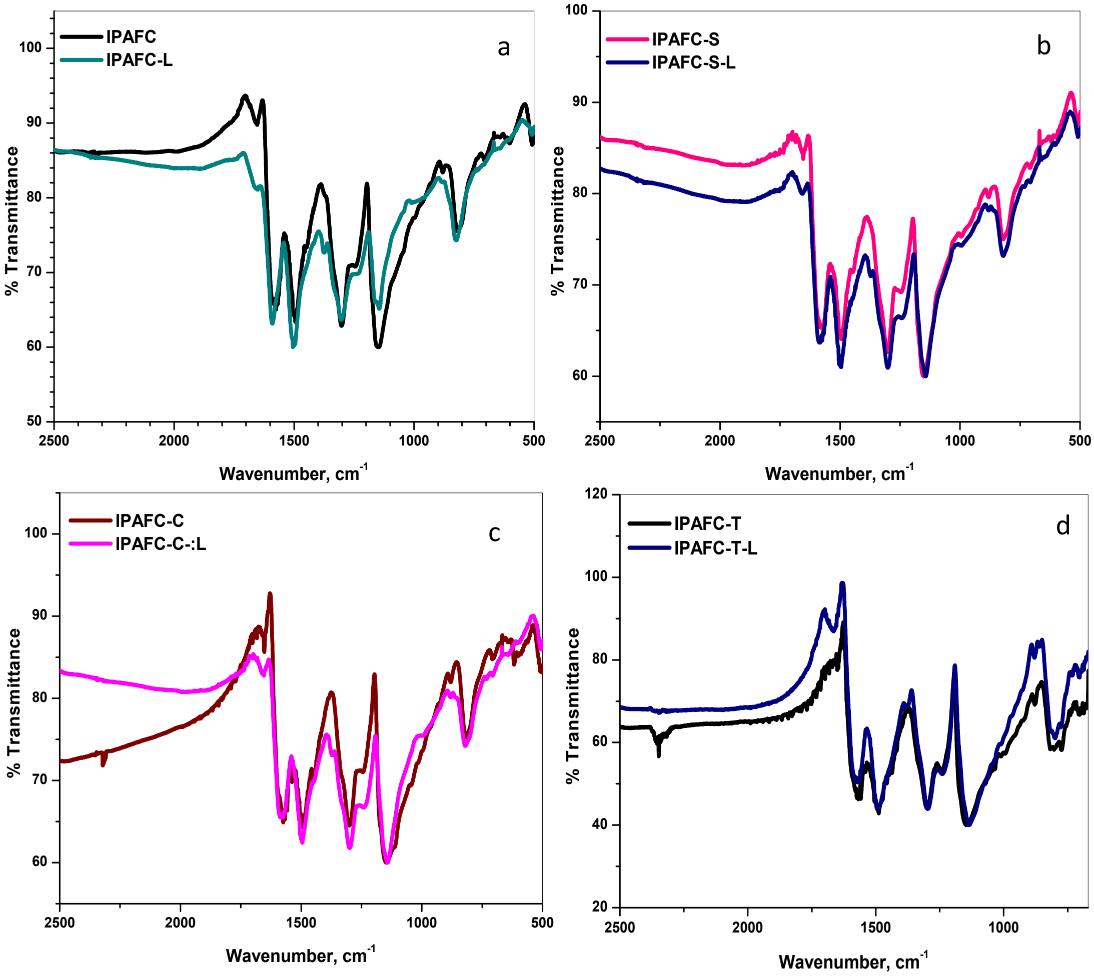


Figure 4.7: FTIR Spectra of un-leached and leached polymers of aniline-formaldehyde a) IPAFC b) IPAFC-S c) IPAFC-C d) IPAFC-T

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 (were B denotes benzenoid ring). The 1558–1560 cm^{-1} bands are assigned to –N=Q=N–structure (where Q denotes quinone) [Ding *et al.*, 2008; Trchova *et al.*, 2006; Shao *et al.*, 2009; Kuczynska *et al*., 2010; Hino *et al.*, 2006; Guimard *et al.*, 2007; Ayad *et al.*, 2009].

Incorporation of surfactants can be confirmed by the peaks in the range 2500-3200 cm^{-1}, which corresponds to the $-CH_2-$ stretching vibrations [Kuczynska *et al.*, 2010, Han *et al.*, 2013]. From the spectra of polymers of aniline synthesized in presence of surfactants, peaks can be observed in the region of 2500-3200 cm^{-1}. Removal of surfactants from the polymer can be confirmed by the absence of these peaks in the spectra of leached polymers.

In case of aniline formaldehyde polymer (Figure 4.7), an additional peak was observed at 1650 cm^{-1}. Surfactant based aniline formaldehyde polymer exhibits similar characteristic peaks as that of aniline [Ho *et al*., 2007]. Here also removal of surfactants for leached polymers can be confirmed by absence of peaks in the region 2500-3200 cm^{-1}.

4.4.3 Morphology by SEM

The SEM images of imprinted polymers of aniline in presence of surfactants are given in Figure 4.8. From the images effect of surfactants in directing the morphology can be understood. The morphology changed from spherical in imprinted polyaniline [Milja *et al.*, 2014] to aggregated fiber like structure.

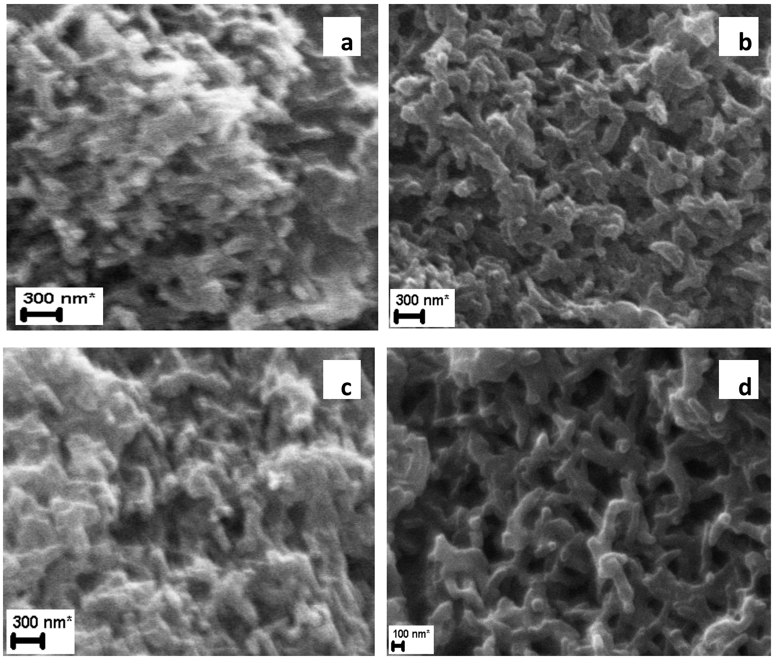


Figure 4.8: SEM images of polymers of aniline a) IPAN-S b) IPAN-C, c) IPAN-T d) IPAN-T-L

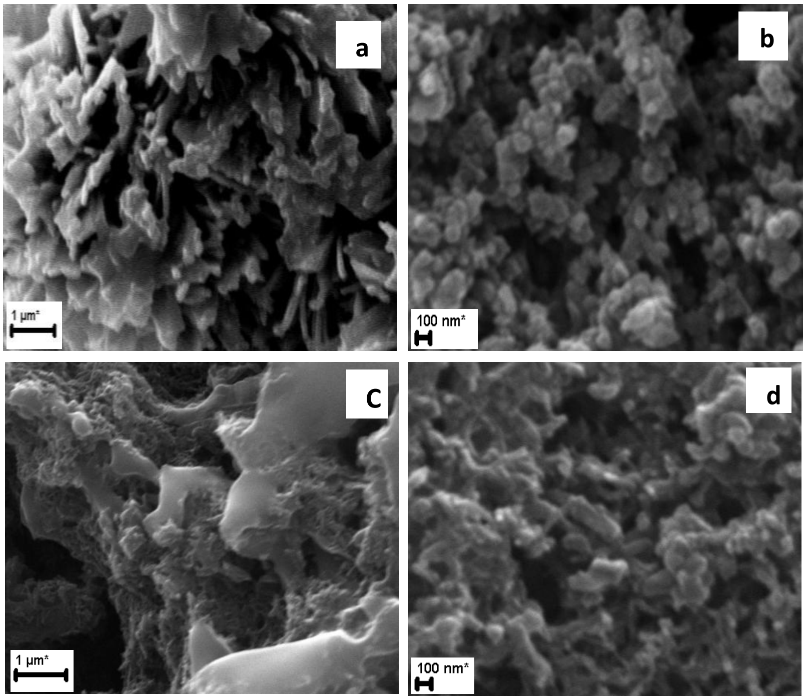


Figure 4.9: SEM images of polymers of aniline-formaldehyde a) IPAFC b) IPAFC- S c) IPAFC-C d) IPAFC-T

SEM image of IPAN-T (Figure 4.8 d) was taken after leaching in 1M HCL/ ethanol to confirm that leaching does not affect the morphology of the material. In case of imprinted aniline-formaldehyde polymer, a flower like morphology was obtained (Figure 4.9 a). But a bulk structure resulted in case of CTAB incorporated polymer (Figure 4.9 c) and aggregated fibers were obtained for polymers with SDS and TX-100 (Figure 4.9 b and c). Here also leaching did not affect the morphology (figure not shown).

4.4.4 Electrochemical characterisation

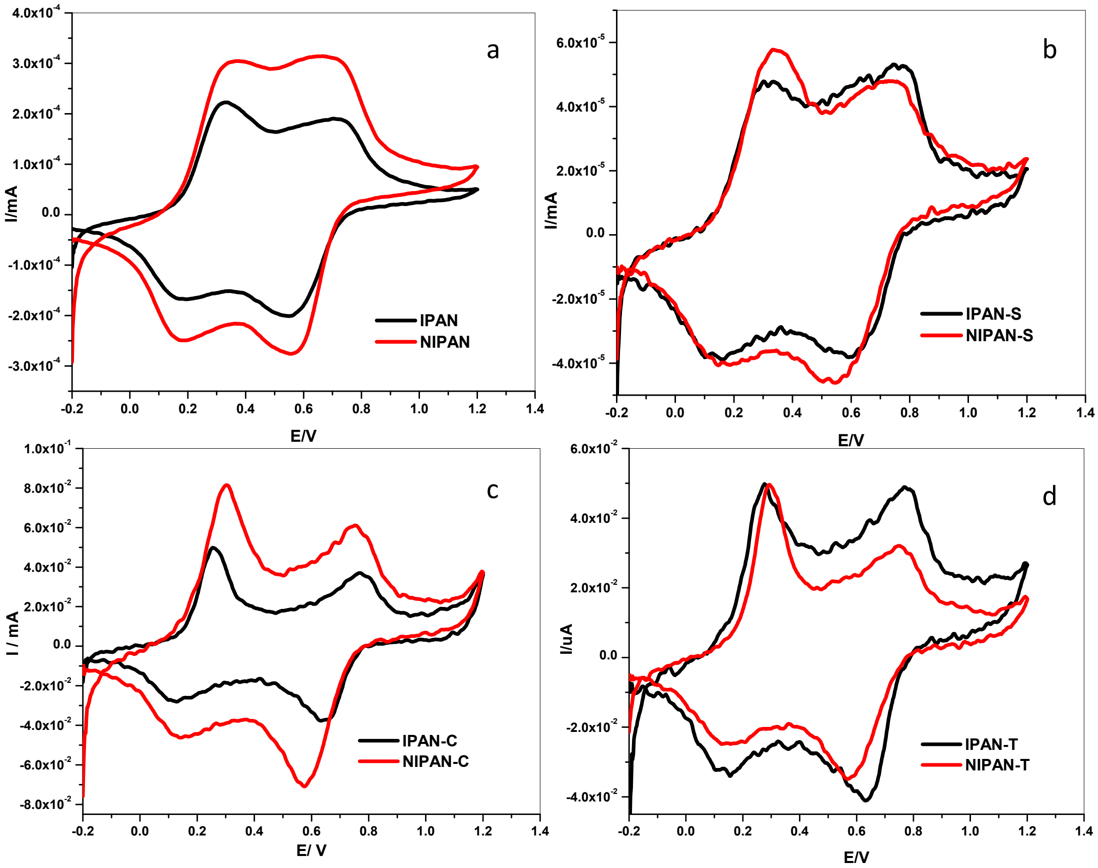


Figure 4.10: Cyclic voltammograms of imprinted and non-imprinted polymers of aniline a) IPAN b) IPAN-S c) IPAN-C, d) IPAN-T

Electrochemical characterisation of polymers of aniline was done by CV. The sample after dispersing in acetone was drop casted 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 potentials are given in Table 4.1.

Table 4.1: Red-ox 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
IPAN-S	0.300	0.114	0.774	0.608
NIPAN-S	0.327	0.147	0.760	0.576
IPAN-C	0.254	0.132	0.769	0.650
NIPAN-C	0.300	0.112	0.762	0.579
IPAN-T	0.266	0.110	0.755	0.637
NIPAN-T	0.288	0.148	0.745	0.581

In the voltammogram given in Figure 4.10, two redox peaks appears for all the polymers. The first one at~ 0.320 V is due to the formation of radical cations (polaronic emeraldine) and the second one at ~0.728 V is due to formation of di-radical dications by oxidation of polyaniline. 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 [Kolla *et al.*, 2005; Stilwell and Park, 1988; Nabid and Entezami, 2005; Yang and Ven, 1994]. But the CV of aniline formaldehyde polymers showed only two oxidation peaks and that too having very low current.

4.4.5 TG

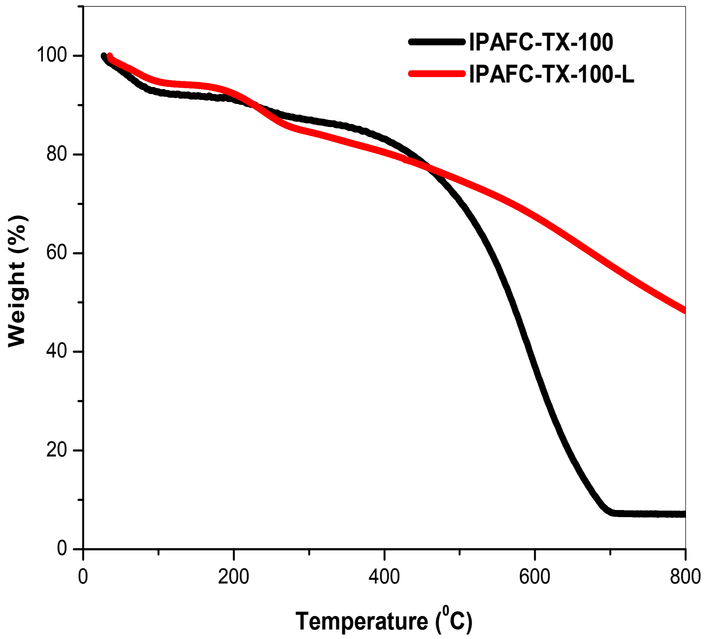


Figure 4.11: TG curves of IPAFC-T and IPAFC-T-L

Thermal stability of imprinted polymers was measured using TG (Figure 4.11). IPAFC-T and IPAFC-T-L were used for the study as they gave complete uranium removal. From the Figure, we can see that the curve for IPAFC-T-L is similar to that of imprinted polyanilines reported by Milja *et al.* [2014]. The first weight loss is observed at 100 ^{0}C due to desorption of water. The second weight loss starts at about 200 ^{0}C due to dedoping and the third weight loss from around 450 ^{0}C is due to the disintegration of polymer back bone [Ho *et al.,* 2007; Sun *et al.*, 2013; Wanga *et al.*, 2009]. In the case of IPAFC-T, though the weight loss occurs at the same temperatures, decomposition is not complete even at 800 ^{0}C. This may be due to the presence of uranyl ions.

4.4.6 Surface area and pore size analysis

Surface area and pore size analysis was carried out to check the effect of surfactants on the porosity of the materials synthesized in aniline-formaldehyde matrix. Leached materials were used for the study. The data obtained is compiled in Table 4.2.

Table 4.2: Surface area and pore size analysis

Material	BET surface area m^2/g	Pore volume cm^3/g	Average pore diameter (Å)
IPAFC	24.2	0.034	60.0
IPAFC-S	22.0	0.035	63.0
IPAFC-C	35.6	0.062	67.4
IPAFC-T	26.0	0.045	64.0

The data shows that surfactants do not have a significant effect on the surface area of aniline-formaldehyde polymer. Among the polymers, the one with CTAB has higher surface area, pore volume and average pore diameter. But complete removal was obtained with polymer synthesized in presence of TX-100. Hence it can be concluded that surface area does not have major effect on the uptake of imprinted polymers [Milja *et al.*, 2011, de Oliveira *et al.*, 2013]. But the high pore diameter obtained may be contributing towards the decrease in preconcentration time. Therefore we have provided a mechanism based on formation of binding sites in presence of surfactants for the observed results.

4.5 Solid phase extraction studies

The synthesized polymers were utilized for uranyl ion removal by SPE. The results compiled in Table 4.3 shows that imprinted polyanilines with surfactants give a fairly good uptake at neutral pH with 10^{-3} M ammonium acetate as buffer.

But it was observed that the percentage of removal of uranyl ion was not stable. It decreased with increasing days of storage. In order to obtain a stable material, aniline-formaldehyde ion imprinted polymer with and without surfactants were synthesized. Surfactant incorporated aniline formaldehyde polymers gave better results in terms of stability and percent removal. Complete removal of uranium was obtained with TX-100 incorporated aniline. Formaldehyde is generally added as a crosslinker during synthesis of aniline and here it helps in keeping the binding sites intact, hence increasing the stability of the material. A possible reason for the high percentage of uranium removal for the polymer synthesized with neutral surfactant can be given by considering the formation of nitrogen coordinated binding sites inside the polymer matrix as given in Figure 4.12.

Table 4.3: Solid phase extraction studies with imprinted polymers

		Removal (%)	
Matrix	Material	40 mg	50 mg
Polyaniline	IPAN	59.0	76.3
	IPAN-S	63.5	89.8
	IPAN-C	67.8	67.9
	IPAN-T	76.1	78.5
Aniline-Formaldehyde Copolymer	IPAFC	65.7	69.7
	IPAFC- S	80.0	84.4
	IPAFC-C	78.4	97.5
	IPAFC-T	82.5	>99

In case of cationic surfactant, the repulsion with positively charged uranyl ion can minimize its chance to get coordinate to nitrogen of aniline. For the anionic surfactant, its negative end can attract some uranyl cations reducing the possibility of nitrogen coordination. Since neutral surfactants are charge less they provide a better opportunity for nitrogen coordination and hence formation of more specific binding sites inside the polymer.

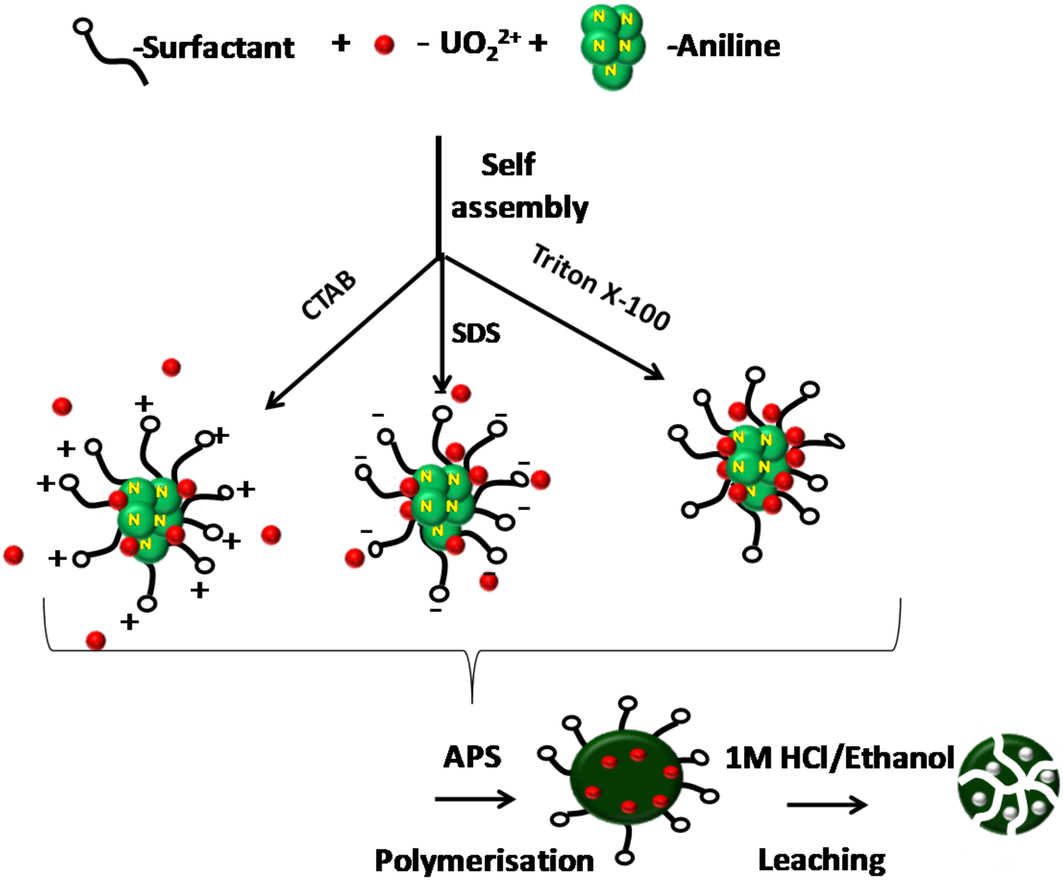


Figure 4.12: Scheme for uranyl ion imprinting in presence of surfactants

Dai *et al.*, [2000] had compared the removal efficiency of hierarchically imprinted polymers synthesized with different surfactants and had obtained >99% removal with all these polymers. They had imprinted after isolating the metal ion-ligand complex. Hence surfactants here do not have any role in formation of binding sites.

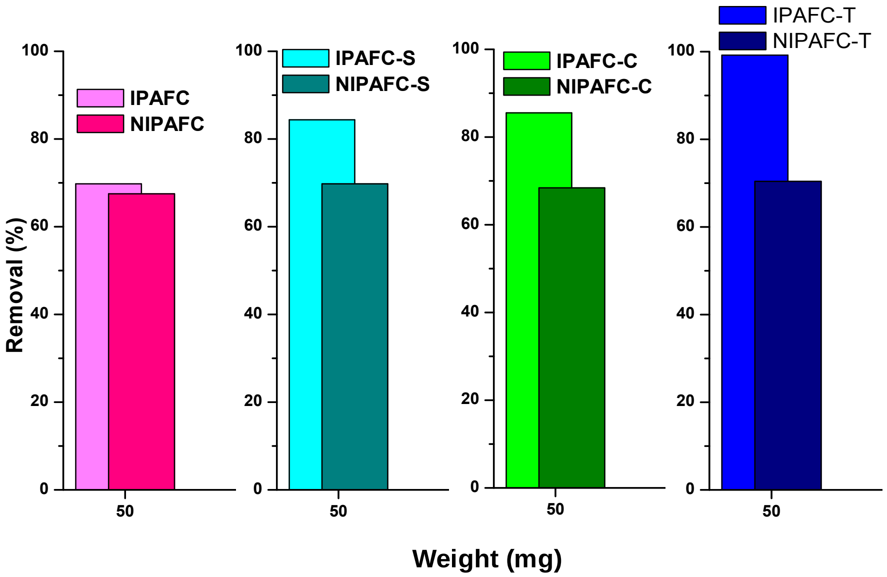


Figure 4.13: Comparison of removal efficiency of imprinted and non-imprinted polymers

All other reports use CTAB as the surfactant and comparison studies have not yet been carried out. SPE studies with non-imprinted polymers, given in Figure 4.13, also show that all of them exhibit almost similar removal efficiency as they are synthesized in the absence of uranyl ion. From the Figure it can be observed that the removal efficiency and imprinting effect is the highest for polymer synthesized with neutral surfactant TX-100.

Weight variation studies given in Table 4.3 shows that 50 mg of TX-100 incorporated aniline formaldehyde is the efficient material for removal of uranium. Removal efficiency at various pH were done with 50 mg of imprinted polymers in aniline and aniline formaldehyde matrix using 10^{-3} M ammonium acetate buffer.

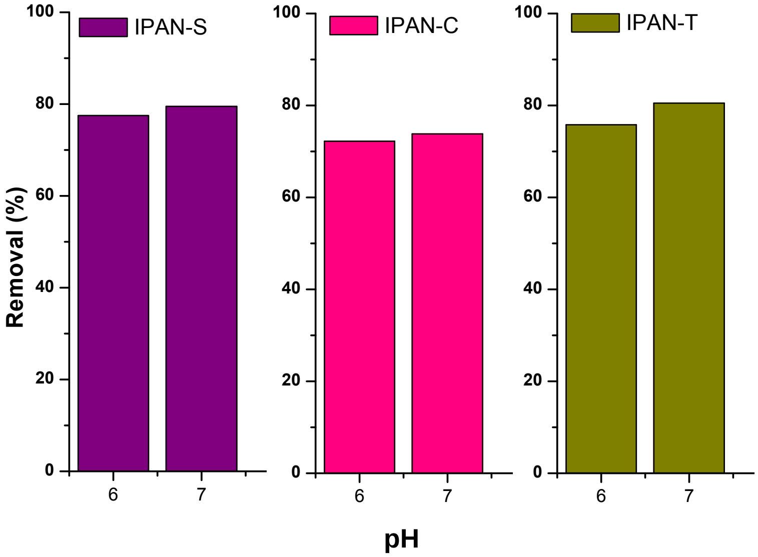


Figure 4.14: pH variation of imprinted polymer in aniline

The studies using imprinted polymers in aniline are given in Figure 4.14. We can see that polymer with TX-100 gives better removal at pH 7.0. But complete removal is not possible. The studies in aniline formaldehyde matrix (Figure 4.15) show that copolymer synthesized with TX-100 gives the desired results at pH 7.0.

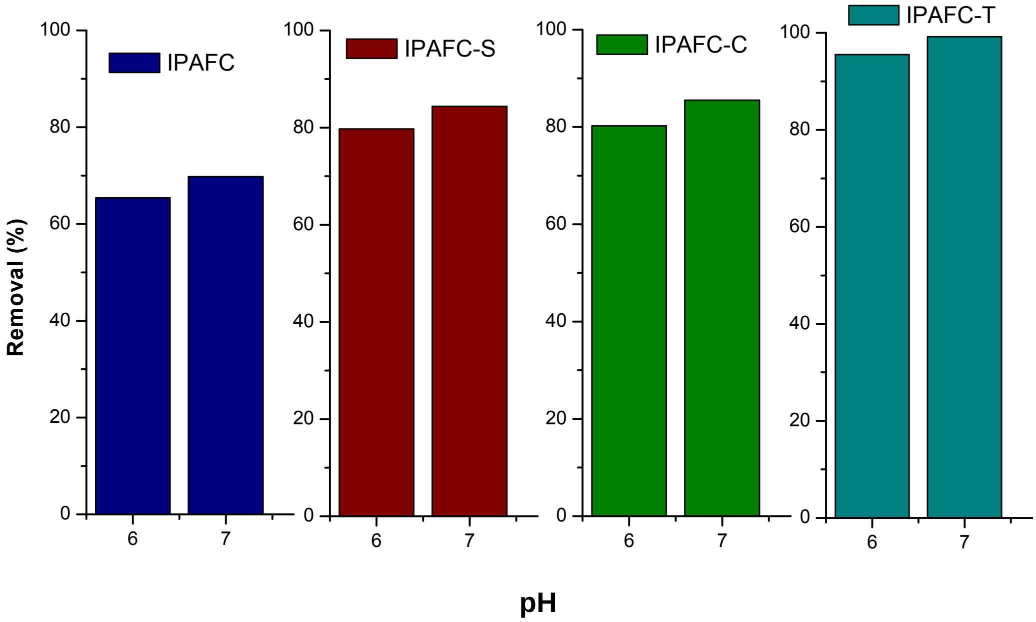


Figure 4.15: pH variation of imprinted polymer in aniline-fomaldehyde

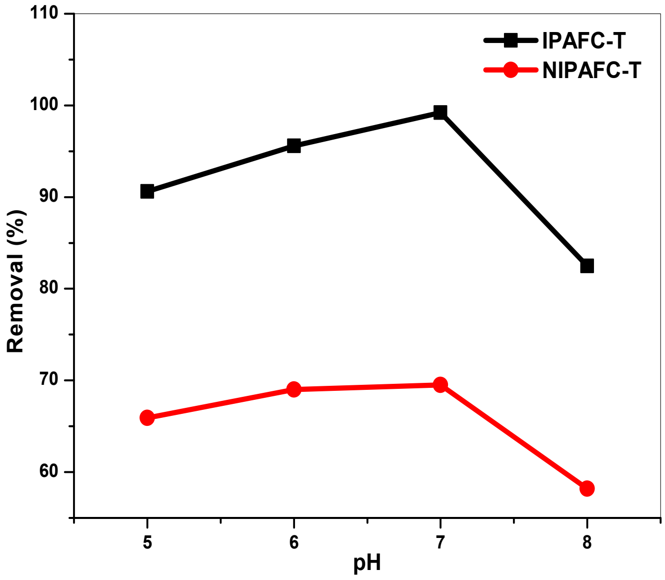


Figure 4.16: pH variation of IPAFC-T-L and NIPAFC-T-L

Hence pH variation studies of the corresponding imprinted and non-imprinted material were conducted at a broader range of 5.0-8.0 (Figure 4.16). From the graph significant imprinting effect can be observed at the measured range and it can be confirmed that neutral pH is the ideal condition for the material to remove uranium.

Further parameters like time of stirring (5, 10, 20 and 30 min) during the pre-concentration and elution of uranium were optimised by checking the removal efficiency of 100 µg of uranyl ion present in 100 mL of aqueous solutions using leached IPAFC-T. The results are given in Table 4.4. Within 5 minutes 95 % removal can be observed and complete removal can be achieved within 10 minutes. At optimised conditions the material exhibited an imprinting effect of 1.4.

Table 4.4: Optimisation of preconcentration and elution time of IPAFC-T-L

Parameters	Uranium removal (%)*
Preconcentration Time (min)	
5	95.5
10	>99
20	>99
30	>99
Elution Time(min)	
5	96.8
10	>99
20	>99
30	> 99

*-Average of duplicate measurements

4.6 Reusability studies

Reusability studies were carried out for five cycles under the optimised conditions. 50 mg of IPAFC-T-L at pH 7.0 was used. After the first cycle, the material was stirred for 30 min in pH 7.0 ammonium acetate buffer for neutralization, since elution is done using 1M HCl and was repeated for the remaining cycles. Even after five cycles, complete removal (>99 %) was obtained which shows the capability of the material in repeated removal of uranium from aqueous samples.

4.7 Retention capacity studies

The maximum amount of pre-concentrated uranyl ion/g of the imprinted material (retention/binding capacity of IPAFC-T-L) was calculated by saturating 50 mg of polymer particles with 10 mg L^{-1} of uranyl ion under optimal conditions. The maximum amount of uranyl ion preconcentrated was eluted with 1.0 M HCl and determined spectrophotometrically by using the arsenazo III procedure. The material gives a retention capacity of 88 μmol g^{-1} and 32 μmol g^{-1} at 10 mg L^{-1} for IPAFC-T-L and NIPAFC-T-L respectively. This shows that the material has high retention capacity which can be utilized for removal of uranium.

4.8 Selectivity studies

To evaluate the selectivity of the material for uranyl ion over other inorganic ions, 50 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 optimised conditions. The concentration of uranyl ion was then determined by spectrophotometry, after elution with 10 mL of 1M HCl.

The distribution ratio and selectivity coefficients of uranyl ion with respect to other inorganics using imprinted and non-imprinted particles are shown in Table 4.5. The selectivity coefficients of imprinted polymer for uranium are greater by 10^2 –10^3 fold as compared to other ions.

Table 4.5: Selectivity data of IPAFC-TX-100 and NIPAFC-TX-100

Metal ions	Distribution Ratio (D)		Selectivity Coefficient (S)		Imprinting coefficient (K')
	NIPAFC	IPAFC	NIPAFC	IPAFC	
UO_2^{2+}	3.0	99	-	-	-
Na^+	0.87	0.18	3.4	$5.2x10^2$	152.9
Ca^{2+}	0.83	0.19	3.6	$5.1x10^2$	141.7
Mg^{2+}	0.90	0.21	3.3	$4.5x10^2$	136.4
Cu^{2+}	0.92	0.45	3.2	$4.8x10^2$	150.0
Zn^{2+}	0.64	0.08	4.7	$9.8x10^3$	2085.1
Mn^{2+}	0.64	0.16	4.7	$3.9x10^2$	82.9
Fe^{3+}	0.70	0.16	4.3	$4.5x10^2$	104.6
Co^{2+}	0.70	0.22	4.5	$5.6x10^2$	124.4
Ni^{2+}	0.65	0.19	4.6	$1.6x10^3$	347.8

The imprinting coefficients for various co-existing species lie in the range 82.9 (Mn^{2+}) to 2085.1 (Zn^{2+}). From the results shown in Table 4.5, it is clear that uranyl ion can be removed selectively from several inorganic species present in dilute aqueous solutions.

4.9 Experimental

4.9.1 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. Formaldehyde was purchased from E Merck. All other chemicals used in this work are of reagent grade and were used as received. The solutions were prepared in distilled water.

4.9.2 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 was done using a TG/DTA-6200 (SII Nano Technology Inc., Japan). Surface area and pore size analysis was done using a BET surface area analyzer (Gemini 2360, Micromeritics, Norcross, USA).

4.9.3 Leaching of uranyl ion and surfactants from imprinted polymers

Uranyl ion was leached from the imprinted polymer by stirring the polymer in 1M HCl/EtOH for 48 h in order to remove the template and the surfactant molecule. After 48 h, the material was filtered and washed with large amount of distilled water and dried in an oven at 50 ^{0}C. 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).

4.9.4 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 µg 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.

4.9.5 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 [Snell, 1978].

4.10 Conclusions

A simple method is described for aqueous phase synthesis of nanostructured imprinted polymers in aniline and aniline-formaldehyde matrix using cationic, anionic and neutral surfactants. A comparative study with these hierarchically imprinted polymer materials for the removal efficiency of uranium from aqueous samples and a possible explanation for the observed results has been provided. Leaching out the surfactant after imprinting improved the overall kinetics as >95 % removal was attained within 5 minutes. Imprinted polymer synthesized with neutral surfactant was found to give good selectivity, retention capacity and imprinting effect. Therefore the material has immense potential to be utilised in removal of toxic uranium and other metal ion toxins for a cleaner and safer environment.

Summary of the thesis

Imprinting is a way of making artificial locks for molecular or ionic keys. Imprinted polymers have gained considerable attraction in research field due to their high selectivity for a specific target species and remarkable stability. These properties make them suitable for application in a variety of fields; from biomedical assays to solid phase extraction. There is a growing concern over the increasing pollution due to toxic inorganic metal ions in the environment. Among them uranium is a recent addition to the list. Though only weakly radioactive, U(VI) exerts chemical toxicity due to its solubility and mobility. Therefore we have exploited the possibilities of metal ion imprinted polymers for removal of uranium from aqueous samples using solid phase extraction.

The first chapter gives a brief introduction on the origin of imprinting. Different strategies of molecular imprinting, matrices and the components used have also been mentioned. This is followed by a description on the importance of uranium and a thorough literature survey on the use of imprinted polymers in uranium removal. The scope of the work involving the synthesis of various imprinted polymers for uranium detoxification is given towards the end of the chapter.

Second chapter points out the advantage of surface imprinting over commonly used method of bulk imprinting. Surface imprinted silica nanospheres with 8-hydroxyquinoline as complexing agent was synthesised and utilized for uranium removal from simulants of environmental samples. The virtues of using imprinted nanospheres over bulk particles are demonstrated using solid phase extraction studies. 20 mg of the material is sufficient for complete removal. The material works in the pH 5.0-7.0, has good selectivity towards uranium in presence of 10^2-10^3 fold interferents and a retention capacity of 23.3 mg g^{-1}. Application of the material in removal of uranium from simulants of sambhar salt lake and ground water is also provided.

Synthesis of imprinted polymer in aqueous phase using aromatic monomers has been brought out in chapter 3. The highlight of this work is the absence of crosslinker, organic solvents and vinylated compounds in the polymer recipe. Aniline and 8-hydroxyquinoline functionalised aniline were used as the functional monomers for imprinting uranium. The material works in the pH range 6.0 to 7.0 and selectively removes uranium in presence of 10^2-10^3 times of other inorganic metal ions. It has a retention capacity of 19.7 mg g^{-1} and is reusable. Complete removal of up to 1000 ppb of uranium is possible from aqueous samples with 40 mg of the polymer.

Fourth chapter utilizes the concept of hierarchical imprinting for synthesis of uranium imprinted polymers in presence of surfactants. Here also aqueous phase polymerisation was done with aniline and aniline-formaldehyde as the matrix. Effect of neutral (Triton X-100), anionic (sodium dodecyl sulphate) and cationic (cetyltrimethylammonium bromide) surfactants on the imprinted polymers of aniline and aniline-formaldehyde for removal of uranium by solid phase extraction has been studied. Complete removal is possible at neutral pH with 50 mg of the polymer synthesized in presence of neutral surfactant. This material also exhibits good selectivity in presence of 10^2-10^3 fold interfering metal ions and has a retention capacity of 20.9 mg g^{-1}. The polymer was found to be reusable for five cycles.

Recent thrust in research is for providing a cleaner and safer environment. Imprinted polymers can play an effective role in achieving the goal. The polymers synthesized in aniline have the advantage of providing a conductive matrix suitable for sensing applications. Another benefit of using aniline as the matrix is its solubility in organic solvents. This property can be utilized to study the binding events inside the polymer using spectroscopic methods. All the methods proposed here for synthesis of imprinted polymers has relevance in the field of detoxification of toxic metal ions from environmental samples and decontamination of metal biotoxins from biological fluids such as serum and urine.

References

Ahmadi, S. J., O. Noori-Kalkhoran, S. Shirvani-Arani, "Synthesis and characterization of new ion-imprinted polymer for separation and preconcentration of uranyl (UO_2^{2+}) ions", *J. Hazard. Mater.*, 175, **2010**, 193-197.

Alexander, C.; Andersson, H. S.; Andersson, L. I.; Ansell, R. J.; Kirsch, N.; Nicholls, I. A.; Mahony, J. O.; Whitcombe, M. J., "Molecular imprinting science and technology: a survey of the literature for the years up to and including 2003", *J. Mol. Recognit.*, 19, **2006**, 106-180.

Alizadeh, T.; Amjadi, S., "Preparation of nano-sized Pb^{2+} imprinted polymer and its application as the chemical interface of an electrochemical sensor for toxic lead determination in different real samples", *J. Hazard. Mater.,* 190, **2011**, 451-459.

Alizadeh, T.; Amjadi, S., "Synthesis of nano-sized Eu^{3+}-imprinted polymer and its application for indirect voltammetric determination of europium", *Talanta*, 106, **2013**, 431-439.

Alizadeh, T.; Ganjali, M. R.; Nourozi, P.; Zare, M.; Hoseini, M., "A carbon paste electrode impregnated with Cd^{2+} imprinted polymer as a new and high selective electrochemical sensor for determination of ultra-trace Cd^{2+} in water samples", *J. Electroanal. Chem.*, 657, **2011**, 98-106.

Alizadeh, T.; Ganjali, M. R.; Zare, M.; "Application of an Hg^{2+} selective imprinted polymer as new modifying agent for the preparation of a novel highly selective and sensitive electrochemical sensor for the determination of ultratrace mercury ions", *Anal. Chim. Acta*. 689, **2011**, 52–59.

Alizadeh, T.; Rashedi, M., "Synthesis of nano-sized arsenic-imprinted polymer and its use as As^{3+} selective ionophore in a potentiometric membrane electrode: Part 1", *Anal. Chim. Acta.*, 843, **2014**,7-17.

Alves, K. G. B.; Melo, E. F.; Andrade, C. A. S.; de Melo, C. P., "Preparation of fluorescent polyaniline nanoparticles in aqueous solutions", *J .Nanopart. Res.*, 15, **2013**, 1-11.

Araki, K.; Maruyama, T.; Kamiya, N.; Goto, M., "Metal ion-selective membrane prepared by surface molecular imprinting", *J. Chromatogr. B.*, 818, **2005,** 141-145.

Arshady, R.; Mosbach, K., **"**Synthesis of substrate-selective polymers by host-guest polymerization", *Macromol. Chem. Phy.*, 182, **1981**, 687-692.

Ashkenani, H.; Taher, M. A., "Determination of cadmium(II) using carbon paste electrode modified with a Cd-ion imprinted polymer", *Microchim. Acta.,* 178, **2012**, 53–60.

Ashkenani, H.; Taher, M. A., "Selective voltammetric determination of Cu(II) based on multiwalled carbon nanotube and nano-porous Cu-ion imprinted polymer*", J. Electroanal., Chem.* 683, **2012**, 80–87.

Asir S, Uzun L, Türkmen D, Say R, Denizli A., "Ion-selective imprinted superporous monolith for cadmium removal from human plasma", *Sep. Sci. Technol.*, 40, **2005**, 3167–3185.

Ayad, M. M.; Amer, W. A.; Stejskal, J., "Effect of iodine solutions on polyaniline films"*, Thin Solid Films,* 517, **2009**, 5969-5973.

Bae, S. Y.; Southard, G. L.; Murray, G. M., "Molecularly imprinted ion exchange resin for purification, preconcentration and determination of UO_2^{2+} by spectrophotometry and plasma spectrometry, *Anal. Chim. Acta.* 397, **1999**, 173-181.

Bahrami, A.; Besharati-Seidani, A.; Abbaspour, A.; Shamsipur, M., "A highly selective voltammetric sensor for sub-nanomolar detection of lead ions using a carbon paste electrode impregnated with novel ion imprinted polymeric nanobeads", *Electrochim. Acta*., 118, **2014,** 92-99.

Bajwa, S. Z.; Dumler, R.; Lieberzeit, P.A., "Molecularly imprinted polymers for conductance sensing of Cu^{2+} in aqueous solutions", *Sensor. Actuat. B. Chem.*, 192, **2014**, 522-528.

Belokon, Y.N.; Tararov, V.I.; Saveleva, T.F.; Vorobev, M.M.; Vitt, S.V.; Sizoy, V.F.; Sukhacheva, N.A.; Vasilev, G.V.; Belikov, V.M., "Memory of a polymeric matrix, stabilizing the initial conformation of potassium bis[N-(5-methacryloylamino)-salicylidene-(S)-norvalinato]-cobaltate(III) in the deuterium-exchange", *Macromol. Chem. Phy*., 184, **1983**, 2213-2223.

Bernal, J. P., Rodriguez De San Miguel, E.; Aguilar, J. C.; Salazar, G.; De Gyves, J., "Adsorption of metallic cations on silica gel-immobilized 8-hydroxyquinoline", *J. Sep. Sci. Tech.,* 35, **2000**, 1661-1679.

Bi, X.; Yang, K.L., "Complexation of copper ions with histidine-containing tripeptides immobilized on solid surfaces", *Langmuir*, 23, **2007**, 11067-11073.

Biju, V. M.; Gladis, J. M.; Rao, T. P., "Ion imprinted polymer particles: synthesis, characterization and dysprosium ion uptake properties suitable for analytical applications", *Anal. Chim. Acta*., 478, **2003**, 43-51.

Birlik E, Ersöz A, Açikkalp E, Denizli A, Say R., "Cr(III)-imprinted polymeric beads: Sorption and preconcentration studies", *J. Hazard. Mater*., **2007**, 140, 110–116.

Boeva, Z. A.; Sergeyev, V. G., "Polyaniline: synthesis, properties, and application", *Polym. Sci. Ser. C.*, 56, **2014**, 144–153.

Boonpangrak, S.; Whitcombe, M. J.; Prachayasittikul, V.; Mosbach, K.; Ye, L., "Preparation of molecularly imprinted polymers using nitroxide-mediated living radical polymerization", *Biosens. Bioelec.*, 22, **2006**, 349-354.

Branger, C.; Meouche, W.; Margaillan, A., "Recent advances on ion-imprinted polymers", *React. Func. Polym.*, 73, **2013**, 859-875.

Braus, H.; Middleton F.M.; Walton, G., "Organic chemical compounds in raw and filtered surface waters", *Anal. Chem.*, 23, **1951**, 1160-1164.

Buhani; Narsito; Nuryono; Kunarti, E.S., "Production of metal ion imprinted polymer from mercapto-silica through sol-gel process as selective adsorbent of cadmium", *Desalination*, 251, **2010**, 83-89.

Burckhalter, J. H.; Leib, R. I., "Amino- and chloromethylation of 8-quinolinol. Mechanism of preponderant ortho substitution in phenols under mannich conditions", *J. Org. Chem.* 26, **1961**, 4078-4083.

Burns, P. C.; Ewing, R. C.; Miller, M. L., "Incorporation mechanisms of actinide elements into the structures of U^{6+} phases formed during the oxidation of spent nuclear fuel", *J. Nucl. Mat.*, 245, **1997**, 1-9.

Candan, N.; Tüzmen, N.; Andaç, M.; Andaç, C. A.; Say, R. I.;, Denizli, A., "Cadmium removal out of human plasma using ion-imprinted beads in a magnetic column", *Mater. Sci. Eng.: C* , 29, **2009**, 144-152.

Cataldo, F.; Maltese, P., "Synthesis of alkyl and N-alkyl-substituted polyanilines", *Eur. Polym. J.,* 38, **2002**, 1791-1803.

Chanda, M.; Rempel, G. L., "Enhanced copper selectivity and faster sorption kinetics of poly(4-vinylpyridine) crosslinked in presence of copper(II) as template on silica gel", *React. Polym.*, 16, **1992** , 149-158.

Chang, X. J.; Jiang, N.; Zheng, H.; He, Q.; Hu, Z.; Zhai, Y. H.; Cui, Y. M., "Solid-phase extraction of iron(III) with an ion-imprinted functionalized silica gel sorbent prepared by a surface imprinting technique", *Talanta*, 71, **2007**, 38-43.

Chang, X. J.; Wang, X. Y.; Jiang, N.; He, Q.; Zhai, Y. H.; Zhu, X. B.; Hu, Z., "Silica gel surface-imprinted solid-phase extraction of Zr(IV) from aqueous solutions", *Micro. chim. Acta*, 162, **2008,** 113-119.

Chen, J. H.; Li, G. P.; Liu, Q. L.; Ni, J. C.; Wu, W. B.; Lin, J. M., "Cr(III) ionic imprinted polyvinyl alcohol/sodium alginate (PVA/SA) porous composite membranes for selective adsorption of Cr(III) ions", *Chem. Eng. J.*, 165, **2010**, 465-473.

Chen, L.; Xuab, S.; Lia, J., "Recent advances in molecular imprinting technology: current status, challenges and highlighted applications", *Chem. Soc. Rev.*, 40, **2011**, 2922-2942.

Chowdhury, P.; Saha. B.; "Potassium dichromate initiated polymerization of aniline", *Indian J. Chem. Technol.*, 12, **2005**, 671-675.

Craft, E.; Abu-Qare, A.; Flaherty, M.; Garofolo, M.; Rincavage, H.; Abou-Donia, M., "Depleted and natural uranium: chemistry and toxicological effects". *J. Toxicol. Environ. Health B Crit. Rev.*, 7, **2004**, 297-317.

Cui, A.; Singh, A.; Kaplan, D. L., "Enzyme-Based Molecular Imprinting with Metals", *Biomacromolecules*, 3, **2002**, 1353-1358.

Dai, S., Shin, Y.S., Barnes, C.E., Toth, L.M., "Enhancement of uranyl adsorption capacity and selectivity on silica sol-gel glasses via molecular imprinting", *Chem. Mater.*, 9, **1997**, 2521-2525.

Dai, S.; Barleigh, M. C.; Shin, Y., "Imprint-coating synthesis of selective functionalized ordered mesoporous sorbents for separation and sensors", US Patent 6,251,280, **2001**.

Dai, S.; Burleigh, M. C.; Ju, Y.H.; Gao, H. J.; Lin, J. S.; Pennycook, S. J.; Barnes, C.E.; Xue, Z.L., "Hierarchically imprinted sorbents for the separation of metal ions", *J. Am. Chem. Soc.,* 122, **2000**, 992-993.

Dakova, I.; Karadjova, I.; Georgieva, V.; Georgiev, G., "Ion-imprinted polymethacrylic microbeads as new sorbent for preconcentration and speciation of mercury", *Talanta*, 78, **2009**, 523-529.

Dam, H. A.; Kim, D., "Selective copper(II) sorption behavior of surface-imprinted core-shell-type polymethacrylate microspheres", *Ind. Eng. Chem. Res.*, 48, **2009**, 5679-5685.

Daniel, S.; Babu, P. E. J.; Rao, T. P., "Preconcentrative separation of palladium(II) using palladium(II) ion-imprinted polymer particles formed with different quinoline derivatives and evaluation of binding parameters based on adsorption isotherm models", *Talanta,* 65, **2005**, 441-452.

de Oliveira, F. M.; Somera, B.F.; Ribeiro, E. S.; Segatelli, M. G.; Yabe, M. J. S.; Galunin, E.; Tarley, C. R. T., "Kinetic and isotherm studies of Ni^{2+}adsorption on poly (methacrylic acid) synthesized through a hierarchical double-imprinting method, using a Ni^{2+} ion and cationic surfactant as templates". *Ind. Eng. Chem. Res*., 52, **2013**, 8550–8557.

Demiralay, E. Ç.; Andac, M.; Say, R.; Alsancak, G.; Denizli, A., "Nickel(II)-imprinted monolithic columns for selective nickel recognition", *J. App. Polym. Sci*., 117, **2010**, 3704-3714.

Deng, H. N.; Gao, L. Y.; Zhang, S. F.; Yuan, J. S., "Preparation of a Copper Ion Selective Membrane by Surface-Modified Molecular Imprinting", *Ind. Eng. Chem. Res*., 51, **2012**, 14018-14025.

Ding, H.; Shen, J.; Wan, M.; Chen, Z., "Formation mechanism of polyaniline nanotubes by a simplified template-free method". *Macromol. Chem. Phys*. 209, **2008,** 864–871.

Domingo, J. L., "Reproductive and developmental toxicity of natural and depleted uranium: A review", *Reprod. Toxicol.,* 15, **2001**, 603–609.

Ebrahimzadeh, H.; Moazzen, E.; Amini, M. M.; Sadeghi, O., **"**Novel magnetic ion imprinted polymer as a highly selective sorbent for extraction of gold ions in aqueous samples", *Anal. Methods*, 4, **2012**, 3232-3237.

El-Dib, F. I.; Sayed, W. M.; Ahmed, S. M.; Elkodary, M., "Synthesis of polyaniline nanostructures in micellar solutions", *J. App. Polym. Sci*., 124, **2012**, 3200-3207.

Ersöz, A.; Say, R.; Denizli, A., "Ni(II) ion-imprinted solid-phase extraction and preconcentration in aqueous solutions by packed-bed columns", *Anal. Chim. Acta,* 502, **2004**, 91-97.

Fan, Z. F., "Hg(II)-imprinted thiol-functionalized mesoporous sorbent micro-column preconcentration of trace mercury and determination by inductively coupled plasma optical emission spectrometry", *Talanta*, 70, **2006**, 1164-1169.

Fang, G. Z.; Tan, J.; Yan, M. P., "An ion-imprinted functionalized silica gel sorbent prepared by a surface imprinting technique combined with a sol-gel process for selective solid-phase extraction of cadmium(II)", *Anal. Chem*. 77, **2005**, 1734-1739.

Fasihi, J.; Ammari Alahyari, S.; Shamsipur, M.; Sharghi, H., Charkhi, A., **"**Adsorption of uranyl ion onto an anthraquinone based ion-imprinted copolymer", *React. Func. Polym*., 71, **2011**, 803-808.

Fletcher, K. E.; Boyano, M. I.; Thomas, S. H.; Wu, Q.; Kemner, K. M.; Loffler, F. E., "U(VI) reduction to mononuclear U(IV) by desulfitobacterium species", *Environ. Sci. Technol*., 44, **2010**, 4705–4709.

Fu, X. C.; Wu, J.; Nie, L.; Xie, C. G.; Liu, J. H.; Huang, X. J., "Electropolymerized surface ion imprinting films on a gold nanoparticles/single-wall carbon nanotube nanohybrids modified glassy carbon electrode for electrochemical detection of trace mercury(II) in water", *Anal. Chim. Acta*., 720, **2012**, 29-37.

Fujii, Y.; Matsutani, K.; Kikuchi, K., **"**Formation of a specific coordination cavity for a chiral amino-acid by template synthesis of a polymer Schiff base cobalt(III) complex", *J. Chem. Soc. Chem. Comm*., 7, **1985,** 415-417.

Gao, B. J.; An, F. Q.; Zhu, Y., **"**Novel surface ionic imprinting materials prepared via couple grafting of polymer and ionic imprinting on surfaces of silica gel particles", *Polymer*, 48, **2007**, 2288-2297.

Gao, D.; Z. Zhang, M.; Wu, C.; Xie, G.; Guan, D.; Wang, A., "Surface functional monomer-directing strategy for highly dense imprinting of TNT at surface of silica nanoparticles", *J. Am. Chem. Soc*., 129, **2007**, 7859-7866.

Gawin, M.; Konefal, J.; Trzewik, B.; Walas, S.; Tobiasz, A.; Mrowiec, H.; Witek, E., "Preparation of a new Cd(II)-imprinted polymer and its application to determination of cadmium(II) via flowinjection-flame atomic absorption spectrometry", *Talanta,* 80, **2010**, 1305-1310.

Germiniano, T. O.; Corazza, M. Z.; Segatelli, M. G.; Ribeiro , E. S.; Yabe, M. J. S.; Galunin, E.; Tarley, C. R. T., "Synthesis of novel copper ion-selective material based on hierarchically imprinted cross-linked poly(acrylamide-co-ethylene glycol dimethacrylate)", *React. Func. Polym*., 82, **2014**, 72-80.

Gilman, A. P.; Villencuve, D. C.; Seccours, V. E.; Yagminas, A. P.; Tracy, B. L.; Quinn, J. M.; Valli, V. E.; Willes, R. J.; Moss, M. A., "Uranyl nitrate: 28 days and 91 days toxicity studies in the Sprague-Dawley rat", *Toxicol. Sci.*, 41, **1998**, 117-128.

Gladis, J. M.; Rao, T. P., "Synthesis and analytical applications of uranyl ion imprinted polymer particles", *Anal. Lett.*, 36, **2003**, 2107-2121.

Gladis, J. M.; Rao, T.P., "Effect of porogen type on the synthesis of uranium ion imprinted polymer materials for the preconcentration/separation of traces of uranium", *Micro. Chim. Acta*, 146, **2004**, 251-258.

Gospodinova, N.; Terlemezyan, L., "Conducting polymers prepared by oxidative polymerization: polyaniline", *Prog. Polym. Sci.*, 23, **1998**, 1443–1484.

Greibrokk, T.; Sellergren, B., "Molecular imprinting in separation science", *J. Sep.Sci.*, 32, **2008**, 3263-3264.

Guimard, N. K.; Gomez, N.; Schmidt, C. E., "Conducting polymers in biomedical engineering"*, Prog. Polym. Sci.* 32, **2007**, 876-921.

Hamaya, T.; Hiratani, K.; Ohashi, K., "Ultraviolet spectrophotometric studies of the reactivity of a water-soluble polymer containing pendant 8-hydroxy quinoline moieties with metal ions", *Macromol. Chem. Phys.* 195, **1994**, 2739-2746.

Han, J.; Dai,J.; Zhou, C.; Guo, R., "Dilute cationic surfactant-assisted synthesis of polyaniline nanotubes and application as reactive support for various noble metal nanocatalysts", *Polym. Chem.*, 4, **2013**, 313-321.

Haupt, K.; Mosbach, K., "Molecularly Imprinted Polymers and their use in biomimetic sensors", *Chem. Rev.*, 100, **2000**, 2495-2504.

He, Q.; Chang, X.J.; Zheng, H.; Jiang, N.; Wang, X.Y., "Determination of chromium(III) and total chromium in natural waters using a surface ion-imprinted silica gel as selective adsorbent", *Int. J. Environ. Anal. Chem.*, 88, **2008**, 373-384.

Heeger, A. J., "Semiconducting and metallic polymers: The fourth generation of polymeric materials", *Angew. Chem., Int. Ed.*, 40, **2001**, 2591–2611.

Hino, T.; Namiki, T.; Kuramoto, N., "Synthesis and characterization of novel conducting composites of polyaniline prepared in the presence of sodium dodecylsulfonate and several water soluble polymers", *Synth. Met.*, 156, **2006**, 1327-1332.

Ho, K. S.; Huang, Y. J.; Kuo, C. W.; Lee, S. W.; Hsieh, T. H.; Chuang, C. N., "Effect of aniline-formaldehyde resin on the reduced conjugation length of doped polyaniline: thermal studies", *J. App. Polym. Sci.,*103, **2007**, 2120-2128.

Hoai, N. T.; Yoo, D. K.; Kim, D., "Batch and column separation characteristics of copper-imprinted porous polymer micro-beads synthesized by a direct imprinting method:, *J. Hazard. Mater.,* 173, **2010**, 462-467.

Homayon, A. P.; Marjaneh, S. Z.; Simin. T., "Nickel adsorption from environmental samples by ion imprinted aniline -formaldehyde polymer", *Iran. J. Chem. Chem. Eng.,* 31, **2012**, 35-43.

Huang, J., "Syntheses and applications of conducting polymer polyaniline nanofibers", *Pure Appl. Chem.*, 78, **2006**, 15-27.

Huang, L. M.; Wen, T. C.; Gopalan, A., "Synthesis and characterization of soluble conducting poly(aniline-co-2, 5-dimethoxyaniline)", *Mater. Lett,.* 57, **2003**, 1765-1774.

Huo, H. Y.; Su, H. J.; Tan, T. W., "Adsorption of Ag^+ by a surface molecular-imprinted biosorbent", *Chem. Eng. J.*, 150, **2009**, 139-144.

Hwang, K. O.; Yakura, Y.; Ohuchi, F. S.; Sasaki, T., "Template-assisted assembly of metal binding sites on a silica surface", *Mat. Sci. Eng. C-Bio S.*, 3, **1995**, 137-141.

Ishikawa, S. I.; Suyama, K.; Isamu, S., "Biosorption of actinides from dilute waste actinide solution by egg-shell membrane", *Appl. Biochem. Biotech.*, 78, **1999**, 521-533.

James, D.; Gladis, J. M.; Pandey, A. K.; Naidu, G. R. K.; Rao T. P., "Design of two-dimensional biomimetic uranyl optrode and its application to the analysis of natural waters", *Talanta*, 74, **2008**, 1420-1427.

James, D.; Venkateswaran, G.; Rao, T. P., "Removal of uranium from mining industry feed simulant solutions using trapped amidoxime functionality within a mesoporous imprinted polymer material", *Micropor. Mesopor. Mat.* 119, **2009**, 165-170.

Jerome, C.; Martinot, L.; Jerome, R., "Binding and release of metallic cations by a polyaniline-based resin", *Radiochim. Acta.*, 88, **2000**, 39-46.

Jiang, N.; Chang, X. J.; Zheng, H.; He, Q.; Hu, Z., "Selective solidphase extraction of nickel(II) using a surface-imprinted silica gel sorbent", *Anal. Chim. Acta,* 577, **2006**, 225-231.

Jiang, W.; Su, H. J.; Huo, H. Y.; Tan, T. W., "Synthesis and properties of surface molecular imprinting adsorbent for removal of Pb^{2+}", *Appl. Biochem. Biotechnol.,* 160, **2010**, 467-476.

John, J. M.; Nigel, P. S.; Saunders, G. D.; Walton, P. H., "Detection and extraction of an ion in a solution, particularly uranium ion". European Patent 1019555B1, **1999**.

Kabanov, V. A.; Efendiev, A. A.; Orujev, D. D., "Complex forming polymeric sorbents with macromolecular arrangement favourable for ion sorption", *J. Appl. Polym. Sci*., 24, **1979**, 259-267.

Kala, R.; Biju, V. M.; Rao, T. P., "Synthesis, characterization, and analytical applications of erbium(III) ion imprinted polymer particles prepared via [gamma]-irradiation with different functional and crosslinking monomers", *Anal. Chim. Acta*., 549, **2005**, 51-58.

Kato, M.; Nishide, H.; Tsuchida, E., "Complexation of metal-ion with poly(1-vinylimidazole) resin prepared by radiation- induced polymerization with template metal-ion", *J. Polym. Sci. Polym. Chem. Ed*., 19, **1981**, 1803-1809.

Kimaro, A.; Kelly, L. A.; Murray, G. M., "Molecularly imprinted ionically permeable membrane for uranyl ion", *Chem. Comm*., 14, **2001**, 1282-1283.

Kolla, H. S.; Surwade, S. P.; Zhang, X.; MacDiarmid, A. G.; Manohar, S. K., "Absolute molecular weight of polyaniline", *J. Am. Chem. Soc*. 127, **2005**, 16770-16771.

Kuchen, W.; Schram, J., "Metal-ion-selective exchange resins by matrix imprint with methacrylates", *Angew. Chem. Int. Ed*., 27, **1988**, 1695-1697.

Kuczynska, A.; Uygun, A.; Kaim, A.; Wilczura-Wachnik, H.; Gul Yavuzb, A.; Aldissi, M., "Effects of surfactants on the characteristics and biosensing properties of polyaniline", *Polym. Int.*, 59, **2010**, 1650-1659.

Kushwaha, S.; Sudhakar, P. P., "Noncovalent surface grafting of uranium complexed cucurbit[5]uril oligomer onto palm shell powder: a novel approach for selective uranyl ion extraction", *Analyst*, 137, **2012**, 3242-3245.

Lan, C. R.; Yang, M. H., "Synthesis, properties and applications of silica-immobilized 8-quinolinol part 1. Characterization of silica-immobilized 8-quinolinol synthesized via a mannich reaction", *Anal. Chim. Acta*, 287, **1994**, 101-109.

Li C. X.; Pan J. M.; Gao J.; Yan Y. S., "A novel Ce(III)-imprinted polymer supported by attapulgite: synthesis, characterization and adsorption behaviours towards Ce(III) in aqueous solution", *Int. J. Mater. Struct. Integr*. 3, **2009**, 294–308.

Li, F.; Jiang, H. Q.; Zhang, S. S., "An ion-imprinted silica-supported organic-inorganic hybrid sorbent prepared by a surface imprinting technique combined with a polysaccharide incorporated sol-gel process for selective separation of cadmium(II) from aqueous solution", *Talanta*, 71, **2007**, 1487-1493.

Li, H. L.; Perkas, N.; Li, Q. L.; Gofer, Y.; Koltypin Y.; Gedanken, A., "Improved silanization modification of a silica surface and its application to the preparation of a silica-supported polyoxometalate catalyst", *Langmuir*, 19, **2003**, 10409-10413.

Li, Q.; Su, H. J.; Li, J.; Tan, T. W., "Application of surface molecular imprinting adsorbent in expanded bed for the adsorption of Ni^{2+} and adsorption model", *J. Environ. Manag*., 85, **2007**, 900-907.

Lin, C. R.; Wang, H. Q.; Wang, Y. Y.; Cheng, Z. Q., "Selective solid-phase extraction of trace thorium(IV) using surface-grafted Th(IV)-imprinted polymers with pyrazole derivative", *Talanta*, 81, **2010**, 30–36.

Liska, I., "Fifty years of solid-phase extraction in water analysis – historical development and overview", *J. Chromatogr. A*, 885, **2000**, 3–16.

Liska, I., "On-line *versus* off-line solid-phase extraction in the determination of organic contaminants in water: Advantages and limitations", *J. Chromatogr. A,* 655, **1993**, 163-176.

Liu, G.; Freund, M. S., "New Approach for the Controlled Cross-Linking of Polyaniline: Synthesis and Characterization", *Macromolecules*, 30, **1997,** 5660-5665.

Liu, Y. H., Cao, X. H., Hua, R., Wang, Y. Q., Liu, Y. T., Pang, C., Wang, Y., "Selective adsorption of uranyl ion on ion-imprinted chitosan/PVA cross-linked hydrogel", *Hydrometallurgy,* 104, **2010**, 150-155.

Liu, Y. H.; Cao, X. H.; Le, Z. G.; Luo, M. B.; Xu, W. Y.; Huang, G. L., "Pre-Concentration and determination of trace uranium(VI) in environments using ion-imprinted chitosan resin via solid phase extraction", *J. Braz. Chem. Soc.*, 21, **2010**, 533-540.

Lopes Pinheiro, S. C.; Descalzo, A. B.; Raimundo, I. M.; Orellana, G.; Moreno-Bondi, M. C., "Fluorescent ion-imprinted polymers for selective Cu(II) optosensing", *Anal. Bioanal. Chem*., 402, **2012**, 3253-3260.

Lu, Y. K.; Yan, X. P., "An imprinted organic-inorganic hybrid sorbent for selective separation of cadmium from aqueous solution", *Anal. Chem*., 76, **2004**, 453-457.

MacDiarmid, A. G., "Synthetic metals": a novel role for organic polymers", *Angew. Chem., Int. Ed*., 40, **2001**, 2581–2590.

MacDiarmid, A. G.; Chiang, J. C.; Halpen, M.; Huang, W. S.; Mu, S. L.; Nanaxakkara, L. D.; Somasli, N. L.; Wu, W.; Yaniger, S. I., ""Polyaniline": Interconversion of Metallic and Insulating Forms". *Mol. Cryst. Liq. Cryst*., 121, **1985**, 173-180.

Metilda, P. J. M. Gladis, G. Venkateswaran, T. Prasada Rao, "Investigation of the role of chelating ligand in the synthesis of ion-imprinted polymeric resins on the selective enrichment of uranium(VI)". *Anal. Chim.Acta*. 587, **2007**, 263-271.

Metilda, P.; Gladis, J. M.; Rao, T. P., "Influence of binary/ternary complex of imprint ion on the preconcentration of uranium(VI) using ion imprinted polymer materials", *Anal. Chim. Acta*., 512, **2004**, 63-73.

Milja, T. E.; Krupa, V. S.; Rao T. P., "Synthesis, characterization and application of uranyl ion imprinted polymers of aniline and 8-hydroxy quinoline functionalized aniline", *RSC Advances*, 4, **2014**, 30718-30724.

Milja, T. E.; Prathish,K. P.; Rao T. P., "Synthesis of surface imprinted nanospheres for selective removal of uranium from simulants of sambhar salt lake and ground water", *J. Hazard. Mat.*, 188, **2011**, 384–390.

Monreal, M. J.; Diaconescu, P. L., "The riches of uranium", *Nat. Chem*., 2, **2010**, 424.

Mosbach, K., "Molecular Imprinting", *Trends. Biochem. Sci*., 19, **1994**, 9-14.

Murray, G. M., "Polymer based permeable membrane for removal of ions", **2004**, US6780323B2.

Murray, G. M.; Jenkins, A. L.; Bzhelyansky, A.; Uy, O. M., "Molecularly imprinted polymers for the selective sequestering and sensing of ions", *Johns Hopkins Appl. Tech. Digest*, 18, **1997**, 464-472.

Nabid, M. R.; Entezami, A. A., "Comparative study on the enzymatic polymerization of N-substituted aniline derivatives", *Polym. Adv. Techn.* 16, **2005**, 305-309.

Nacano, L. R.; Segatelli, M. G.; Tarley, C. R. T., "Selective sorbent enrichment of nickel ions from aqueous solutions using a hierarchically hybrid organic-inorganic polymer based on double imprinting concept", *J. Braz. Chem. Soc.*, 21, **2010**, 419-430.

Nancharaiah, Y. V.; Joshi, H. M.; Mohan, T. V. K.; Venugopalan, V. P.; Narasimhan, S. V., "Aerobic granular biomass: a novel biomaterial for efficient uranium removal", *Curr. Sci*. 91, **2006**, 503-508.

Ng, S. M.; Narayanaswamy, R., “Fluorescence sensor using a molecularly imprinted polymer as a recognition receptor for the detection of aluminium ions in aqueous media”, *Anal. Bioanal. Chem*., 386, **2006**, 1235-1244.

Nishide, H.; Tsuchida, E., “Selective adsorption of metal ions on poly(4-vinyl pyridine) resins in which the ligand chain is immobilized by crosslinking”, *Makromol. Chem*., 177, **1976**, 2295-2310.

Ober, C. K.; Cheng, S. Z. D.; Hammond, P. T.; Muthukumar, M.; Reichmanis, E.; Wooley, K. L.; Lodge, T. P., “Research in macromolecular science: challenges and opportunities for the next decade”, *Macromolecules*, 42, **2009**, 466-471.

Ohga, K.; Kurauchi, Y.; Yanase, H., **“**Adsorption of Cu^{2+} or Hg^{2+} ion on resins prepared by cross-linking metal-complexed chitosans”, *Bull. Chem. Soc. Jap*., 60, **1987**, 444-446.

Otero-Romaní, J.; Moreda-Piñeiro, A.; Bermejo-Barrera, P.; Martin-Esteban, A., **“**Ionic imprinted polymer for nickel recognition by using the bi-functionalized 5-vinyl-8-hydroxyquinoline as a monomer: Application as a new solid phase extraction support”, *Micro. Chem. J*., **93**, **2009**, 225-231.

Owens, G. S.; Southard, G. E.; Van Houten, K. A.; Murray, G. M., “Molecularly imprinted ion-exchange resin for Fe^{3+}”, *Sep. Sci. Technol*. 40, **2005**, 2205-2211.

Özkara, S.; Andaç, M.; Karakoç, V.; Say, R.; Denizli, A., “Ion-imprinted PHEMA based monolith for the removal of Fe^{3+} ions from aqueous solutions”, *J. App. Polym. Sci*., 120, **2011**, 1829-1836.

Pakade, V. E.; Cukrowska, E. M.; Darkwa, J.; Darko, G.; Torto, N.; Chimuka, L., “Simple and efficient ion imprinted polymer for recovery of uranium from environmental samples”, *Water. Sci. Technol.,* 65, **2012**, 728-36.

Pan, J. Y.; Wang, S.; Zhang, R. F., "A novel Pb(II)-imprinted IPN for selective preconcentration of lead from water and sediments", *Int. J. Environ. Anal. Chem.,* 86, **2006**, 855-865.

Perez-moral, N.; Mayes, A. G.; "Applications in molecular imprinting of polymers". Landes Bioscience: Texas, **2006**.

Philipse, A. P.; Vrij, A., "Preparation and properties of nonaqueous model dispersions of chemically modified, charged silica spheres", *J. Colloid. Interface. Sci*. 128, **1989**, 121-136.

Piletsky, S. A.; Piletska, E. V.; Bossi, A.; Karim, K.; Lowe, P.; Turner, A. P. F., "Substitution of antibodies and receptors with molecularly imprinted polymers in enzyme-linked and fluorescent assays", *Biosens. Bioelectron*., 16, **2001**, 701–707.

Polk, B. J.; Potje-Kamloth, K.; Josowicz, M.; Janata, J., "Role of protonic and charge transfer doping in solid-state polyaniline". *J. Phys. Chem. B*., 106, **2002,** 11457–11462.

Preetha, C. R.; Gladis, J. M.; Rao, T. P.; Venkateswaran, G., **"**Removal of toxic uranium from synthetic nuclear power reactor effluents using uranyl ion imprinted polymer particles". *Environ. Sci. Tech,* 40, **2006**, 3070-3074.

Qiu, J. D.; Guo, J.; Liang, R. P.; Xiong, M., "A nanocomposite chitosan based on ferrocene-modified silica nanoparticles and carbon nanotubes for biosensor application", *Electroanalysis,* 19, **2007**, 2335-2341.

Rajabi, H. R.; Roushani, M.; Shamsipur, M., **"**Development of a highly selective voltammetric sensor for nanomolar detection of mercury ions using glassy carbon electrode modified with a novel ion imprinted polymeric nanobeads and multi-wall carbon nanotubes", *J. Electroanal. Chem*., 693, **2013**, 16-22.

Ramkumar, J.; Chandramouleeswaran, S., "Separation of uranyl ion using polyaniline", *J. Radioanal. Nucl. Chem*. 298, **2013**, 1543-1549.

Rammika, M.; Darko, G.; Torto, N., "Incorporation of Ni(II)-dimethylglyoxime ion-imprinted polymer into electrospun polysulphone nanofibre for the determination of Ni(II) ions from aqueous samples", *Water Sci. Technol*., 37, **2011**, 539-546.

Rannou, P.; Nechtschein, M., "Aging studies on polyaniline: conductivity and thermal stability"*, Synth. Met.,* 84, **1997**, 755-756.

Rao, T. P.; Daniel, S.; Gladis, J. M., "Tailored materials for preconcentration or separation of metals by Ion Imprinted polymers for solid-phase extraction (IIP-SPE)", *Trends. Anal. Chem*., 23, **2004**, 28-35.

Rao, T. P.; Kala, R.; Daniel, S., "Metal ion-imprinted polymers-novel materials for selective recognition of inorganics", *Anal. Chim. Acta*., 578, **2006**, 105–116.

Ren, Y. M.; Zhang, M. L.; Zhao, D., "Synthesis and properties of magnetic Cu(II) ion imprinted composite adsorbent for selective removal of copper", *Desalination,* 228, **2008**, 135-149.

Riley, J. P.; Taylor, D., "The analytical concentration of traces of dissolved organic materials from sea water with Amberlite XAD-1 resin", *Anal. Chim. Acta,* 46 **1969**, 307-309.

Rosatzin, T.; Andersson, L. I.; Simon, W.; Mosbach, K., "Preparation of Ca^{2+} selective sorbents by molecular imprinting using polymerizable ionophores", *J. Chem. Soc. Perk. Trans.,* 2, **1991**, 1261-1265.

Saatçilar, Ö.; Satiroglu, N.; Say, R.; Bektas, S.; Denizli, A., "Binding behavior of Fe^{3+} ions on ion-imprinted polymeric beads for analytical applications" *J. Appl. Polym. Sci,.* 101, **2006**, 3520-3528.

Sadeghi, S.; Aboobakri, E., “Magnetic nanoparticles with an imprinted polymer coating for the selective extraction of uranyl ions”, *Microchim. Acta*., 178, **2012**, 89-97.

Sadeghi, S.; Mofrad, A. A., “Synthesis of a new ion imprinted polymer material for separation and preconcentration of traces of uranyl ions”, *React. Func. Polym*., 67, **2007**, 966-976.

Saraji, M.; Yousefi, H., **“**Selective solid-phase extraction of Ni(II) by an ion-imprinted polymer from water samples”, *J. Hazard. Mater.,* 167, **2009**, 1152-1157.

Saunders, G. D.; Foxon, S. P.; Walton, P. H.; Joyce, M. J.; Port, S. N., “A selective uranium extraction agent prepared by polymer imprinting”, *Chem. Comm.*, 4, **2000**, 273-274.

Say, R.; Ersöz, A.; Denizli, A., **“**Selective separation of uranium containing glutamic acid molecular-imprinted polymeric microbeads”, *Sep. Sci. Tech.*, 38, **2003**, 3431-3447.

Sellergren, B., “Direct drug determination by selective sample enrichment on an imprinted polymer”, *Anal. Chem*., 66, **1994**, 1578-1582.

Sellergren, B., “Molecularly imprinted polymers-man made mimics of antibodies and their applications in analytical chemistry”, Elsevier, Amsterdam, **2001.**

Sellergren, B.; “Shaping enzyme inhibitors”, *Nat. Chem*., 2, **2010**, 7-8.

Shamsipur, M., Fasihi, J., Ashtari, K., “Grafting of ion-imprinted polymers on the surface of silica gel particles through covalently surface-bound initiators: A selective sorbent for uranyl ion”, *Anal. Chem*., 79, **2007**, 7116-7123.

Shao, L.; Qiu, J. H.; Feng, H. X.; Liu, M. Z.; Zhang, G. H.; An, J. B.; Gao, C. M.; Liu, H. L., “Structural investigation of lignosulfonate doped polyaniline”, *Synth. Met*., 159, **2009**, 1761–1766.

Shawky, H. A., “Synthesis of ion-imprinting chitosan/PVA crosslinked membrane for selective removal of Ag(I)”, *J. App. Polym. Sci.*, 114, **2009**, 2608-2615.

Shirvani-Arani, S.; Ahmadi, S. J.; Bahrami-Samani, A.; Ghannadi-Maragheh, M., “Synthesis of nano-pore samarium(III)-imprinted polymer for preconcentrative separation of samarium ions from other lanthanide ions via solid phase extraction”, *Anal. Chim. Acta,* 623, **2008**, 82-88.

Sid Kalal, H., Pakizevand, N., Hoveidi, H., Taghiof, M., Tavangari, S., Panahi, H. A., “Adsorption of Strontium (II) on new ion-imprinted solid-phase support: determination, isotherms, thermodynamic and kinetic studies”, *Caspian J. Env. Sci.,* 11, **2013**, 53-63.

Silva, Claudio H. B.; Da Costa Ferreira, Ana M.; Constantino, Vera R. L; Temperini, Marcia L. A., “Hybrid materials of polyaniline and acidic hexaniobate nanoscrolls: high polaron formation and improved thermal properties”. *J. Mater. Chem. A,* 2, **2014**, 8205-8214.

Silverman, L.; Moudy, L.; Hawley, D. W., “Small amounts of uranium in presence of iron, colorimetric determination with 8-quinolinol”, *Anal. Chem*, 25, **1953**, 1369-1373.

Simpson, N. J. K, “Solid-Phase Extraction: Principles, Techniques, and Applications”, Marcel Dekker, New York, **2000**.

Singh, D. K.; Mishra, S., “Synthesis and characterization of UO_2 $^{2+}$-ion imprinted polymer for selective extraction of UO_2^{2+}”, *Anal. Chim. Acta*. 644, **2009**, 42-47.

Snell, F. D., “Photometric and Fluorimetric Methods of Analysis - Metals Part 2”, Wiley, New York, **1978**.

Sobhi, D. J.; Gladis, J. M.; Rao, T. P., "Synthesis of imprinted polymer material with palladium ion nanopores and its analytical application", *Anal. Chim. Acta*., 488, **2003**, 173-182.

Steed, J. W.; Atwood, J. L., "Supramolecular chemistry", Wiley, UK, **2009**.

Stilwell, D. E.; Park, S. M., "Electrochemistry of conductive polymers: II. Electrochemical studies on growth properties of polyaniline", *J. Electrochem. Soc.,.* 135, **1988**, 2254-2262.

Stöber, W.; Finker, A.; Bohn, E., "Controlled growth of monodisperse silica spheres in the micron size range", *J. Colloid Interface Sci*. 26, **1968**, 62-69.

Su, H. J.; Wang, Z. X.; Tan, T. W., "Preparation of a surface molecular imprinted adsorbent for Ni^{2+} based on Penicillium chrysogenum", *J. Chem. Technol. Biotechnol.*, 80, **2005**, 439–444.

Subden, R. E.; Brown, R. G.; Noble, A. C., "Determination of histamines in wines and musts by reversed-phase high-performance liquid chromatography", *J. Chromatogr. A*, 166, **1978**, 310-312.

Sun, Y.; Shao, D.; Chen, C.; Yang, S.; Wang, X., "Highly efficient enrichment of radionuclides on graphene oxide-supported polyaniline", *Environ. Sci. Technol*. 47, **2013**, 9904-9910.

Tan, C. J.; Tong, Y. W., "Molecularly imprinted beads by surface imprinting", *Anal. Bioanal. Chem.* 389, **2007**, 369-376.

Tang, S. J.; Wang, A.T.; Lin, S. Y.; Huang, K. Y.; Yang, C.C.; Yeh, J.M.; Chiu, K. C., "Polymerization of aniline under various concentrations of APS and HCl". *Polym. J.,* 43, **2011**, 667-675.

Tarley, C. R. T.; Fernandes, F. F.; Luccas, P. O.; Segatelli, M. G., "Enhanced selectivity and sensitivity for flow injection spectrophotometric determination of cobalt using solid phase extraction with a 2d ion-imprinted adsorbent", *Anal. Lett.* 44, **2011**, 216-231.

Tran, H. D.; D'Arcy, J. M.; Wang, Y.; Beltramo, P. J.; Strong, V. A.; Kaner, R. B., "The oxidation of aniline to produce "polyaniline": a process yielding many different nanoscale structures", *J. Mat. Chem*., 21, **2011**, 3534-3550.

Trchova, M.; Sedenkova, I.; Konyushenko, E. N.; Stejskal, J.; Holler, P.; Ciric-Marjanovic, G., "Evolution of polyaniline nanotubes: the oxidation of aniline in water", *J. Phys. Chem. B.,* 110, **2006**,9461–9468.

Uezu, K.; Nakamura, H.; Goto, M.; Murata, M.; Maeda, M.; Takagi, M.; Nakashio, F., "Novel metal ion-imprinted resins prepared by surface template polymerization with W/O emulsion", *J. Chem. Eng. Jpn*., 27, **1994**, 436-438.

Vatanpour, V.; Madaeni, S. S.; Zinadini, S.; Rajabi, H. R., "Development of ion imprinted technique for designing nickel ion selective membrane", *J. Membrane. Sci*., 373, **2011**, 36-42.

Walas, S.; Tobiasz, A.; Gawin, M.; Trzewik, B.; Strojny, M.; Mrowiec, H.; "Application of a metal ion-imprinted polymer based on salen-Cu complex to flow injection preconcentration and FAAS determination of copper", *Talanta*, 76, **2008**, 96-101.

Wang, Z.; Qin, Y.; Wang, C.; Sun, L.; Lu, X.; Lu, X., "Preparation of electrochemical sensor for lead(II) based on molecularly imprinted film", *Appl. Surf. Sci.,* 258, **2012**, 2017-2021.

Wanga, G.; Zhaoa, J.; Li, X.; Li, C.; Yuan, W., "Synthesis and characterization of electrically conductive and fluorescent poly(N-[5-(8-hydroxyquinoline) methyl] aniline)/V_2O_5 xerogel hybrids", *Synth. Met*. 159, **2009**, 366-371.

Whitcombe, M. J.; Kirsch, N.; Nicholls, I. A., “Molecular imprinting science and technology: a survey of the literature for the years 2004-2011”, *J. Mol. Recognit.,* 27, **2014**, 297- 401.

Whitcombe, M. J.; Rodriguez, M. E.; Villar, P.; and Vulfson, E., “A new method for the introduction of recognition site functionality into polymers prepared by molecular imprinting- synthesis and characterization of polymeric receptors for cholesterol”, *J. Am. Chem. Soc*., 117, **1995**, 7105–7111.

WHO: Guidelines for Drinking Water Quality, 2nd edition, Addendum to Vol.2. “Health criteria and other supporting information”, WHO/EOS/98.1, Geneva, **1998**.

WHO: Guidelines for Drinking Water Quality, 3rd edition, Geneva, **2003**.

Wu, G.; Wang, Z.; Wang, J.; Hea, C., “Hierarchically imprinted organic–inorganic hybrid sorbent for selective separation of mercury ion from aqueous solution”, *Anal. Chim. Acta*., 582, **2007**, 304–310.

Wu, H. G.; Ju, X. J.; Xie, R., Liu, Y. M.; Deng, J. G.; Niu, C. H.; Chu, L. Y., “ A novel ion-imprinted hydrogel for recognition of potassium ions with rapid response”, *Polym. Adv. Tech*., 22, **2011,** 1389-1394.

Wu, M.; Liao, L.; Zhao, M.; Lin, Y.; Xiao, X.; Nie, C., “Separation and determination of trace uranium using a double-receptor sandwich supramolecule method based on immobilized salophen and fluorescence labeled oligonucleotide”, *Anal. Chim. Acta*., 729, **2012**, 80-84.

Wulff G.; Sarhan A., “Use of polymers with enzyme analogous structures for resolution of racemates”, *Angew. Chem. Int. Ed. Engl*., 11, **1972**, 341-343.

Wulff, G.; "Molecular imprinting in cross-linked materials with the aid of molecular templates-a way towards artificial antibodies", *Angew. Chem. Int. Ed. Engl.*, 34, **1995**, 1812–1832.

Xia, Y.; Wiesinger, J. M.; MacDiarmid, A. G.; Epstein, A. J.; "Camphorsulfonic acid fully doped polyaniline emeraldine salt: conformations in different solvents studied by an ultraviolet/visible/near-infrared spectroscopic method". *Chem. Mater*. 7, **1995**, 443–445.

Yadav, D. N.; Sarin, M. M., "Geo-chemical behavior of Uranium in the Sambhar Salt Lake, Rajasthan (India): Implications to "source" of salt and uranium "sink"", *Aquat. Geochem.,* 15, **2009**, 529-545.

Yadav, D. N.; Sarin, M. M.; Krishnaswami, S., "Hydrogeochemistry of Sambhar Salt Lake, Rajasthan: Implication to Recycling of Salt and Annual Salt Budget", *Geol. Soc. India*, 69, **2007**, 139-152.

Yan, H.; Kyung, H. R., "Characteristic and synthetic approach of molecularly imprinted polymer", *Int. J. Mol. Sci*. 7, **2006**,155-178.

Yan, H.; Row, K. H., "Molecularly imprinted solid-phase extraction for determination of enrofloxacin and ciprofloxacin in chicken muscle", *Bull. Korean Chem. Soc*. 29, **2008**, 1173-1178.

Yan, M.; Ramstrom, O., "Molecular imprinted materials: science and technology", Marcel Dekker, USA, **2005**.

Yang, C.H.; Wen, T.C., "Electrochemical copolymerization of aniline and para-phenylenediamine on IrO_2-coated titanium electrode", *J. Appl. Electrochem.*, 24, **1994**, 166-178.

Yasuda, A.; Shimidzu, T., "Chemical oxidative polymerization of aniline with ferric chloride", *Polym. J.*, 25, **1994**, 329-338.

Yavuz, H.; Andaç, M.; Uzun, L.; Say, R.; Denizli, A., "Molecular recognition based iron removal from human plasma with imprinted membranes", *Int. J. Artif. Organs.*, 29, **2006**, 900-911.

Yu, K. Y.; Tsukaghoshi, K.; Maeda, M.; Takagi, M., "Metal ion-imprinted microspheres prepared by reorganization of the coordinating groups on the surface", *Anal. Sci.,* 8, **1992**, 701-703.

Zambrzycka, E.; Roszko, D.; Lesniewska, B.; Wilczewska, A. Z.; Godlewska-Zylkiewicz, B., "Studies of ion-imprinted polymers for solid-phase extraction of ruthenium from environmental samples before its determination by electrothermal atomic absorption spectrometry". *Spectrochim. Acta. B.*, 66, **2011**, 508-516.

Zamora, M. L.; Tracy, B. L.; Zielinski, J. M.; Meyerhof, D. P.; Moss, M. A., "Chronic ingestion of uranium in drinking water: a study of kidney bioeffects in humans", *Toxicol Sci.*, 43,**1998**, 68-77.

Zhai, Y. H.; Yang, D.; Chang, X. J.; Liu, Y. W.; He, Q., "Selective enrichment of trace copper(II) from biological and natural water samples by SPE using ion-imprinted polymer", *J. Sep. Sci.* 31, **2008**, 1195–1200.

Zhai, Y. H.; Liu, Y. W.; Chang, X. J.; Chen, S. B.; Huang, X. P., "Selective solid-phase extraction of trace cadmium(II) with an ionic imprinted polymer prepared from a dual-ligand monomer", *Anal. Chim. Acta*, 593, **2007**, 123-128.

Zhang, H. J.; Liang, H. L.; Chen, Q. D.; Shen, X. H., "Synthesis of a new ionic imprinted polymer for the extraction of uranium from seawater", *J. Radioanal. Nucl. Ch.,* 298, **2013**, 1705-1712.

Zhang, M. L.; Zhang, Z. H.; Liu, Y. N.; Yang, X.; Luo, L. J.; Chen, J. T.; Yao, S. Z., "Preparation of core-shell magnetic ion-imprinted polymer for selective extraction of Pb(II) from environmental samples", *Chem. Eng. J.*, 178, **2011**, 443–450.

Zhang, N.; Hu, B.; Huang, C. Z., "A new ion-imprinted silica gel sorbent for on-line selective solid-phase extraction of dysprosium(III) with detection by inductively coupled plasma-atomic emission spectrometry", *Anal. Chim. Acta,* 597, **2007**, 12–18.

Zhang, N.; Suleiman, J. S.; He, M.; Hu, B., "Chromium(III)-imprinted silica gel for speciation analysis of chromium in environmental water samples with ICP-MS detection", *Talanta,* 75, **2008**, 536-543.

Zhang, Z. H.; Zhang, H. B.; Hu, Y. F.; Yang, X.; Yao, S. Z., **"**Novel surface molecularly imprinted material modified multi-walled carbon nanotubes as solid-phase extraction sorbent for selective extraction gallium ion from fly ash", *Talanta*, 82, **2010**, 304-311.

Zhang, Z. T.; Dai, S.; Hunt, R. D.; Wei, Y.; Qiu, S. L., **"**Ion-imprinted zeolite: A surface functionalization methodology based on the "ship-in-bottle" technique", *Adv. Mat.,* 13, **2001**, 493-496.

Zheng, H.; Yang, S. L.; Wang, J. C.; Sun, W. F., "Highly selective determination of rhodium(III) using silica gel surface-imprinted solid phase extraction", *Int. J. Environ. Anal. Chem*., 91, **2011**, 1013-1023.

Zheng, H.; Zhang, D.; Wang, W.Y.; Fan, Y.Q.; Li, J.; Han, H.P., **"**Highly selective determination of palladium(II) after preconcentration using Pd(II)-imprinted functionalized silica gel sorbent prepared by a surface imprinting technique", *Microchim. Acta*, 157, **2007**, 7-11.

Zhou, L.; Shang, C.; Liu, Z.; Huang, G.; Adesina, A. A., "Selective adsorption of uranium(VI) from aqueous solutions using the ion-imprinted magnetic chitosan resins", *J. Colloid Interface Sci.*, 366, **2012**, 165-172.

Zhu, X. B.; Cui, Y. M; Chang, X. J.; Zou, X. J.; Li, Z. H., "Selective solid phase extraction of lead(II) from biological and natural water samples using surface-grafted lead(II)-imprinted polymers", *Microchim. Acta.,* 164, **2009**, 125-132.

List of Publications

Book Chapters

1. T. Prasada Rao, Dhanya James and **Milja T. Elias**, "Electrochemical Sensing of Deadly Toxin-Atrazine: An Overview" Chapter 5, **2011**, 1-38 in Advances In Environmental Research, Vol. 8, Ed. Justin A. Daniels, Nova Science, Publishers, USA.
2. T. Prasada Rao, Dhanya James and **Milja T. Elias,** "Optical sensors for monitoring trace inorganic toxins". Chapter 4, **2012**, 147-174, in Handbook of Molecular Imprinting: Advanced Sensor Applications. Eds: S. Lee & T. Kunitake, Pan Stanford publishing Pvt. Ltd.

Papers

1. Synthesis of surface imprinted nanospheres for selective removal of uranium from simulants of sambhar salt lake and ground water, **T.E. Milja**, K. P. Prathish and T. Prasada Rao., *J. Hazard. Mat.*, 188, **2011**, 384–390.
2. Synthesis, characterization and application of uranyl ion imprinted polymers of aniline and 8-hydroxy quinoline functionalized aniline, **T.E. Milja**, V. S. Krupa and T. P. Rao., *RSC Advances*, 4, **2014**, 30718-30724.
3. Hierarchically imprinted polymers of aniline and aniline-formaldehyde for selective removal of uranium. **T.E. Milja**, V. S. Krupa and T. P. Rao (to be communicated)
4. Highly selective cyclic voltammetric detection and quantification of parts per billion amounts of arsenic (III). **Milja, T.E**., Nithya, S., Dhanya, S., Rao, T.P., (to be communicated).
5. Dhanya, S, Nair, V.V.P, **Milja, T.E**, Ramakrishnan, K, Rao, T.P, Virtually specific UV-molecular probe for nitrite sensing, *Indian Journal of Chemistry - Section B Organic and Medicinal Chemistry*, 51, **2012**, 1607-1612.

Conference Proceedings

1. Surface grafted silica based imprinted nanomaterials for chemical winning of nuclear fuel grade uranium. **T.E. Milja**, K. P. Prathish and T. Prasada Rao (Poster presented in International Conference on Materials for the Millennium-MATCON 2010), held at Cochin during 11-13 January.
2. Biomimetic functionalized nanomaterials for uranium harnessing or decontamination of simulants of Sambhar salt lake waters, India. **T.E. Milja** and T. Prasada Rao, in MIP2010: The 6th International Conference on Molecular Imprinting, held at New Orleans, LA during August 9-12, 2010.
3. Optical molecular probes in specific sensing of nitrite, Dhanya S.**,** S. Saritha, J. Jaisy, **Milja T. E**, T. Prasada Rao, Proceedings of 13 th CRSI National symposium in chemistry held during Febraury 4-6, 2011 at KIIT Univ., Bhubaneswar.