SYNTHESIS, CHARACTERIZATION AND APPLICATIONS OF POLYMERIC SORBENTS

By

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As members of the Viva Voce Committee, we certify that we have read the dissertation prepared by Remya Devi P.S entitled Synthesis, characterization and applications of polymeric sorbents and recommend that it may be accepted as fulfilling the thesis requirement for the award of Degree of Doctor of Philosophy.

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I, hereby declare that the investigations presented in the thesis have been carried out by me. The work is original and has not been submitted earlier as a whole or in part for a degree / diploma at this or any other Institution / University.

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a. Journal

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2. Evaluation of the effect of heating on the ion exchange capacity of polyaniline. **P.S. Remya Devi**, M.N. Deo, S. Kawadiya, N. Raje, S.R. Vishwakarma , R. Verma and A.V.R. Reddy, *Synthetic Metals*, **2015**, *210 /B*, 297-303.
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b. Symposia

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c. Others:

1. Effect of gamma radiation on organic ion exchangers. **P.S. Remya Devi**, Shreeram Joshi, Rakesh Verma, A.M. Lali, L.M. Gantayet, *Radiation Physics and Chemistry*, **2010**, *79*, 41-45.
2. Ion-exchange separation of ^{60}Co and ^{125}Sb from zirconium for radioactive waste management. **P.S. Remya Devi**, Shreeram Joshi, Rakesh Verma, A.V.R. Reddy, A.M. Lali, and L.M. Gantayet, *Nuclear technology*, **2010**, *171*, 220-227.

(Remya Devi. P.S)

Dedicated to

My Husband and Kids

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(Remya Devi P.S)

CONTENTS

SYNOPSIS

Synthetic polymeric sorbents are extensively used as ion exchangers in analytical separations, effluent treatment, recovery of valuables, catalysis and other applications. One can design and tailor these polymers to meet specific end-use, provided the structure-property relations are well-understood. Polymerization/immobilization of organic compounds on inorganic/organic support not only provides better mechanical, thermal and radiation stability but also may result in materials with different properties. This also provides a method to obtain sorbents with large surface area and controlled thickness.

Synthetic organic-polymers, having cross linked hydrocarbon chains, derivatized with ionogenic groups, are the most common ion exchange materials used for industrial applications. Majority of the commercial resins are styrene-divinylbenzene based, because of its good chemical resistance and excellent physical strength. Usually, commercial resins contain ionogenic groups at a concentration of 2.5-5 mmol g^{-1}. The nature of ionogenic groups varies from strong acidic cation exchangers ($-SO_3^-$) to strong basic anion exchangers ($-(CH_3)_3N^+$) and to chelating agents.

During service and regeneration, polymeric sorbents are subjected to a variety of physical and chemical stresses which can cause damage to both the matrix and the functional groups [1]. Various parameters like chemical environment, temperature and radiation are reported to influence the performance of these sorbents. Chemical stability has been evaluated and reported for various sorbents.

Nuclear industry is one of the largest consumers of polymeric sorbents, where these are used for ion exchange separation of radioactive species [2]. When these ion exchangers are exposed to ionizing radiation, chemical changes may occur due to direct energy transfer to the polymer or by the indirect effects of radicals produced by radiolysis of the medium. Extensive studies have been carried out on the effects of ionizing radiation on synthetic organic polymers by Pillay [3] and, Marinsky and Guiffrida [4]. These effects are manifested in terms of either or all of the following: reduction in ion exchange capacity, chain scission or cross-linking, evolution of gases and decomposition of the polymer. Hence, still efforts are on to obtain a radiation-resistant polymer for sorption applications.

Temperature is one of the key factors influencing the kinetics of sorption in ion exchange chromatographic processes [5]. The exchange rate was reported to increase rapidly at elevated temperatures, during the anion exchange chromatographic separation of ^{235}U and ^{238}U using strong anion exchange resins in HCl medium [5]. However, conventional organic anion exchangers start losing their exchange capacity on heating at temperature >60^{o}C under aerated conditions and hence are seldom used at elevated temperatures [6]. Thus there is an increasing urge for stable and efficient sorbent material which can withstand ionizing radiation as well as high temperature.

Conducting polymers, a special class of organic polymers, have been extensively used in electronic industry. Among the conducting polymers, polyaniline (PAni) stands out due to its ease of synthesis and pH-dependent reversible chemistry. Conductivity of PAni has been well investigated by various researchers for a multitude of applications [7, 8]. A few reports are available on application of PAni as an ion exchanger [9-11]. Detailed work on chemical stability of PAni has been reported in the literature [12, 13]. However, stability of PAni towards ionizing radiation as well as at elevated temperatures is yet to be established.

Applications of polymeric sorbents, with the scope for either new or modified materials have been discussed in this thesis. The work done on the above-mentioned theme has been organized in seven chapters which have been described briefly in what follows.

PAni as well as its various composites were synthesized, characterized and used for metal ions sorption applications. Silica gel, XAD, calcium alginate and silane were chosen as substrates for preparing various composites, keeping in mind the specific applications. Stability of PAni towards ionizing radiation and thermal agitation was evaluated. Preconcentration of Hg, on PAni as well as its composites, from acidic media was investigated. The resultant improvement in detection limits of Hg during EDXRF determinations is discussed and compared with that of cold vapour atomic absorption spectroscopy (CVAAS). Additionally, distribution ratios of Zr, Co, Sb and Nb on PAni from various acidic media were evaluated, to facilitate the process design for separation of these metal ions.

Chapter 1: Introduction

This chapter provides an extensive literature survey on polymeric sorbents and composites, with special emphasis on their ion exchange applications. Reports on the effects of high energy radiation and heat on their structure and properties are summarized. Current status of synthetic organic-polymers as ion exchangers and scope of the present work are discussed. Existing literature on the applications of Polyaniline (PAni), a well-known conducting polymer is reviewed and compared with the conventional anion exchangers. The reversible chemistry of PAni, in conjunction with weak anion exchange capacity suggests that it can be used for sorption /separation of negatively charged species from acidic media. Recent developments on the application-specific modification of

PAni, either through structure or combination with materials having the desired features, are discussed.

The review of existing literatures suggests that enough scope exists for carrying out work on PAni. The objectives of the present thesis were to investigate the radiation and thermal stability of PAni, determination of ion exchange capacity of PAni and applications of PAni and its composites for sorption /separation of various metals ions from acidic solutions.

Chapter 2: Synthesis and characterization of polyaniline and its composites

Chemical synthesis and characterization of PAni and its composites are discussed in this chapter. PAni was synthesized in the powder form via chemical oxidative polymerization of aniline in HCl medium. Further, the base as well as salt form of PAni was obtained through appropriate chemical conversion. PAni was synthesized in-situ on XAD resin and silica gel beads to form the respective composites. PAni was loaded on calcium alginate beads and silane discs, during their synthesis itself. Both, powder form and composites of PAni were characterized using physicochemical methods and compared vis-à-vis reported in the literature. Elemental analysis, UV-visible spectroscopy, FT-IR spectroscopy, viscometry and ion exchange capacity were used as the characterization tools. Principles and optimization of analytical parameters for each technique are described. Ion exchange capacity of PAni was determined in terms of ionizable chlorine atoms, using Energy Dispersive X-ray Fluorescence (EDXRF) Spectroscopy and Neutron Activation Analysis (NAA). These results were validated by gravimetric determination of chloride as AgCl.

Chapter 3: Evaluation of radiation stability of polyaniline

One of the several applications of ion exchangers is in the separation of radioactive elements either for recovery or decontamination purpose. Decontamination and recycling of used pressure tubes from Indian Pressurized Heavy Water Reactors, demands essentially the separation of long-lived radioactive cobalt (^{60}Co, $t_{1/2}$ = 5.27 y) and antimony (^{125}Sb, $t_{1/2}$ = 2.77 y) from zirconium. Previously, ion exchange separation strategies were developed and demonstrated in our laboratory, for achieving the required decontamination with respect to these two radionuclides using commercially available ion exchange resins [14].

PAni, being an anion exchanger, is a promising candidate for the separation of Sb from Zr from acidic media. However, it is essential to evaluate the radiation stability of PAni, before carrying out further investigations, since these separations are carried out in radioactive environments.

Evaluation of the stability of PAni towards gamma irradiation is discussed in this chapter. The radiation stability of PAni was evaluated by subjecting it to gamma radiation, followed by physicochemical characterization. To determine the extent and nature of radiation damage, batch experiments were performed. Both the salt and base forms of PAni in different media were subjected to gamma radiation from a ^{60}Co source and the cumulative dose was varied from 1.2 to 3.6 MGy. It was found that the ion exchange capacity of PAni decreased on irradiation and the decrease was a function of the exposure dose, chemical form of PAni and irradiation conditions. The decrease in the capacity on irradiation in aqueous medium was attributed mainly to the indirect effects of radiation. FT-IR analysis revealed minor radiation damage to the structural integrity of PAni on irradiation. Chloride-PAni was found to be more stable to γ-radiation than the base-PAni.

In addition to this, chloride-PAni showed superior radiation resistance, compared to that reported in the literature for Dowex 1x4 resins, in terms of reduction in ion exchange capacity. These studies revealed the radiation stability characteristics of PAni with respect to ion exchange capacity, suggesting its potential for ion exchange separation applications in radioactive environments.

Chapter 4: Evaluation of thermal stability of polyaniline

Thermal stability of PAni was evaluated to assess its use as ion-exchanger at elevated temperature. Thermogravimetric analysis of salt (chloride) and base form of PAni revealed the decomposition pattern and volatile products produced. Structural modifications in PAni upon heating upto 500°C were studied using UV-visible spectroscopy, Fourier Transform Infrared Spectroscopy and viscometry. The gaseous decomposition products of polyaniline were identified using high resolution infrared spectroscopy. Anion exchange capacity of polyaniline, in terms of ionizable chlorine, determined using Energy Dispersive X-ray Fluorescence spectrometry, was found to be 3.25 meq g^{-1}. Polyaniline was found to retain ~ 90% of the original capacity on heating upto 200°C. These studies evinced the superior thermal stability of polyaniline over conventional anion exchangers.

Chapter 5: Sorption of Hg(II) from acidic solutions using polyaniline

Hg(II) was sorbed on polyaniline from aqueous solutions, followed by determination using energy dispersive X-ray fluorescence spectrometry. Distribution ratio of Hg(II) on polyaniline was about $4x10^3$ in water, whereas distribution ratio was $1.2x10^4$ at 0.1 M HCl and decreased drastically with increase in HCl concentration. Rapid kinetics of sorption was evinced by the 80% uptake within the initial 1 min and quantitative sorption within 5 min of equilibration. The sorption was found to follow Langmuir isotherm model and the Langmuir capacity was calculated as 19.7 mg g^{-1}. The ability of polyaniline to form stable and homogeneous pellets facilitated the energy dispersive X-ray fluorescence determination without recourse to elution. Detection limit of Hg was 166 ng, as obtained from the calibration plot. The apparent detection limit was 42 pg, as the preconcentration factor of Hg(II) on polyaniline was $4x10^3$. The developed method is at par with the established method for mercury determination, viz. cold vapour atomic absorption spectrometry.

Chapter 6: Determination of distribution ratio of Zr(IV), Co(II), Sb(V) and Nb(V) in polyaniline

Long-lived radioactive isotopes of Co and Sb (viz. ^{60}Co and ^{125}Sb) are formed as a result of neutron activation of zircaloy material of, the pressure tubes in Indian Pressurized Heavy Water Reactors (PHWR). Need for the separation of radioisotopes of Co and Sb arises from the decontamination requirements of used pressure tube zircaloy. Zircaloy is being replaced by Zr-Nb, due its better mechanical strength and greater resistance to hydride attack. In the case of Zr-Nb alloy, the long-lived ^{94}Nb ($t_{1/2}$ = 20000 y) needs to be separated to fulfill the decontamination requirements. Distribution ratios of these metal ions in PAni from various acid media viz. HCl, HF, oxalic acid and mixture of HCl-HF were determined. Quantification of all the metal ions in solution was carried out using the respective radiotracers and the results were compared with those obtained using ICPOES. Appropriate combination of the media is suggested to improve the separation factors in order to achieve the required separation efficiency. These distribution ratio data will be of use in designing a separation process.

Chapter 7: Conclusions and future perspectives

In this chapter, a brief summary of the highlights of the present investigations as well as future perspectives for exploration on practical ion exchange applications, utilizing the established thermal and radiation stability of PAni is given.

Following conclusions could be drawn from the present work:

(i) PAni was stable towards gamma irradiation upto a dose of 3.6 MGy and retains ~ 80% of the ion exchange capacity

(ii) Structural stability and retention of ion exchange capacity (~ 90%) of PAni on heating upto 200°C was established.

(iii) Sorption of Hg(II) on PAni could improve the detection limits to 42 pg in EDXRF determinations.

(iv) Separation factors of Co(II), Sb(V) and Nb(V) with respect to Zr (V) were highest in 1 M HCl medium, using PAni as the anion exchanger.

This work resulted in one peer reviewed publication and two communications, besides five symposia presentations.

Future perspectives are:

(i) Anion exchange property of PAni can also be used for separation and preconcentration of metal ions like Au(III), Pt(IV), Pd(II), As(V) which form anionic species in acidic media.

(ii) Distribution ratio data for Zr(IV), Co(II), Sb(V) and Nb(V) can be used for designing a separation process applicable to aqueous solutions of these metal ions.

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Chapter 1

Introduction

1.1 Analytical Chemistry - The central science

Analytical chemistry is the science of inventing and applying the concepts and principles for measuring the chemical systems /species. It is applied to all branches of science and hence is called the central science. Analytical chemistry involves both qualitative or quantitative analysis and the analytical skill lies in extracting the true value of the analyte, free from interferences of matrix as well as the analytical reagents. A few analytical techniques are either selective or specific and can be used without prior separation. However, most of the techniques require either separation or preconcentration of the analytes, in order to obtain statistically significant and representative results. Towards meeting these objectives, various methodologies are being developed that are analyte-specific and efficient for the separation and recovery of valuable analytes from complex matrices. In most of these studies, separation /preconcentration of the analyte plays a very important role in reaching the required detection limits. Thus, analytical science in general, and separation science in particular, plays an important role for the determination of the analytes that are present at decision levels and yet their determination is crucial to take informed decisions in the areas like medico-legal, forensic, high purity materials and environmental sciences.

1.2 Separation: An inevitable element of Analytical Chemistry

Separation is a process that is used to isolate two or more distinct components in a mixture of substances, of which, at least one is enriched in one or more of the mixture’s constituents for either preparative or analytical purposes. Separation science aims to achieve rapid and efficient separation of the analytes required for both analytical methodologies and preparative scale up of new compounds. In some cases, it becomes imperative to preconcentrate the analytes from sample matrices. It is essential that the chemical forms of the analytes often have to be preserved while the preconcentration procedures are applied. This requirement is scientifically challenging and often results in the development of new methodologies that have to be validated. The development of new methodologies are expected to result in the simplification and miniaturization of sample preparation procedures leading to minimum solvent and reagent consumption and drastic reduction of laboratory wastes. The theme of this thesis revolves around the development of new methodologies essentially for the preconcentration and determination of the analytes of interest.

Depending on the ease of operation, chemistry and end-use requirements like separation factors or precision, various analytical techniques are adopted for separation or preconcentration of the analytes from sample matrices. Solvent extraction, ion exchange, membrane separation, precipitation and filtration are the commonly used techniques in analytical laboratories for this purpose. Ion exchange separation processes, being clean, efficient and easy to adopt, have been reported in the literature for separation of various metal ions in different media. These processes make use of ion exchange materials, which are either organic or inorganic sorbents, capable of interacting with the analyte through physical or chemical bonding. Ion exchangers /sorbents are characterized by their structure, stability, sorption capacity and reusability. Most of the organic ion exchangers contain synthetic polymers as their backbone, with the required functional groups attached either in the main or side chain in their structure.

1.3 Synthetic polymeric sorbents for ion exchange separation of analytes

Polymers are macromolecules composed of repeating structural units that are connected by covalent bonds. They include a variety of materials, both natural and synthetic, like adhesives, foams, coatings, packing materials, textile and industrial fibres, composites, electronic devices and sorbents, which possess varying properties. Natural polymers include proteins, starch, cellulose and latex. Polyethylene, polyvinyl chloride, polystyrene and nylon are a few synthetic polymers, produced on commercial scale and used in a variety of applications. Synthetic polymeric sorbents are extensively used as sorbents or ion exchangers in analytical separations, effluent treatment, recovery of valuables and catalysis. They are commonly available in the form of powder, beads or sheets /membranes.

One can tailor these synthetic polymers to meet the application-specific requirements, provided that their structure-property relations are well-understood. Synthetic polymers, with pre-defined properties, are fabricated by (i) optimizing the synthesis conditions, (ii) incorporating the requisite functional groups, either during or after the synthesis and (iii) making composites with suitable substrates. Synthetic organic-polymers, having cross linked hydrocarbon chains, derivatized with ionogenic groups, are the most common ion exchange materials used for industrial applications. Majority of the commercial resins are styrene-divinylbenzene based, because of its good chemical resistance and excellent physical strength. Usually, commercial resins contain ionogenic groups at a concentration of 2.5-5 mmol g^{-1}. The nature of ionogenic groups varies from strong acidic cation exchangers, (for example, $-SO_3^-$) to strong basic anion exchangers (for example, $-(CH_3)_3N^+$) and to chelating agents. In order to obtain ion exchange materials with improved mechanical, chemical or radiation stability, polymerization /immobilization of organic molecules is carried out on inorganic /organic supports. Usually, these composite materials possess large surface area, with the ion exchange functionalities coated on the surface. The thickness of these surface coatings can be controlled by tuning the synthesis conditions.

During service and regeneration, polymeric sorbents are subjected to a variety of physical and chemical stress which can cause damage to both the matrix and the functional groups [1]. Various parameters are reported to influence the performance of these sorbents: chemical, thermal, environmental, and radiation, to name a few. Chemical stability of various sorbents has been evaluated and well-documented in the literature. Reports on the stability of sorbents to radiation and thermal fields are sparse.

Nuclear industry is one of the largest consumers of polymeric sorbents, where these are used for ion exchange separation of radioactive species [2]. When these ion exchangers are exposed to ionizing radiation, chemical changes may occur due to direct energy absorption by the polymer or by the indirect effects of radicals produced by radiolysis of the medium. Extensive studies have been carried out on the effects of ionizing radiation on synthetic organic polymers by Pillay [3] and, Marinsky and Guiffrida [4]. These effects are manifested in terms of either or all of the following: reduction in ion exchange capacity, chain scission or cross-linking, evolution of gases and decomposition of the polymer. Hence, efforts are still under way to obtain a radiation-resistant polymer for sorption applications in such environments.

Temperature is one of the key factors influencing the kinetics of sorption in ion exchange chromatographic processes [5]. The exchange rate was reported to increase rapidly at elevated temperatures, during the anion exchange chromatographic separation of ^{235}U and ^{238}U using strong anion exchange resins in HCl medium [5]. However, conventional organic anion exchangers start losing their exchange capacity on heating at temperatures above 60^{o}C, in air, and hence are seldom used for elevated temperature applications [6]. Thus, there is an increasing need for stable and efficient sorbent materials which can withstand ionizing radiation as well as high temperature.

One of the ways out is to look for a material, which can easily dissipate the received energy either internally or by transferring to the surroundings. Intrinsically conducting polymers are one such option, which possess either semiconductivity or metallic conductivity, by way of which they are expected to endure the received energy in an efficient manner. In recent years, conducting polymers have become the focus of researchers, especially for electronic materials, catalysts, electro-chromic displays and microelectronic devices [7, 8]. A large number of conducting polymers such as polyacetylene, polypyrrole, polythiophene and polyaniline have been synthesized and characterized. Among the conducting polymers, polyaniline stands out due to its ease of synthesis, environmental stability and pH-dependent reversible chemistry [9-14].

1.4 Polyaniline: Introduction, history, chemistry and state of the art

The term polyaniline (PAni) refers to a class of polymers, the base form of which has the general formula as shown in Fig. 1, containing ‘y’ reduced and (1-y) oxidized repeat units [9].

In principle, ‘y’ can be varied continuously from one, the completely reduced material, to zero, to give the completely oxidized polymer. The various oxidation states of PAni, namely the leucoemeraldine, emeraldine and pernigraniline, are characterized by the ratio of imine to amine nitrogen atoms. In other words, PAni is basically poly(paraphenylene amineimine) in which the oxidation state can be varied from the fully oxidized (pernigraniline) to the fully reduced (leucoemeraldine) states [15]. The most stable emeraldine state is the 50%-oxidized form of PAni.

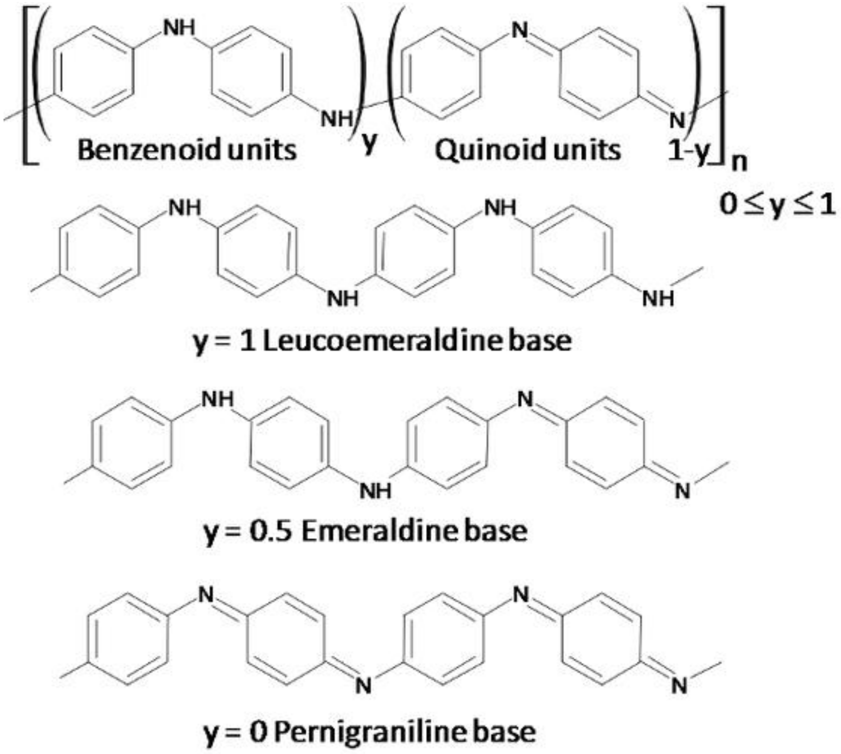


Fig. 1.1 Structure and various oxidation states of PAni [9]

Discovery of PAni could be traced back to the experiments by Runge, almost180 years ago, who reported the formation of a dark green substance upon heating a mixture of Cu(II) chloride and aniline nitrate at 100^{o}C [16]. Later, during the period 1840-43, Fritzsche reported the formation of a dark green precipitate, changing colour to black, upon oxidation of aniline-salt with chromic acid [17]. In 1862, Letheby reported the formation of a dark blue product at the anode, upon electrolysis of aniline sulfate [18]. It was widely used in dyeing industry under the common name aniline black. Various forms of PAni, their synthesis and redox chemistry were studied in the 20th century [19]. An increasing interest in the chemistry, physics and engineering of PAni, was observed in the past 20 years. Pioneers in conducting polymers research, Alen Hegeer, Mac Diarmid and Shirakawa were awarded the Nobel Prize in chemistry in 2000.

A number of studies on polyaniline relating to its synthesis, structure, morphology, electro-chromic and solid-state properties have been reported in the literature [20-24]. Chemical or electrochemical routes are adopted for synthesizing PAni, by various researchers, depending on the specific end use [25-28]. Usually, the chemical route generates PAni in the powder form [29] and electrochemical route generates PAni films [30]. Recently, various processable forms of PAni are reported, where they had used substituted anilines as the starting materials for the synthesis [31-33].

The reversible chemistry of PAni in the emeraldine oxidation state (y = 0.5), upon treatment with acid and alkali, is depicted in Fig. 1.2. The anions, ‘A^-’, in the acid form of PAni, are responsible for the anion exchange property of PAni in acidic media [13].

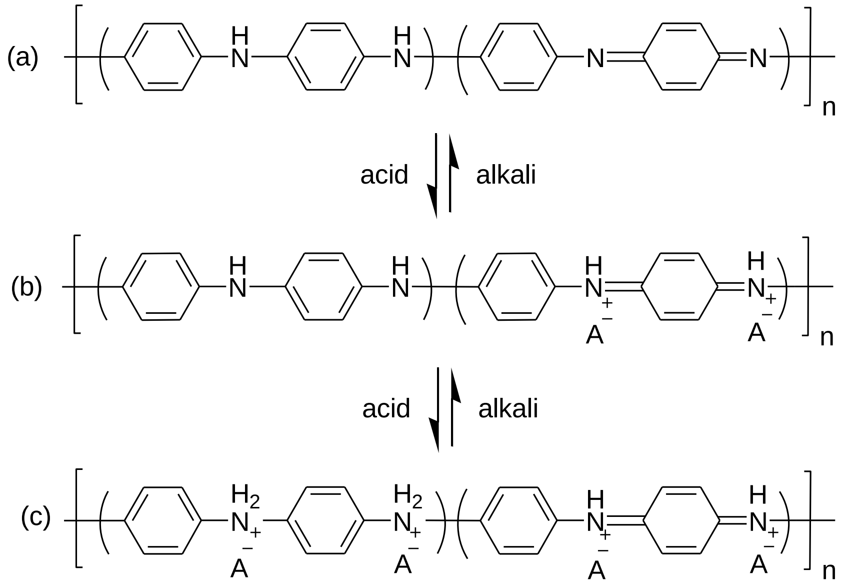


Fig.1.2 Reversible chemistry of emeraldine form of PAni [13]

The reversible chemistry, i.e., interconvertability of the base and acid forms of PAni is the key to its applications, especially in ion exchange separations. PAni contains two types of nitrogen atoms, amine and imine [9]. On equilibration of the base form of PAni with acid solutions, nitrogen atoms get protonated, and the extent of protonation increases with increasing acidity. The protonation of amine nitrogens starts only below pH = 1. Though the amine nitrogens are more basic than the imine nitrogens, the latter are preferentially protonated, as it imparts more stability to PAni, through different resonating structures.

In the case of PAni, contrary to other conjugated systems, not only the aromatic π-electrons, but also the lone pairs of electrons in the nitrogen atoms, participate in extending the delocalization and hence the structural stability [34]. In addition to this, relatively strong interactions between amine and imine groups in neighbouring chains via hydrogen bonds are present in the emeraldine base [35, 36]. These phenomena are responsible for the very difficult processability of PAni in the base form [34]. Partial dissolution of PAni-base is possible only when the solvent-polymer hydrogen bonding interactions replace inter-chain interactions. A few solvents dissolve emeraldine base, for example, NMP (N-methyl-2-pyrrolidinone), TMU (tetramethylurea), DMA (N,N-dimethylacetamide) etc. Sometimes, gelation process is observed in concentrated solutions of PAni [34].

Several devices are fabricated using PAni as the core, for pH, humidity and ammonia gas sensing applications [37-39]. Among the various properties of PAni, conductivity has been well investigated by several researchers for a multitude of applications [40, 41]. PAni is the essential component in sensors, rechargeable batteries, field effect transistors, super-capacitors, electro-rheological fluids, non-linear optical and light emitting diodes, digital memory equipments, erasable optical information storage and electro-chromic devices, anti static and anti-corrosion coatings. [42-46].

The reversible chemistry of PAni, in conjunction with weak anion exchange property, suggests that it can be used for sorption /separation of negatively charged species from acidic media. PAni functions as an anion exchanger solely in acidic media and hence is a weak ion exchanger. PAni has been shown to possess ion exchange properties in acidic media [46, 47]. It has been used for the separation of noble metals like Pt, Pd, Ir, and Au [48, 49] and mercury from aqueous solution [50-52].

Excellent chemical stability of PAni in both strongly acidic and alkaline media has been reported [53]. Detailed work on chemical stability of PAni has been reported in the literature [53, 54]. However, stability of PAni towards ionizing radiation and at elevated temperatures is yet to be established.

1.5 Scope of the present work

A review of the literature suggests that enough scope exists for carrying out research work on PAni and its composites in separation science to develop methodologies for the possible applications in environmental sciences and radioisotope separations. The main challenges include modification of materials and their suitability in harsh conditions like radiation and elevated temperatures. The objectives of the present work were to investigate the radiation and thermal stability of PAni, determination of ion exchange capacity and applications of PAni and its composites for the sorption /separation of various metals ions from acidic solutions.

As part of this thesis work, PAni and its composites were synthesized by chemical route. These were characterized by various physico-chemical methods and their ion exchange capacities were determined. These materials showed good stability in both radiation field and at elevated temperatures as evaluated from simulated experimental investigations. PAni and its composites were used to preconcentrate and determine Hg from aqueous solutions. In addition, Hg(II) loaded PAni-alginate beads and PAni-silane discs were evaluated for the possible use of secondary EDXRF standards. Since PAni showed good radiation stability, distribution ratios of Zr(IV), Co(II), Sb(V) and Nb(V) were determined from various acidic media. Based on these data, a separation strategy for the decontamination of Zr materials in solution from long-lived radioactive isotopes, namely ^{60}Co, ^{125}Sb and ^{94}Nb, can be designed. In view of these encouraging results from this work, it is felt that there is enough scope for the development and application of polymeric sorbents, with either new or modified materials.

Chapter 2

Synthesis and characterization of polyaniline and its composites

Executive summary

Polyaniline (PAni) was synthesized in the powder form by chemical oxidative polymerization of aniline with ammonium persulphate in HCl medium. Further, composites of PAni with beads of silica gel, XAD and calcium alginate were prepared by in-situ chemical polymerization of aniline. Pre-formed base-PAni and tetraethoxysilane were used as precursors for the synthesis of PAni-silane composite discs. PAni powder and its composites were characterized by elemental analysis, UV-visible and FTIR spectroscopy, TG-DSC, SEM, molecular weight and ion exchange capacity measurements. Ion exchange capacity of PAni powder was found to be 3.25 ± 0.084 meq g^{-1}*. These studies revealed the suitability of PAni and its composites for ion exchange /sorption applications and were used in various studies pertaining to this thesis, details of which are described in Chapters 3-6.*

2.1 Synthesis of polyaniline powder

As detailed in Chapter 1, polyaniline (PAni) is obtained by the oxidation of aniline. It can be synthesized either in the form of powder or film, via the chemical or electrochemical polymerization of aniline, respectively. Chemical polymerization is the preferred route, owing to the ease of synthesis. Chemical routes produce polyanilines having relatively higher conductivity, crystallinity, smaller particle size and more number of quinoid rings, compared to those obtained via the electrochemical routes. These reactions are carried out using oxidizing agents in acidic media, where aniline exists as anilinium cations. Various oxidizing agents like ammonium persulphate, potassium dichromate, ceric sulphate and hydrogen peroxide were explored by many researchers. Among these, ammonium persulphate has been reported as the most efficient oxidizing agent. Use of ammonium persulphate has the added advantage of getting a cleaner product, compared to the other oxidizing agents, since the resulting polymer does not contain metal ion impurities. Hence, chemical route involving ammonium persulphate is commonly adopted by researchers for various analytical applications. Huang et al reported the synthesis of PAni using ammonium persulphate in HCl medium [28].

In the present studies, ammonium persulphate was chosen as the oxidizing agent for the chemical synthesis of PAni in HCl medium. The synthesis was carried out at controlled temperatures, in the range of 0-5^{o}C, in order to obtain uniform and high molecular weight polymer. Details of the synthesis of PAni can be found from our earlier work [48, 52] and a brief description is given here. Aniline (0.55 mol) was dissolved in 1.5 L of 1 M HCl and cooled to < 5^{0}C in an ice bath. Ammonium persulphate powder (0.55 mol) was added to the above solution with constant stirring, using a mechanical stirrer. Stirring was continued for ~ 2 h, maintaining the temperature below 5^{0}C. The reaction mixture was filtered after 24 h using a Buchner funnel. The solid was washed with excess of 1M HCl, followed by acetonitrile and then vacuum dried for ~ 16 h. As-synthesized PAni was further purified as follows. PAni powder was first converted to the base form by equilibration with 1 M NH_4OH, followed by washing with water and air-drying. Base-PAni was reconverted to the salt / chloride form by equilibration with 1 M HCl and washing with water till the washings become neutral. Both the base and salt forms of PAni were air-dried and stored in desiccator. The synthesis is schematically shown in Fig. 2.1.

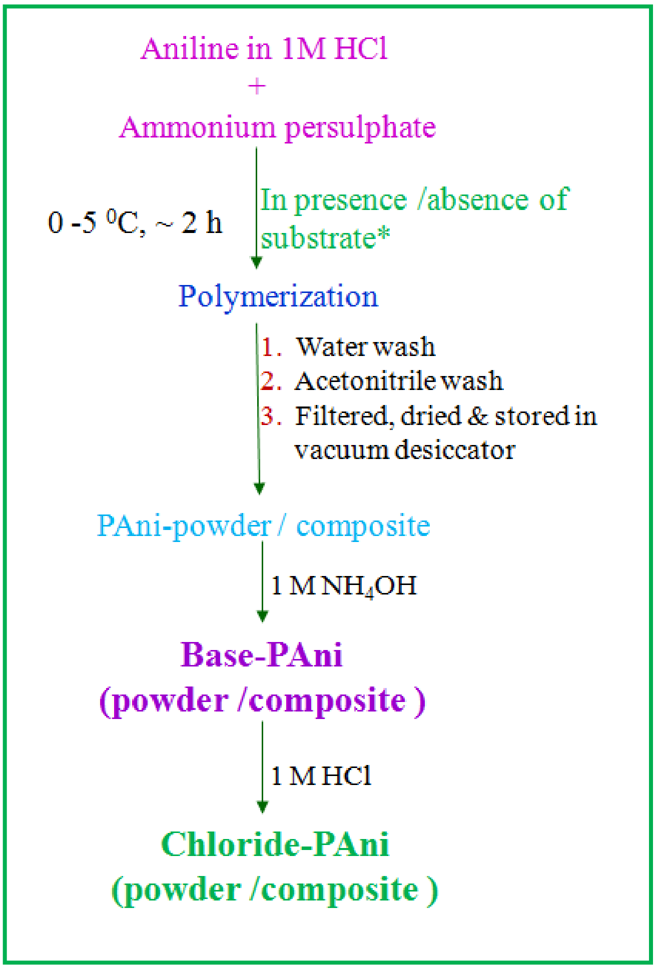


Fig. 2.1 Scheme for the chemical synthesis of PAni and its composites
(*Required substrate was added in this step, to prepare PAni-composites)

2.2 Synthesis of composites of PAni

Processability of PAni is a major limitation for its use as ion exchanger in column operations, as the conventional synthesis route generates the polymer in the form of fine powder. During the present studies, four different composites of PAni were explored for various analytical applications. PAni-coated silica gel and XAD beads were prepared by in-situ polymerization of aniline on the bare beads. PAni-calcium alginate composite beads were obtained by incorporating PAni in the beads during their formation. Pre-formed base-PAni and tetraethoxysilane were the precursors for the synthesis of PAni-silane discs. Composites in the form of beads were prepared for investigating the feasibility of column operation for metal ions sorption. PAni composites in the form of discs were synthesized for reducing the post-sorption processing steps as well as facilitating the determination of sorbed metals using EDXRF spectrometry.

2.2.1 Preparation of PAni-silica gel composite beads

PAni-coated silica gel beads were prepared by in-situ polymerization of aniline on the bare beads. Approximately 10 g of silica gel beads (30-60 mesh, S.D. Fine Chem Ltd., Mumbai) were taken in a 500 mL glass beaker. To this, 10 mL of freshly distilled aniline and 100 mL of 1 M HCl were added and kept below 5^{o}C. In another glass beaker, 30 g of ammonium persulphate was dissolved in 200 mL of 1 M HCl and cooled to < 5^{o}C. After 3 h, ammonium persulphate solution was added to the mixture of silica gel and aniline. The mixture was stirred for 2 h, maintaining the temperature below 5^{o}C. The mixture was kept undisturbed overnight. Finally, the solution was filtered through a Whatman 541 filter paper. PAni-coated silica gel beads were washed with about 1 L of 1 M HCl, followed by water till the washings were neutral. Then it was washed with acetonitrile to remove soluble oligomers of aniline. The air-dried composite beads were sieved and kept in desiccator and characterized by FTIR spectroscopy.

2.2.2 Preparation of PAni-XAD composite beads

Amberlite XAD resin beads, (S.D. Fine Chem Ltd., Mumbai), were washed thoroughly with de-ionized water after equilibration with 1 M NaOH for 4 h, till the washings were neutral. In the case of XAD beads, HCl was not a suitable medium, since these beads floated in HCl and the coating did not occur. Among the various media investigated, acetic acid, in combination with acetone was found to be the most appropriate medium, for the in-situ polymerization and coating of PAni on XAD resin beads. The optimized composition of the reaction mixture was as follows: approximately 10 g of XAD, 20 mL of freshly distilled aniline and 200 mL of solvent system containing 18 mL of glacial acetic acid, 32 mL of acetone and 150 mL of deionized water. This system was cooled to 0-5^{o}C for 3 h and 60 g of ammonium persulphate was added to 200 mL of the solvent mixture. The reaction mixture was stirred for 2 h. Final washing, drying and storage scheme were similar to those described in Section 2.2.1. PAni-XAD composite beads were characterized by FTIR spectroscopy, thermogravimetry and scanning electron microscopy (SEM).

2.2.3 Preparation of PAni-calcium alginate composite beads

Calcium alginate has been reported in the literature for immobilization of sorbents, owing to its thermal stability, easy gel formation at room temperature, high porosity and biocompatibility [55 and references therein].

In the present studies, PAni-alginate composite beads were prepared by in-situ oxidation of aniline in sodium alginate solution in the presence of glutaraldehyde as the cross-linking agent, followed by bead formation. The composite beads were formed by dropping the reaction mixture into calcium chloride solution. The reagents concentration and reaction time were optimized in order to prepare the composite beads having the desired and uniform size distribution. The optimized reaction mixture contained 10 mL of 1% aqueous sodium alginate alongwith 10 µL of distilled aniline, 25 mg of ammonium persulphate and 50 µL of glutaraldehyde. This mixture was stirred for 5-10 mins and dropped into 100 mL of 2% aqueous $CaCl_2$ solution, and the set-up is shown in Fig. 2.2. The dropping height was fixed as 1 cm and a constant flow rate of 4.5 mL min^{-1} was maintained with the help of a peristaltic pump.

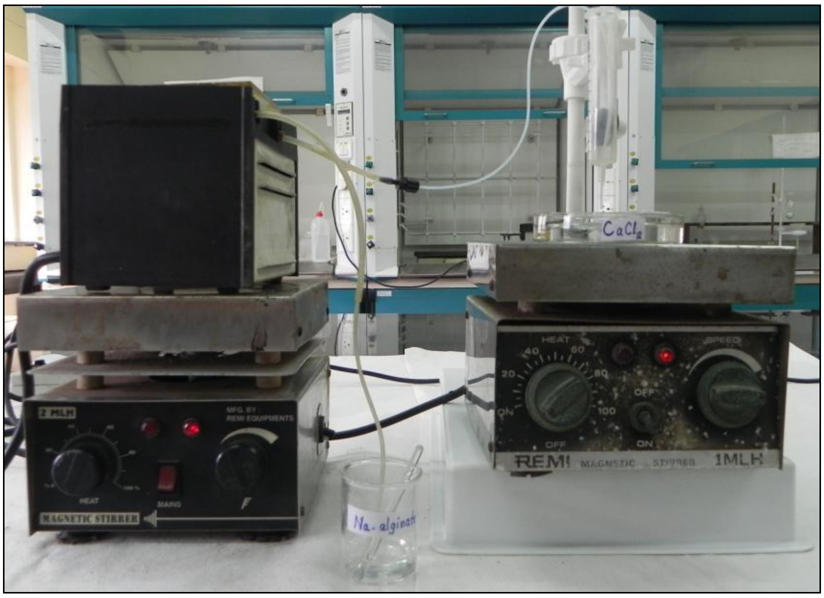


Fig. 2.2 Photograph of the set-up used for the preparation of alginate beads

Bare calcium alginate beads were also synthesized using the above set-up, for comparing and comprehending the characteristics of composite beads. Fig.2.3 depicts the effect of concentration of sodium alginate (0.5 to 5%) and $CaCl_2$ (1 to 10%), respectively, on the formation of calcium alginate beads. Beads shown in Fig. 2.3(a) were obtained by adding dropping concentration sodium alginate to 2% $CaCl_2$ solution and those in Fig. 2.3(b) were obtained by dropping a fixed concentration, i.e., 2% of sodium alginate to varying concentrations of $CaCl_2$.

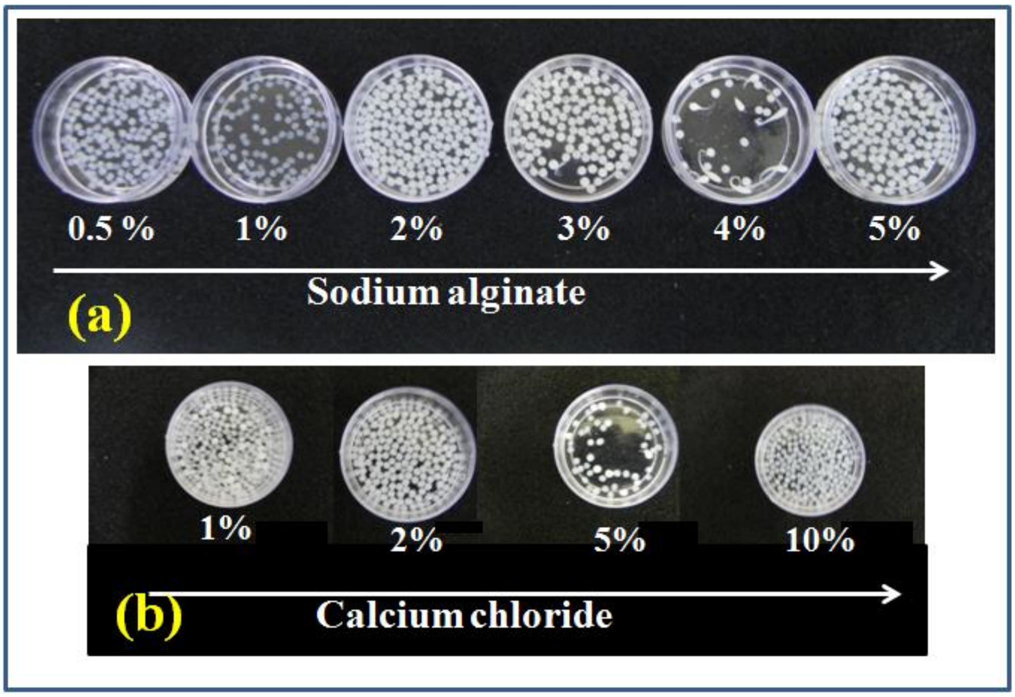


Fig. 2.3 Bare alginate beads prepared with varying concentration of starting materials

Fig. 2.4 shows photographs of (a) PAni-alginate composite and (b) bare alginate beads, where the size of each bead was ~ 2 mm. PAni-composite beads are brown in colour, whereas the bare alginate beads are white and translucent. As-synthesized bare and composite beads were characterized by FTIR spectroscopy, thermogravimetry and SEM.

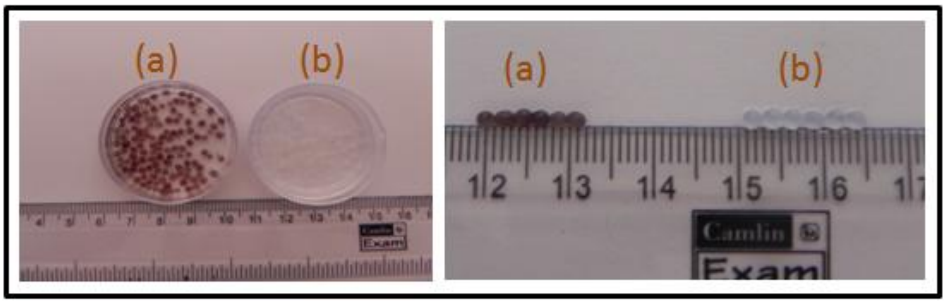


Fig. 2.4 Images of (a) PAni-alginate and (b) bare alginate beads

2.2.4 Preparation of PAni-tetraethoxysilane composite discs

PAni was incorporated in silane discs, during their formation from tetraethoxysilnae via the formic acid assisted hydrolysis and polycondensation. PAni-tetraethoxysilane (PAni-TEOS) composite discs were synthesized at room temperature via the reported procedure [56]. Briefly, base-PAni was dissolved in formic acid (100 mL of 20 g L^{-1}). From this, 10 mL solution was taken in a beaker and equal volume of tetraethoxysilane was added. It was stirred at room temperature for 5 minutes. Three mL solutions were poured into the wells of a six-well plate, made of polystyrene. The well plate was closed and kept undisturbed for 10 days for slow and complete evaporation of the residual formic acid. Green, transparent discs of PAni-silane composites, thus obtained, were stored in desiccator and characterized by FTIR spectroscopy, thermogravimetry and scanning electron microscopy (SEM).

2.3 Characterization of PAni and its composites

2.3.1 Elemental analysis

Carbon, hydrogen and nitrogen in PAni were determined, using CARLO-ERBA elemental analyzer (Model no. 1106). All the samples were air-dried and desiccated prior to elemental analysis. Many analytical techniques have been reported in the literature, for the determination of chlorine in a variety of matrices [57-59]. Chlorine in PAni was determined by neutron activation analysis (NAA), following the procedure reported by Butler and Marsh [59].

C, H, N analysis: Samples were taken in tin crucibles and combusted at 900^{o}C in the presence of limited quantity of oxygen (99.995% pure) and the gases, thus generated, were separated by Porapack QS column and determined by using thermal conductivity detector (TCD), kept at 115°C. High purity helium was used as carrier gas.

Determination of Cl by NAA: About 5-10 mg of accurately weighed PAni samples were packed in clean, dry polyethylene for neutron irradiation. The chlorine standards, used as comparators in NAA, were prepared by evaporating 100 mg of Cl, as NaCl solution, (containing 1 mg mL^{-1} of Cl), on filter paper and packed in polyethylene. Both the samples and standards were double-sealed separately in polyethylene, alongwith a packet containing the filter paper in polyethylene, as the blank. Finally, all packets were packed together in another polyethylene and irradiated for 1 min, in the Pneumatic Carrier Facility (PCF) of Dhruva reactor (BARC, Mumbai, India). Gamma ray spectra of the irradiated samples were acquired using an HPGe detector (30% relative efficiency, Canberra), coupled to an 8k-channel analyzer. Total chlorine in PAni samples was determined by the relative method of NAA and the relevant nuclear data of ^{38}Cl are given in Table 2.1 [60].

Table 2.1 Relevant nuclear data for ^{38}Cl [60]

Natural abundance (%) of ^{37}Cl	(n,γ) cross-section (barns)	Product	Mode of decay	Half-life (min)	γ-ray energy (keV)	γ-ray abundance (%)
24.23	0.43	^{38}Cl	β^- (100 %)	37.25	1642.43	31.9
					2167.54	42.4

Elemental composition of PAni was derived from the measured C, H, N and Cl values, and the results are summarized in Table 2.2. Elemental compositions of both the base and chloride PAni were comparable to those reported in the literature [20]. It can be seen from Table 2.2 that the percentages of C, H, N and Cl added up to ~ 88% for base-PAni and ~ 84% for chloride-PAni. Based on literature reports, it is proposed that the remaining constituents are oxygen and sulphur, present in bound water and sulphonyl groups respectively [20]. It is reported that complete removal of bound water from PAni is difficult to accomplish, due to the inevitable loss of HCl during dehydration [20]. Sulphonation of benzene rings, during the ammonium persulphate-assisted polymerization of aniline in HCl medium, has been reported by Stejskal et. al [20].

Table 2.2 Comparison of measured elemental composition (%) of PAni with the literature reported values

	PAni	C (%)	H (%)	N (%)	Cl (%)
Present work*	Base-PAni	69 ± 2.5	5.3 ± 0.31	13.9 ± 0.21	0.30 ± 0.082
Reported#		75.0	5.0	13.9	0.6
Calculated!		79.5	5.0	15.5	--
Present work*	Chloride-PAni	56 ± 3.2	5.7 ± 0.42	10.9 ± 0.20	11.4 ± 0.62
Reported#		59.7	4.9	10.6	11.1
Calculated!		66.2	4.6	12.9	16.3

*Results of elemental analysis in the present work are rounded off according to ASTM E29-13 [61]. Rule 1: Round the standard deviation to two significant digits; Rule 2: Round the test results to the place of the first significant digit in the standard deviation if the digit is two or higher, to the next place if it is a one.

Based on reference no. [20].

! Based on the empirical formula of PAni.

2.3.2 *Ion exchange capacity determination*

One of the most important characteristics of ion exchangers is their exchange capacity, which is equal to the amount of exchangeable ions, under a set of conditions. It is expressed as milli-equivalents per gram of the dry ion exchanger. The weak anion exchange property of PAni stems from the labile anions attached with the nitrogen atoms in the salt form of PAni.

In the present work, where PAni is synthesized in HCl medium, chloride ions are responsible for the ion exchange capacity of PAni. Chloride-PAni consists of two types of chlorine: ionizable (those attached to nitrogen) and non-ionizable (those attached to the aromatic ring) [62, 63] and the total chlorine is the sum of these two values. Total and covalent chlorine values were determined by NAA of chloride and the base-PAni respectively. Ionizable chlorine was obtained by subtracting the covalent chlorine from total chlorine value. The results were validated by Energy Dispersive X-ray Fluorescence (EDXRF) spectrometry and gravimetric determination of the ionizable chlorine in PAni as AgCl.

2.3.2.1 Neutron activation analysis

Ionizable chlorine in PAni was calculated from the difference between the total chlorine and the non-ionizable (covalently bound) chlorine using NAA. In order to determine the total chlorine, PAni was converted to the chloride form by equilibration with 1 M HCl for 4 h. These solutions were filtered and washed with deionized water, till the washings were neutral and free of chloride, as confirmed by pH and $AgNO_3$ test. Thus obtained chloride-PAni samples were air-dried and the total chlorine was determined by NAA, as described in Section 2.3.1. For determining the non-ionizable chlorine, PAni was equilibrated with 1M NH_4OH, washed with deionized water, air-dried and the chlorine was determined as described above. Ion exchange capacities (milli-equivalents of chloride per gram of PAni) were obtained by subtracting the covalent chlorine from the total chlorine values.

2.3.2.2 Energy dispersive X-ray fluorescence analysis

EDXRF spectrometric determinations were carried out to confirm the ion exchange capacity of PAni, obtained by NAA. XRF measurements were made using an EDXRF spectrometer (EX-3600 M, Jordan Valley, Israel; Resolution = 145 eV for 5.9 keV X-rays).

Both the HCl and NH_4OH-treated PAni samples were pelletized in a KBr press at 10 tons pressure, for the determination of total and covalent chlorine respectively. Pellets of chlorine standard were prepared by evaporating standard NaCl solution in microcrystalline cellulose powder, followed by pelletization. All the sample and standard pellets were of identical dimensions (~ 150 mg weight, 13 mm diameter and 0.4 mm thickness). Ionizable chlorine content in PAni was obtained by subtracting the covalent chlorine from the total chlorine values.

Ion exchange capacity of chloride-PAni was found to be 3.25 ± 0.084 meq g^{-1}, as determined by NAA and EDXRF, and confirmed by gravimetric estimation of chlorine as AgCl.

2.3.3 UV-visible spectroscopy

As-synthesized base-PAni was dissolved (~ 20 µg mL^{-1}) in 0.5% LiCl - N-Methyl-2-pyrrolidinone (NMP) solvent system. UV-visible spectra of these solutions were recorded using a JASCO V-530 spectrophotometer in the wavelength range of 200-800 nm.

Fig. 2.5 shows the UV-visible spectrum obtained in the present studies. UV-visible absorption spectrum of base-PAni in 0.5%LiCl-NMP is reported to have two absorption maxima at approximately 330 nm and 640 nm [64]. Former one is attributed to the π-π^* transition and the latter to a charge-transfer exciton-like transition from benzenoid to quinoid rings [64]. Presence of both benzenoid and quinoid rings could be ascertained in PAni, as is evident from the characteristic bands at 324 and 646 nm in Fig. 2.5.

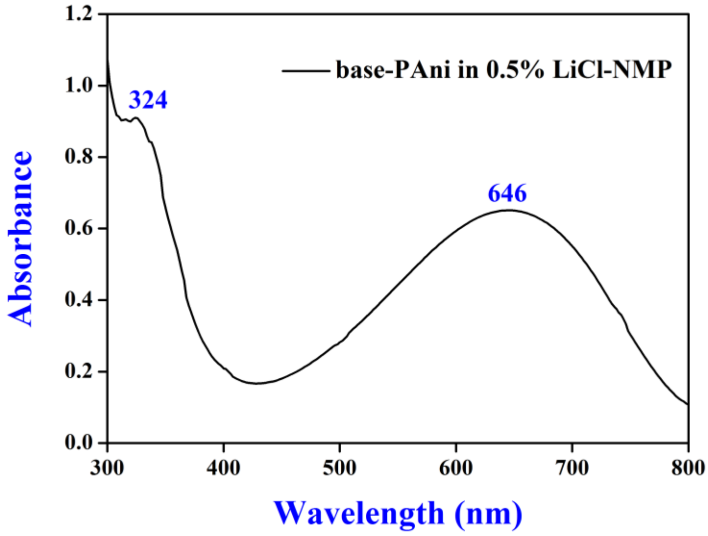


Fig. 2.5 UV-visible spectrum of base-PAni solution in 0.5% LiCl-NMP

2.3.4 FTIR spectroscopy

Infrared spectroscopic measurements were performed on chloride and base PAni, using FTIR spectrometer in transmission mode under vacuum. PAni sample powders were dispersed in CsI matrix (0.5% w/w) and pelletized. The spectra were recorded at room temperature, using Bruker IFS 125 high resolution spectrometer, in the wavenumber range of 400-4000 cm^{-1}. The spectrometer was equipped with a Globar source, KBr beam-splitter and DTGS (MIR) detector. A total of 100 scans at a resolution of 2 cm^{-1} were co-added to obtain statistically significant spectrum. Background spectrum, recorded under similar conditions, using bare CsI pellet was divided in each case to obtain the transmission spectrum. In addition to the pellets, direct analysis of PAni powder and its composites were carried out using the Attenuated Total Reflection (ATR)-

FTIR mode. The spectra were analyzed using Opus 2006 and Origin 8.0 softwares, and are shown in Figs. 2.6-2.10.

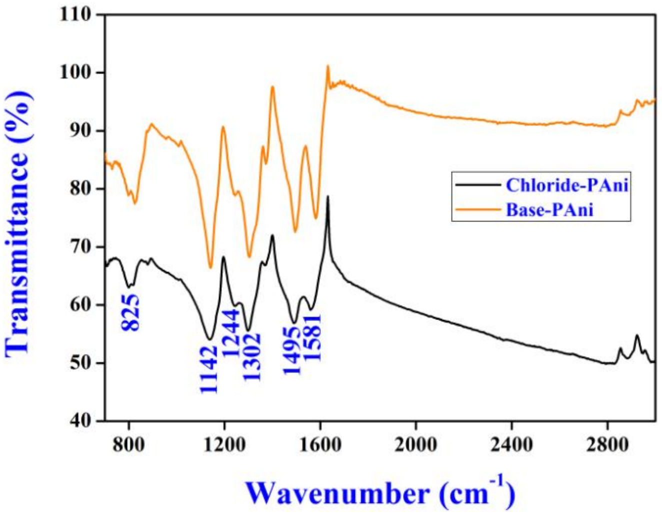


Fig. 2.6 FTIR spectra of chloride and base PAni

Characteristic peaks of PAni identified in Fig. 2.6, have been assigned to the various structural constituents, as shown in Table 2.3 [22, 65, 66]. Thus the structural correspondence of PAni, synthesized during the present work with that reported in the literature [22, 65, 66] was established.

Table 2.3 Peak positions and assignments of characteristic peaks in the FTIR spectrum of PAni [22, 65, 66]

Wavenumber (cm^{-1})	Peak assignment
825	Aromatic C-H out of plane bending of 1,4-disusbtituted benzene
1142	N=Q=N stretching
1244	Stretching of C-N
1302	Stretching of secondary aromatic amine
1495	Benzenoid ring deformation
1581	Quinoid ring deformation

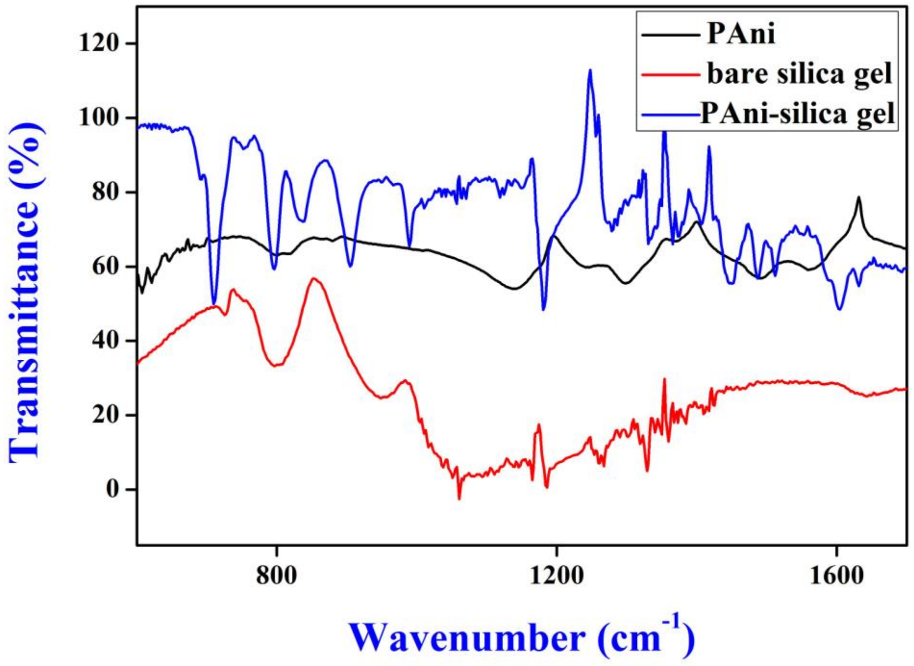


Fig. 2.7 FTIR spectra of PAni, bare silica gel and PAni-silica gel composite beads

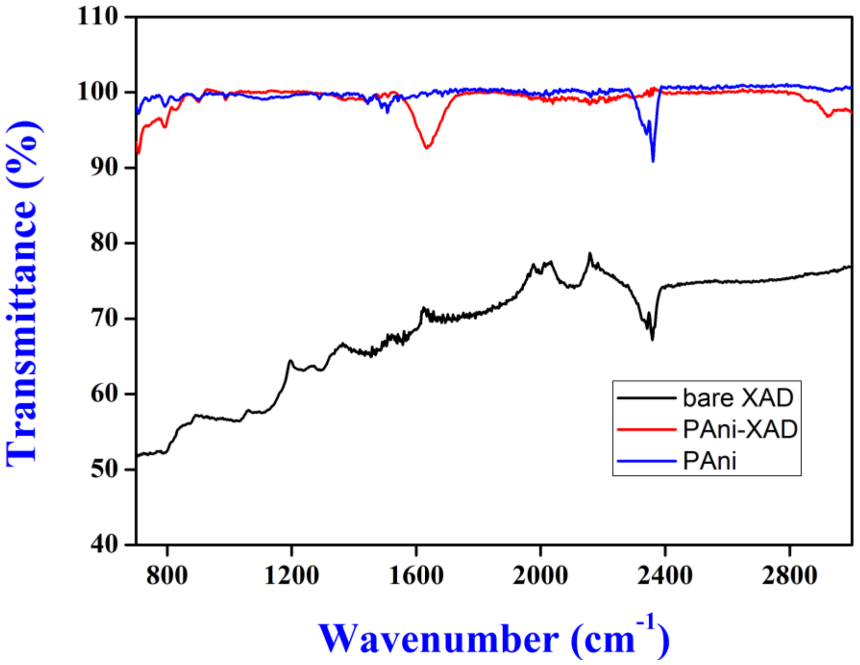


Fig. 2.8 FTIR spectra of PAni, bare XAD and PAni-XAD composite beads

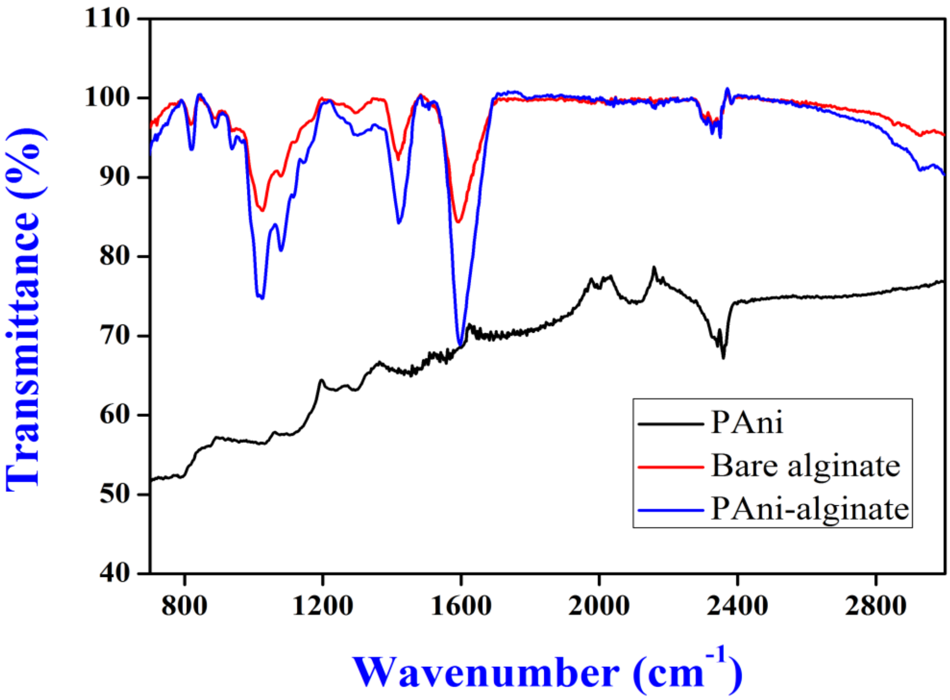


Fig. 2.9 FTIR spectra of PAni, bare alginate and PAni-alginate composite beads

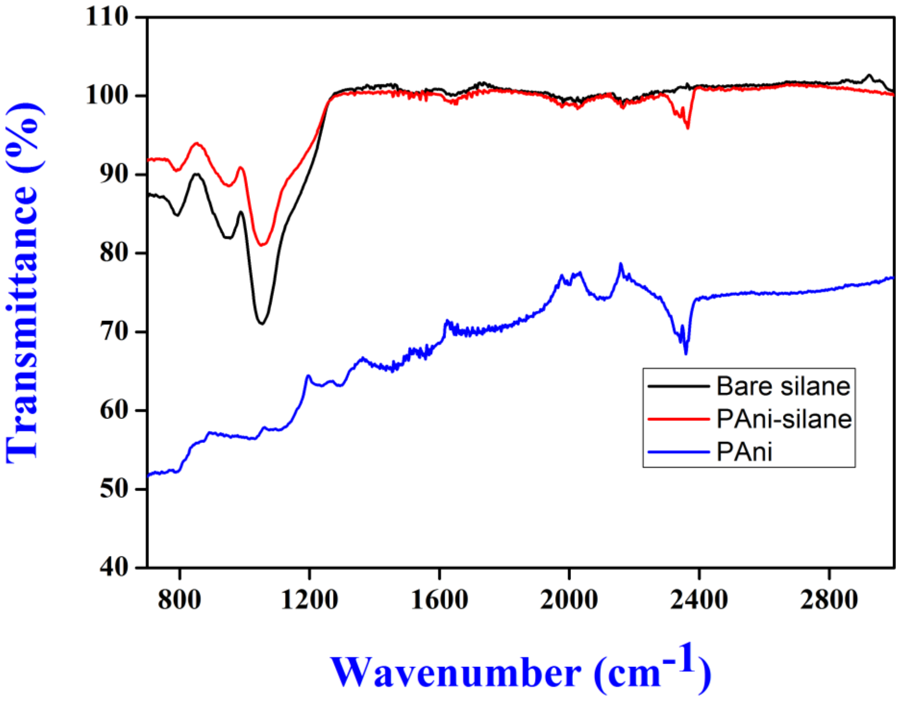


Fig. 2.10 FTIR spectra of PAni, bare silane and PAni-silane composite discs

Formation of composites of PAni with the respective substrates was ascertained by the presence of characteristic peaks of PAni in the FTIR spectra (Figs. 2.7-2.10).

2.3.5 Viscometry

Dilute solution viscometry is one of the several methods for the determination of molecular weight of polymers [67, 68]. Intrinsic viscosity, which represents the capacity of a polymer to enhance the viscosity, increases with the polymer molecular weight. The well-known Mark-Houwink-Sakurada equation (equation 2.1) describes a relation between intrinsic viscosity and molecular weight.

$$[\eta] = K * M^{\alpha} \tag{2.1}$$

where $[\eta]$ is the intrinsic viscosity of the polymer solution, K and α are constants for a polymer-solvent system and M is the molecular weight of the polymer. Here, the molecular weights of polymers can be calculated using viscosity data, provided that the constants K and α are established apriori.

For (PAni - 0.5% LiCl-NMP) system, the literature reported values of K and α are 2.34×10^{-4} and 0.73 respectively [69, 70]. In the present studies, molecular weight of PAni was determined by dilute solution viscometry, using a calibrated Ostwald viscometer and the measurement set-up is shown in Fig. 2.11. Base-PAni was used for studying the viscometric properties, since chloride-PAni is less soluble [19]. Solutions for viscometric measurements were prepared by dissolving base-PAni (2-200 µg mL^{-1}) in 0.5% LiCl-NMP solvent system, at room temperature.

Fig. 2.11 Set-up for viscosity measurements using Ostwald viscometer

Kinematic viscosities, η, of the pure solvent and PAni solutions were calculated from the respective measured times of flow using equation 2.2.

$$\eta = a * t \tag{2.2}$$

where ‘a’ is the calibration constant of the viscometer and ‘t’ is the time of flow of either the pure solvent or the solution. The calculated kinematic viscosities were converted to the reduced viscosities (η_{sp}/C) for each solution, where η_{sp} is the specific viscosity and C is the corresponding concentration of PAni in solution. Intrinsic viscosity of PAni solution was obtained from the Huggin’s plot, where the reduced viscosities were plotted against the concentration of PAni in the solution (equation 2.2) [71].

$$\left(\frac{\eta_{sp}}{C}\right) = [\eta] + k_H * [\eta]^2 * C \tag{2.2}$$

where η_{sp} represents the specific viscosity, (η_{sp}/C) is the reduced viscosity (dL g^{-1}), [η] is the intrinsic viscosity (dL g^{-1}), k_H is the Huggin’s constant and C is the concentration of base-PAni (g dL^{-1}) in solution. Fig. 2.12 shows the Huggin's plot for base PAni-0.5%LiCl-NMP solution system.

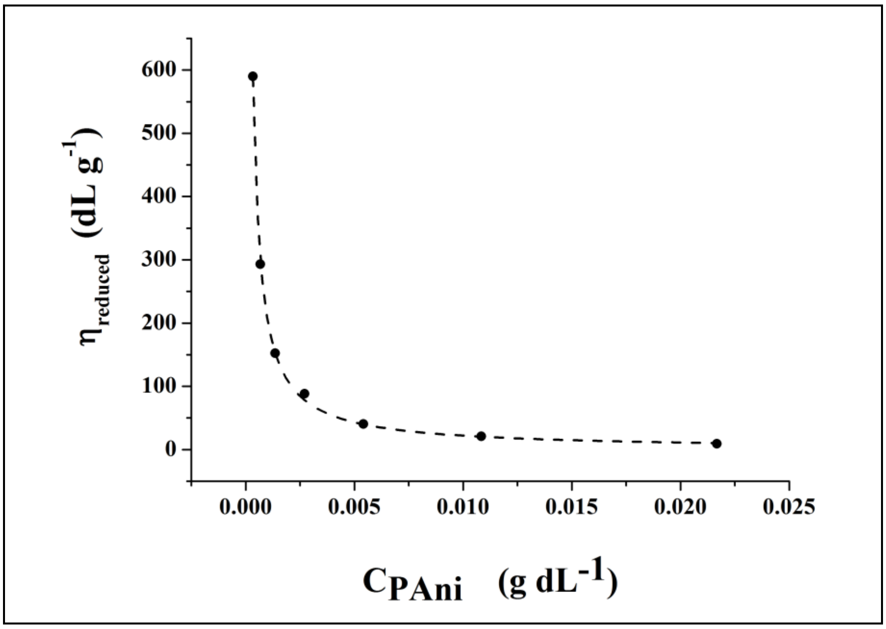


Fig. 2.12 Huggin's plot for base PAni-0.5% LiCl-NMP system for molecular weight determination

Reduced viscosity of the system was found to increase steeply with dilution, which is a clear manifestation of the polyelectrolytic nature of PAni [72]. From Huggin's plot, the intrinsic viscosity was obtained by extrapolation to zero concentration of base-PAni in solution. Molecular weight of as-synthesized PAni was calculated from the intrinsic viscosity, using the reported values of K and α. Average molecular weight of as-synthesized PAni was found to be ~ 68000 Da, which was in agreement with those reported in literature [69, 70, 73, 74].

2.3.6 *Thermogravimetry*

Thermogravimetric analysis is carried out to examine the thermal stability of polymers. In the present studies, thermogravimetric (TG) measurements, alongwith differential scanning calorimetry (DSC), were carried out on 10 mg samples in air as well as nitrogen atmosphere (flow rate: 120 mL min^{-1}) using Netzsch thermal analyzer (Model No.: STA 409 PC Luxx) coupled to Bruker Fourier Transform Infrared (FTIR) system (Model No.: Tensor 27) via a heated Teflon capillary (1 m long, 2 mm internal diameter). Specimen holders, made from recrystallized alumina, were used for thermal measurements. The heating rate of 10^{o}C min^{-1} was maintained in all the measurements. Thermograms and differential scanning calorimetric (TG-DSC) plots are given in Figs. 2.13-2.19 for PAni powder, bare substrates and the respective composites.

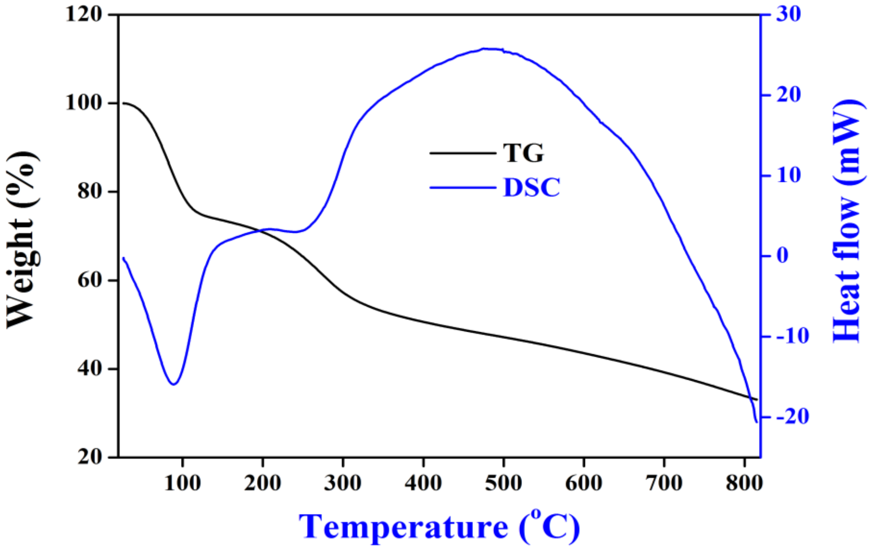


Fig. 2.13 Thermogram (TG) and differential scanning calorimetric (DSC) plot of PAni powder

It is clear from Fig. 2.13 that chloride-PAni undergoes a two-stage weight loss upon heating in air. Initial weight loss is attributed to the loss of bound water and HCl from chloride-PAni. Later on, upon heating beyond 200^{o}C, the polymer chain degradation started and finally ended up with nearly 40% of the initial weight. The residual amount was attributed to unburnt carbon, due to incomplete combustion of the polymer, during heating in air atmosphere. Similar thermograms have been reported in the literature for chloride-PAni [75, 76]. Exothermic peak in the DSC of PAni at 100°C affirms the release of bound water, which was indicated by the thermogram. As could be read from the heat flow rates, endothermic decomposition of polymer chain started upon heating beyond 250°C.

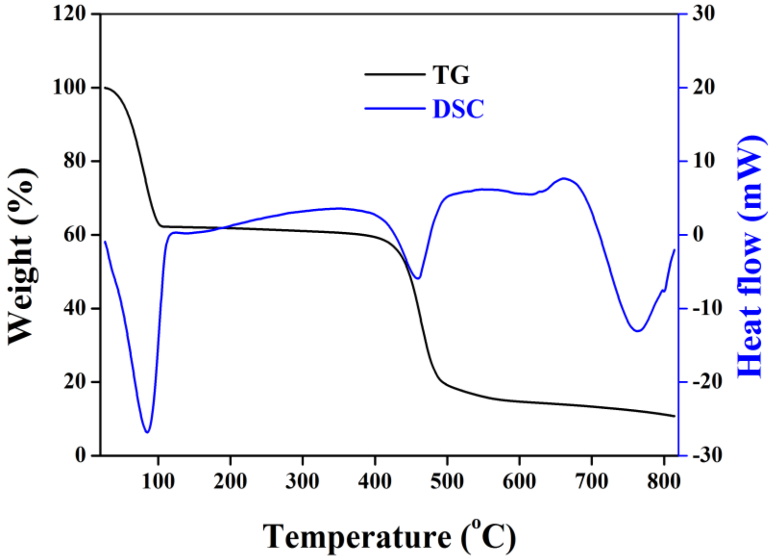


Fig. 2.14 TG-DSC of bare XAD beads

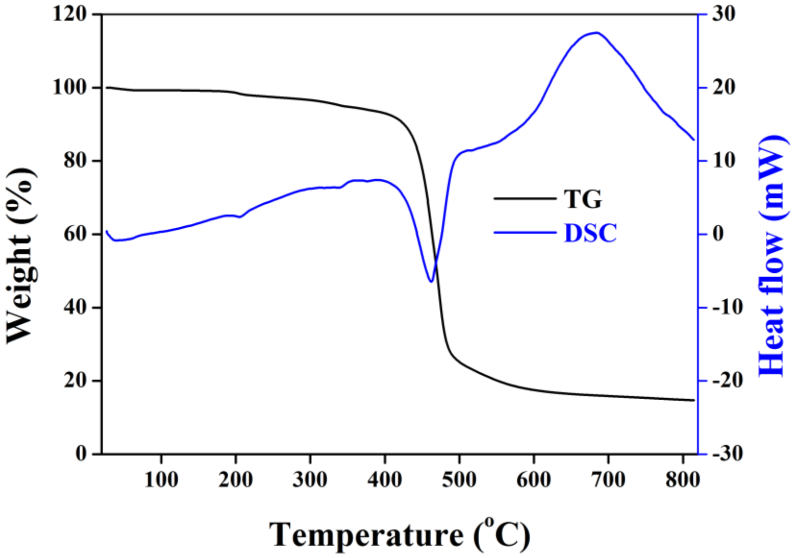


Fig. 2.15 TG-DSC of PAni-XAD composite beads

From Figs. 2.14 and 2.15, it could be inferred that bare XAD beads lost 40% of their weight upon heating upto 400°C and the composites lost only 10% of their initial weight. Hence, the composites are relatively thermally more stable and can be promising sorbents for elevated temperature applications. DSC analyses showed that the composite beads started reacting only beyond 400°C and the endothermic decomposition occurred at still higher temperatures, starting from 500°C.

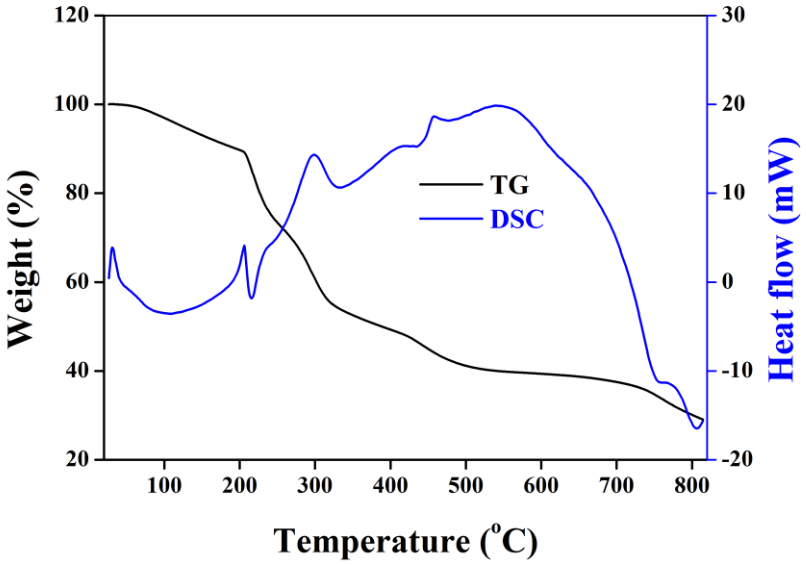


Fig. 2.16 TG-DSC of bare alginate beads

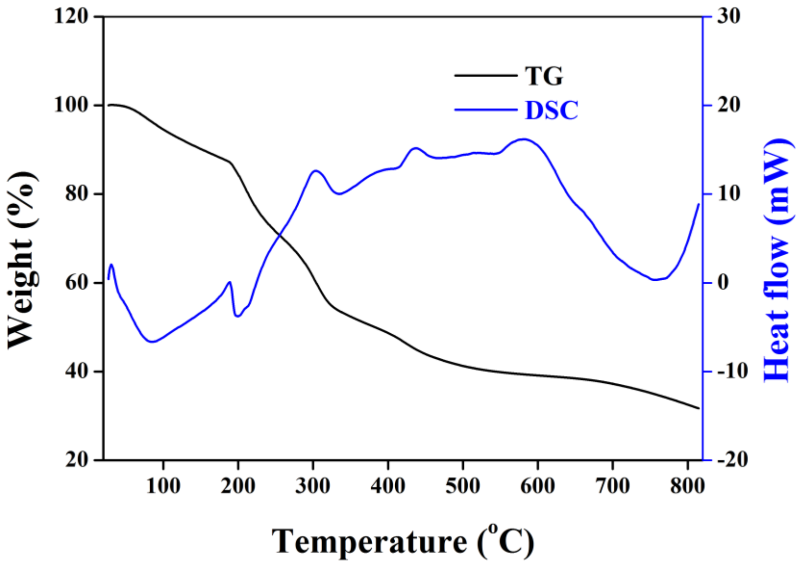


Fig. 2.17 TG-DSC of PAni-alginate composite beads

Thermogravimetric analysis of bare and composite alginate beads (Figs. 2.16 and 2.17) showed that the beads started losing their weight even at nominal temperatures. This behaviour was expected since these beads are known to take up large quantities of water, i.e., ~ 100% or more, which are easily released upon heating. Residual weight was ~ 30% upon heating upto 800^{o}C, which was corresponding to the amount of unburnt carbon [40, 41, 77].

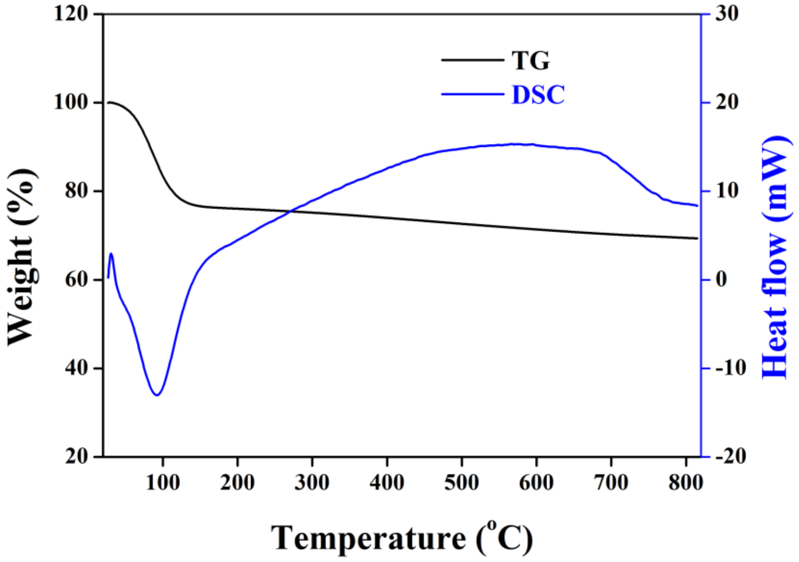


Fig. 2.18 TG-DSC of bare silane discs

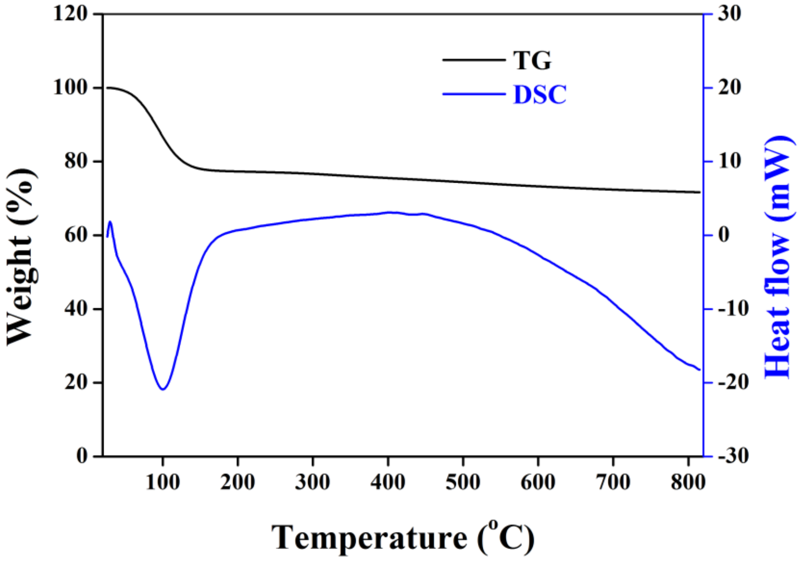


Fig. 2.19 TG-DSC of PAni-silane composite discs

As is vivid from Figs. 2.18 and 2.19, weight loss behavior of PAni-silane composite was similar to that of bare silane, which could be qualified as decomposition of the major matrix. DSC results of both bare and composite silane were identical in the initial phase. Initially, there was a loss of solvent or moisture upon heating upto 150^{o}C. In the latter phase, the behavior was slightly different. The composite discs were stable upto 500^{o}C and started decomposition beyond this temperature, whereas the bare silane discs showed an endothermic decomposition pattern.

2.3.7 SEM imaging

Both bare and composite beads and discs were air-dried and desiccated. In the case of alginate beads, an additional drying at 100^{o}C for 1 h was required, since these beads contained ~ 100 % water by weight. Scanning electron microscopic images of the composites of PAni, alongwith the respective bare substrates were obtained using a PEMTRON-250 instrument and the same are shown in Figs. 2.20-2.25. These images showed the particle size and surface morphology of the bare and composite beads.

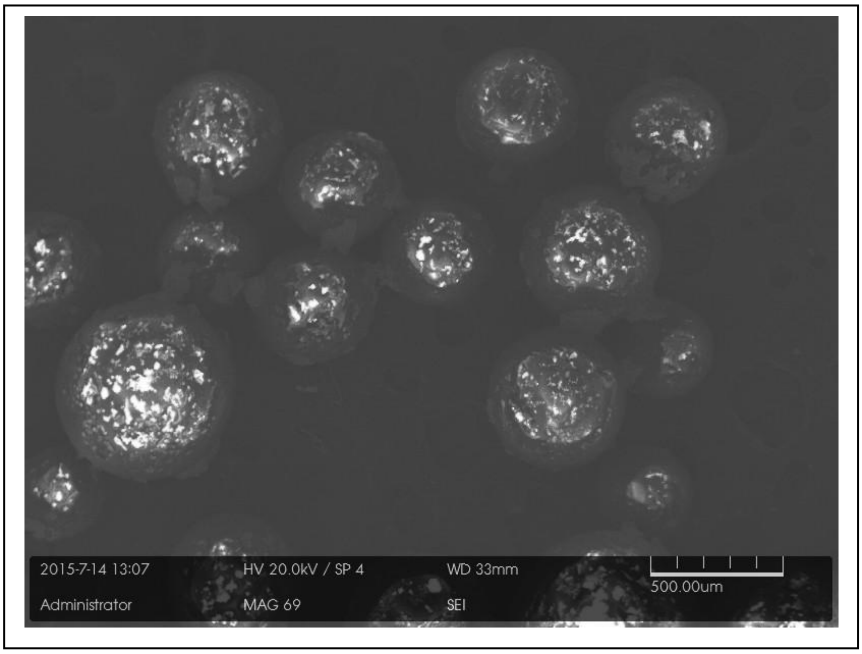


Fig. 2.20 SEM image of bare XAD resin beads

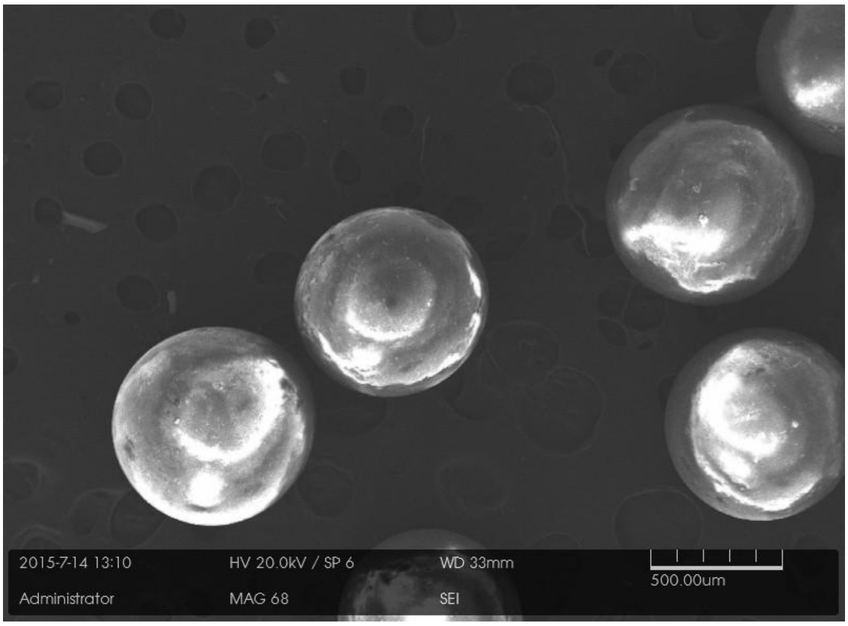


Fig. 2.21 SEM image of PAni-coated XAD resin beads

Since both the XAD and PAni-XAD composite beads (Figs 2.20 and 2.21) showed a distribution of particle sizes between 75 to 600 µm, these beads were sieved and segregated in three size fractions, namely 75-150 µm, 150-300 µm and 300-600 µm.

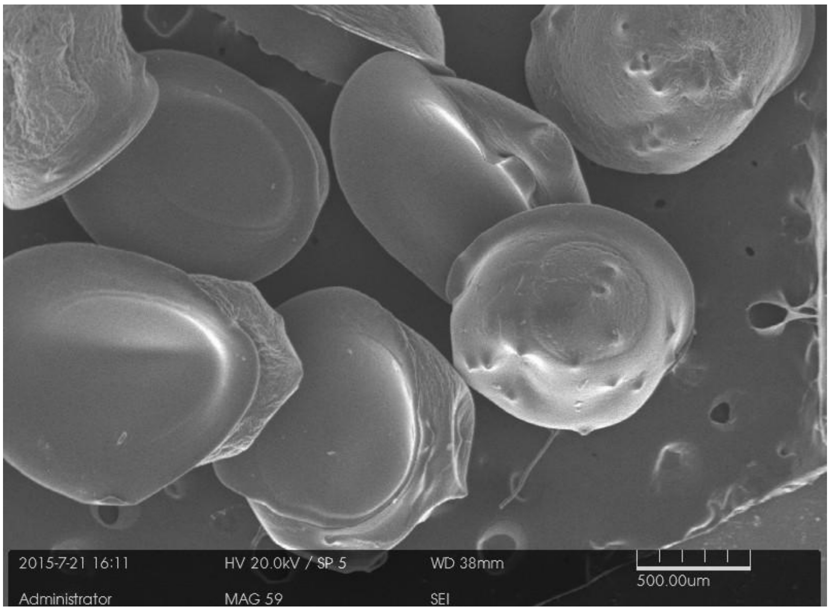


Fig. 2.22 SEM image of bare alginate beads

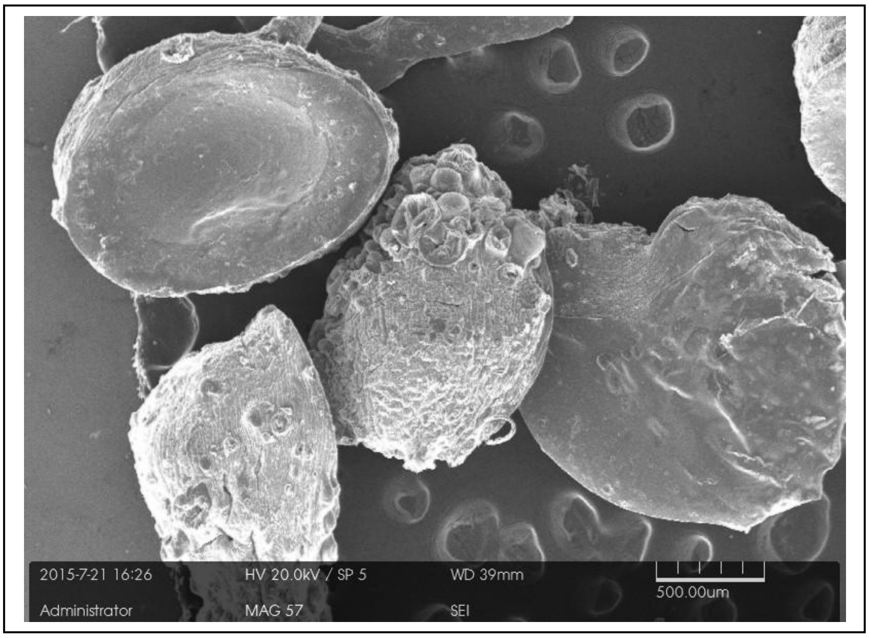


Fig. 2.23 SEM image of PAni-alginate composite beads

From a comparison of the SEM images of bare and PAni-alginate composite beads (Figs. 2.22 and 2.23), it is clear that the beads lose their sphericity upon drying, due to release of absorbed water and blisters generated thereof. The composite surface was rougher, compared to that of the bare alginate beads. This could be due to larger quantity of water released from the composite upon heating, resulting in the formation of blisters and uneven surface structure and shape. PAni has been reported to absorb moisture, especially more so, in the chloride form [20].

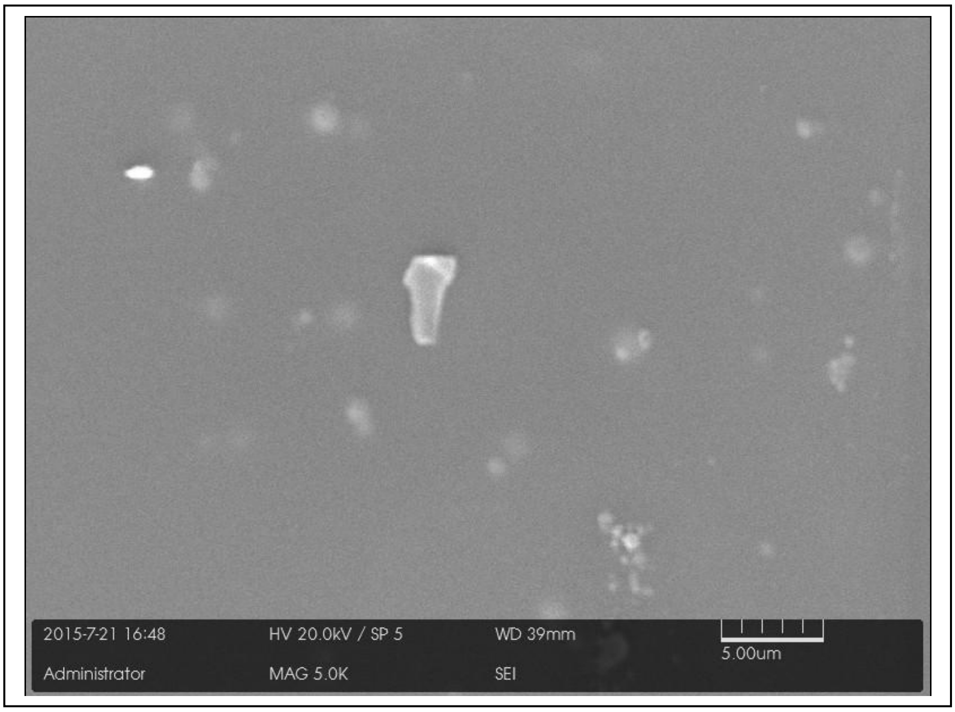


Fig. 2.24 SEM image of a bare silane disc

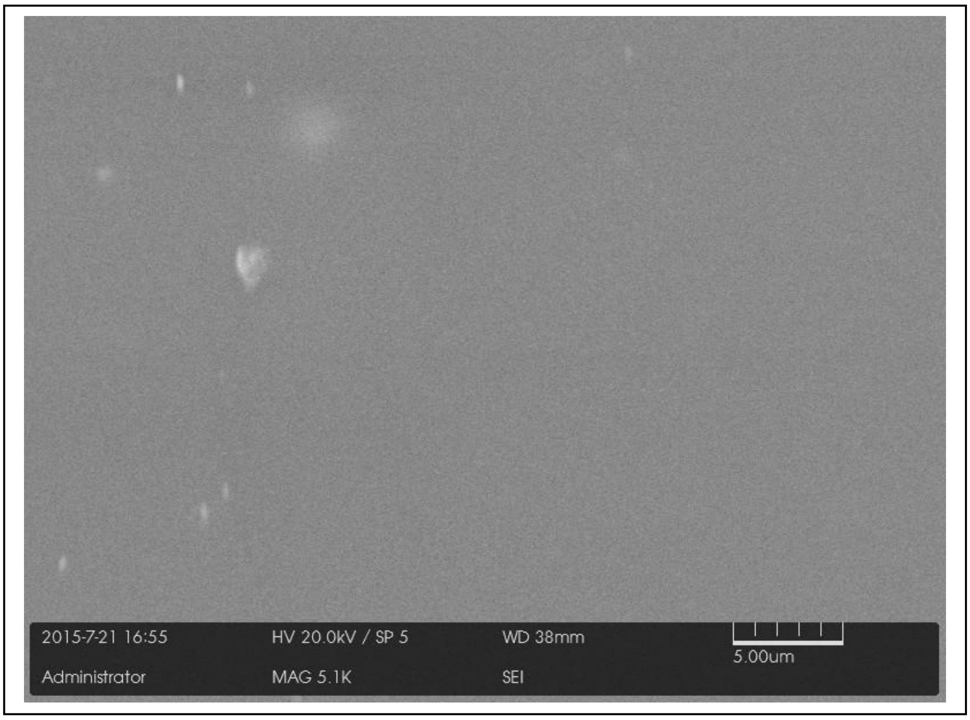


Fig. 2.25 SEM image of a PAni-silane composite disc

Surface morphology of the discs could be visualized from the SEM images in Figs. 2.24 and 2.25. It was observed that PAni has been incorporated uniformly in the composite discs, without affecting the surface smoothness. Hence, it could be inferred that PAni-silane composite discs are ready to use for sorption/separation applications, followed by direct EDXRF determination of the sorbed species such as metal ions.

2.4 Conclusion

PAni was synthesized in the powder form by the chemical oxidative polymerization of aniline in HCl medium and purified. Further, the base as well as salt form of PAni was obtained through appropriate chemical conversion. PAni was synthesized in-situ on XAD resin and silica gel beads to form the respective composites. PAni was loaded on calcium alginate beads and silane discs, during their formation. Both the powder form and composites of PAni were characterized by physico-chemical methods and comparison of the data with those available in the literature. Elemental analysis gave the fractions of C, H, N, S and O in PAni. Ion exchange capacity of PAni powder was found to be 3.25 ± 0.084 meq g^{-1}, as revealed by NAA and confirmed by EDXRF and gravimetry. With the aid of UV-visible spectroscopy and viscometry, information about the benzenoid and quinoid structural constituents and molecular weight of PAni were obtained. FT-IR spectroscopy, thermogravimetry and SEM investigations revealed the structure, thermal stability, size and morphology of PAni and its composites. Physico-chemical characterization indicated the suitability of PAni and its composites for ion exchange /sorption applications.

Chapter 3

Evaluation of radiation stability of polyaniline

Executive summary

Polyaniline (PAni) was synthesized by chemical oxidation of aniline, using ammonium persulphate in 1 M HCl. Radiation stability of PAni was investigated in different aqueous media by subjecting it to gamma radiation from a ^{60}*Co source. Elemental analysis and Fourier Transform Infrared (FTIR) spectroscopic measurements revealed the structural modifications occurring in PAni upon gamma irradiation. Anion exchange capacities of PAni before and after gamma irradiation were determined by neutron activation analysis technique using the measured activity of* ^{38}*Cl. Anion exchange capacity of pristine chloride-PAni was found to be 3.25 ± 0.084 meq* g^{-1}*. The ion exchange capacity decreased with increase in the absorbed dose. Reduction in ion exchange capacity was ~ 20-25% in the case of chloride-PAni and 45-48% in the case of base-PAni, on gamma irradiation upto 3.6 MGy. Chloride form of PAni was more stable towards gamma-radiation compared to the base form and both the forms showed better radiation stability compared to conventional anion exchange resins.*

3.1 Introduction

Synthetic polymers are used as ion exchangers in a multitude of applications. One of the several applications of ion exchangers is in the separation of radioactive elements for either recovery or decontamination purpose. Radiation stability of the chosen ion exchanger is a key factor, to be addressed, before its use in a radioactive environment. Exposure to ionizing radiations, such as alpha, beta, gamma and X-rays, may affect the structural as well as functional properties of organic ion exchanger significantly [78, 79]. Effects of gamma radiation on commercially available organic ion exchangers, like Dowex 1x8, Tulsion and Indion, were reported earlier [80]. Some of the important findings in these reports [78-80] are:

(a) Exposure to gamma radiation dose of 10^{5} Gy results in negligible damage to the ion exchange resins that were studied. An adsorbed dose of 10^{7} Gy or more makes most of the studied ion exchange resins totally unusable.

(b) The strong-acid, sulphonated polystyrene resins are stable up to radiation dose levels of 10^{6} Gy. When exposed to $1.7xl0^{7}$ Gy, about 25% of the total cation-exchange capacity is lost.

(c) The strong-base quaternary amine anion resins are severely damaged by high-intensity radiation. An exposure to $3.8xl0^{6}$ Gy results in a capacity loss of 40-50%, while a dose of $1.7xl0^{7}$ Gy leads to complete degradation of the resin.

(e) Radiation effects on organic ion exchangers result in darkening of their colour, and alteration in particle size and shapes of the resin beads. With increased dose, the resin-colour changes from original shades of amber to brown, dark red and eventually to black. At the same time, particles of the resins become gouged, pitted, cracked and at times even solubilized.

(f) The overall radiation-induced chemical change in ion exchangers is drastically different for a resin irradiated in dry conditions, compared to the same irradiated in the presence of water or aqueous solutions of different pH values.

Polyaniline (PAni), being an anion exchanger, is a promising candidate for the sorption /separation of anionic species from acidic media. However, it is essential to evaluate the radiation stability of PAni, before carrying out further investigations. Effects of ionizing radiation on the electrical properties of PAni are available in literature [81-84].To the best of my knowledge, effects of ionizing radiation on the ion exchange properties of PAni have not been reported till date. Objective of these studies was to study the effects of gamma irradiation on the anion exchange capacity of PAni, for its possible use in radioactive environment.

Radiation stability of PAni was evaluated by subjecting it to gamma radiation, followed by physicochemical characterization. To determine the extent and nature of radiation damage, batch experiments were performed. Both the salt and base forms of PAni in different media were subjected to gamma radiation from a ^{60}Co source. The range of cumulative gamma radiation dose for this study had been chosen as 1.2 to 3.6 MGy, anticipating the highest /most severe radiation damage to PAni, during most of the practical ion exchange applications in radioactive environments. Radiation induced effects on the stability of PAni was evaluated by the data obtained from elemental analysis and Fourier Transform Infrared (FTIR) spectroscopy.

3.2 Experimental

3.2.1 Reagents

Aniline (S. D. fine-chem Ltd.) was distilled under atmospheric pressure at elevated temperature (boiling point = $184^{o}C$) and stored in dark glass bottle, prior to its use. Ammonium persulphate (Merck, purity: 98.5 %), hydrochloric acid (Merck, 11.3 M) and all other reagents were used without further purification. All aqueous solutions were prepared using de-ionized water (Conductivity = 0.05 μS cm^{-1}).

3.2.2 Synthesis of PAni

PAni was synthesized by the method reported earlier [48, 52] and was given in Chapter 2, Section 2.1. However, a brief description is given here. Aniline (0.55 mol) was dissolved in 1.5 L of 1 M HCl, cooled to $0\text{-}5^{0}C$ and ammonium persulphate (0.55 mol) was added. The reaction mixture was filtered after 24 h, washed with 1M HCl, followed by acetonitrile-wash and vacuum drying for 16 h. PAni powder, thus obtained, was converted to the base form by equilibration with 1 M NH_4OH, followed by washing with water and air-drying. Base-PAni was reconverted to the salt /chloride form by equilibration with 1 M HCl and washing with water till the washings become neutral. The salt /chloride PAni was air-dried and stored. Henceforth, the chloride and base forms of PAni will be referred as chloride-PAni and base-PAni respectively.

3.2.3 Gamma-ray irradiation

Gamma chamber GC-5000 (supplied by M/s Board of Radiation and Isotope Technology (BRIT), Mumbai, India) with ^{60}Co gamma radiation source, stationed at Radiation Technology Development Division, BARC, Mumbai, India was used for irradiating the PAni samples. The source had a dose rate of 5 kGy h^{-1}, as measured by Fricke dosimetry.

Figure 3.1 is a schematic representation of the gamma chamber. Following are the specifications of the gamma chamber 5000, used in the present work.

^{60}Co source activity : 5000 Ci
Dose rate : 5 kGy h^{-1}, as determined by Fricke dosimetry
Dose rate uniformity : +25% or better radially;
-25% or better axially
Irradiation volume : ~ 5 L
Size of the sample chamber: 17.2 cm (diameter) × 20.5 cm (height)
Shielding material : Lead & stainless steel

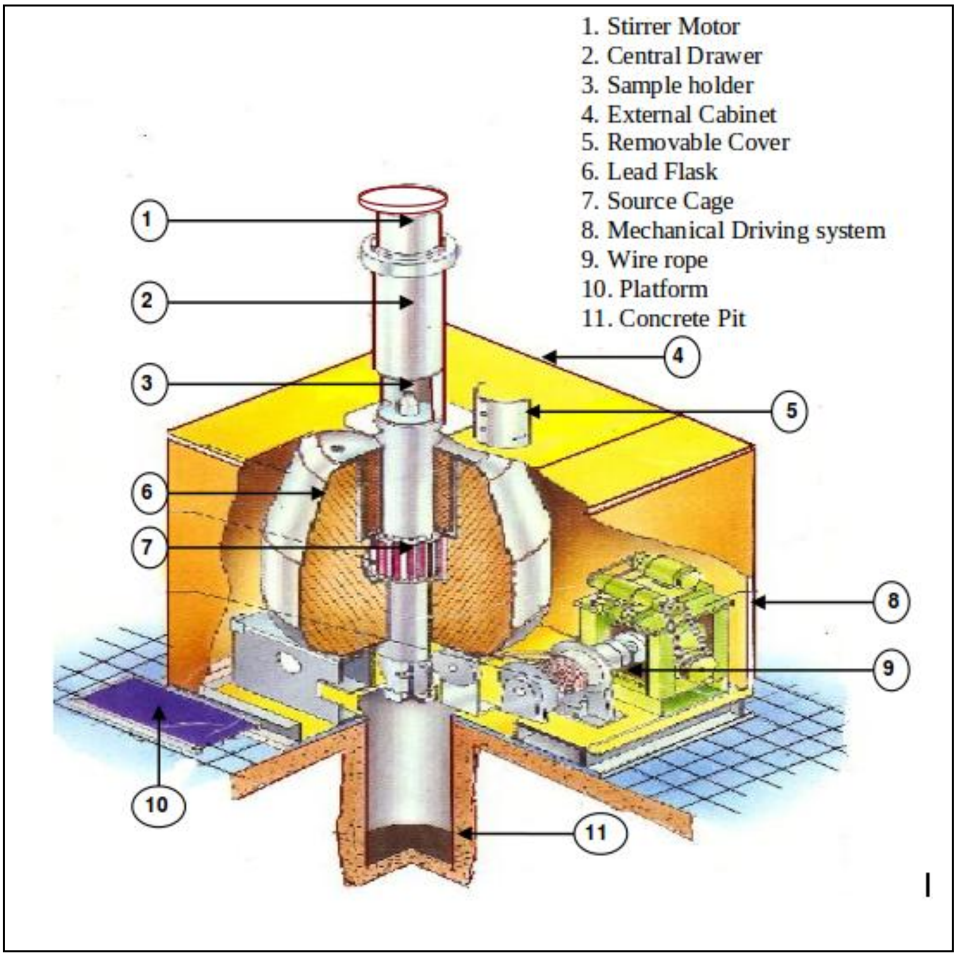


Fig. 3.1 Cross-sectional view of the gamma chamber used for irradiation of PAni samples

Approximately 1 g each of PAni samples (accurately weighed) were subjected to gamma irradiation, in stoppered glass vials (capacity = 50 mL). Base-PAni powder was irradiated in, air as well as water. Chloride-PAni was irradiated in air, water and 1 M HCl media. A constant total solution volume of 40 mL was taken for each irradiation. Cumulative dose was varied between 1.2 to 3.6 MGy.

3.2.4 FTIR spectroscopic measurements

Infrared measurements were performed on unirradiated and irradiated PAni samples, using FTIR spectrometer in transmission mode under vacuum. For FTIR measurements, PAni sample powders were dispersed in CsI matrix (0.5% w/w) and pelletized. The spectra were recorded at room temperature, using Bruker Vertex 80V FTIR spectrometer in the wavenumber range of 400-4000 cm^{-1}. The spectrometer was equipped with a Globar source, KBr beamsplitter and DTGS (MIR) detector. A total of 100 scans at a resolution of 2 cm^{-1} were co-added, for each sample pellet, to obtain statistically significant spectra. Background spectrum, recorded under similar conditions, using bare CsI pellet was divided, in each case, to obtain the transmission /absorption spectrum, derived from instrumental and environmental profiles. The spectra were analyzed using ORIGIN and OPUS (Opus, 2006) softwares.

3.2.5 Elemental analysis

Carbon, hydrogen and nitrogen in PAni were determined, using CARLO-ERBA elemental analyzer (Model no. 1106), as detailed in Chapter 2, Section 2.3.1. All the samples were air-dried and desiccated before elemental analysis. Chlorine in PAni was determined by neutron activation analysis (NAA), following the reported procedure [59]. About 5-10 mg of accurately weighed PAni samples alongwith chlorine standards (100 μL of NaCl solution, containing 1 mg of chlorine per mL) were irradiated for 1 min, in the Pneumatic Carrier Facility (PCF) of Dhruva reactor (BARC, Mumbai, India). The gamma spectra of the irradiated samples were acquired using HPGe detector (30% relative efficiency, Canberra), coupled to an 8k-channel analyzer. Chlorine in PAni samples was determined by the relative method of NAA, as described in Chapter 2, Section 2.3.1 of this thesis.

3.2.6 Determination of ion exchange capacity

Ion exchange capacities of PAni samples, before and after irradiation were determined by NAA, as described in Chapter 2, Section 2.3.2.1.

3.3 Results and discussion

When subjected to high energy radiation, structure and properties of organic polymers may get modified significantly. Extent of these changes depends upon the type of radiation, structure of the polymer and the medium in which the polymer is irradiated. It is well known that scissoring of the polymer chains and breaking of bonds take place during irradiation, leading to enhancement of cross-linking, formation of clusters, liberation of volatile species and formation of new chemical bonds [79]. Quite often, these effects are concomitant, and the rationale of these modifications is attributed mainly to the linear energy transfer (LET) by the radiation. Ionizing radiations, in the dose range of hundreds of kGy, alter the properties of most of the synthetic organic ion exchangers significantly [85-87]. These effects may be classified as either direct or indirect, depending on the type of interaction [78, 88]. In the direct effects, the radiation energy is transferred directly to the ion exchanger. On the other hand, in the indirect effects, the energy transfer occurs through the medium. High absorbed doses may affect exchange capacity, selectivity and exchange kinetics. Radiolytic effects on ion exchangers depend on the nature of the material and chemical composition, ionic form, moisture content, swelling characteristics and the extent of cross-linkage in the macromolecular structure. Radiolytic changes are also affected by the type of radiation, dose rate, absorbed dose as well as the sample's environment during irradiation. The direct and indirect radiolytic effects individually or in synergy may lead to the removal of pendant functional groups, scission of polymer backbone or cross-linking of polymer chains depending on the study conditions.

3.3.1 Gamma radiation effects on the structure of PAni

FTIR spectroscopy, alongwith ^{13}C NMR spectroscopy was used by Traboulsi et al [89] for evaluating the radiation stability of Amberlite IRA 400 towards gamma ray irradiation, where they concluded that the presence of oxygen and absorbed dose were the two important parameters which decide the degradation of anion exchange resins. Better radiation stability of aromatic polyesters was reported with increased delocalization, by Bell and Pezdirtz [90].

PAni consists of both reduced units (benzenoid) and oxidized units (quinoid) as shown in Fig. 1.1 in Chapter 1, and a part of it is given below as Fig. 3.2 [9].

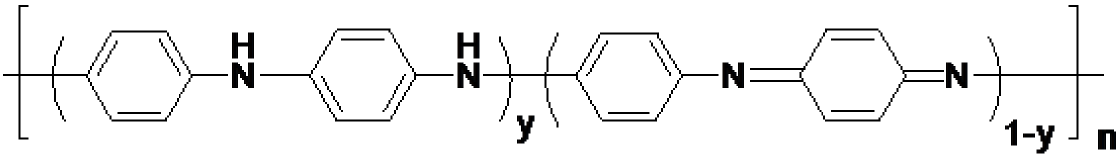


Fig.3.2 General structure of the base form of PAni (y and n are positive integers) [9]

FTIR structural characterization of PAni, synthesized in the present studies, has been discussed in Chapter 2, Section 2.3.4. Fig. 3.3 shows the FTIR spectra of unirradiated and irradiated base-PAni. It can be seen that the characteristic peaks (viz. 1590 cm^{-1}, 1500 cm^{-1}, 1300 cm^{-1}, 1140 cm^{-1} and 825 cm^{-1}) are retained and there are no indications of additional bond formation. This suggests that gamma irradiation has only marginal effect on the structure of PAni. It has been well documented that the presence of aromatic rings in the backbone or in the side chain provides radiation stability to the matrix, due to delocalization of electrons. Extended conjugation of the aromatic electrons throughout the polymer chain brings in the observed stability to PAni towards ionizing radiation.

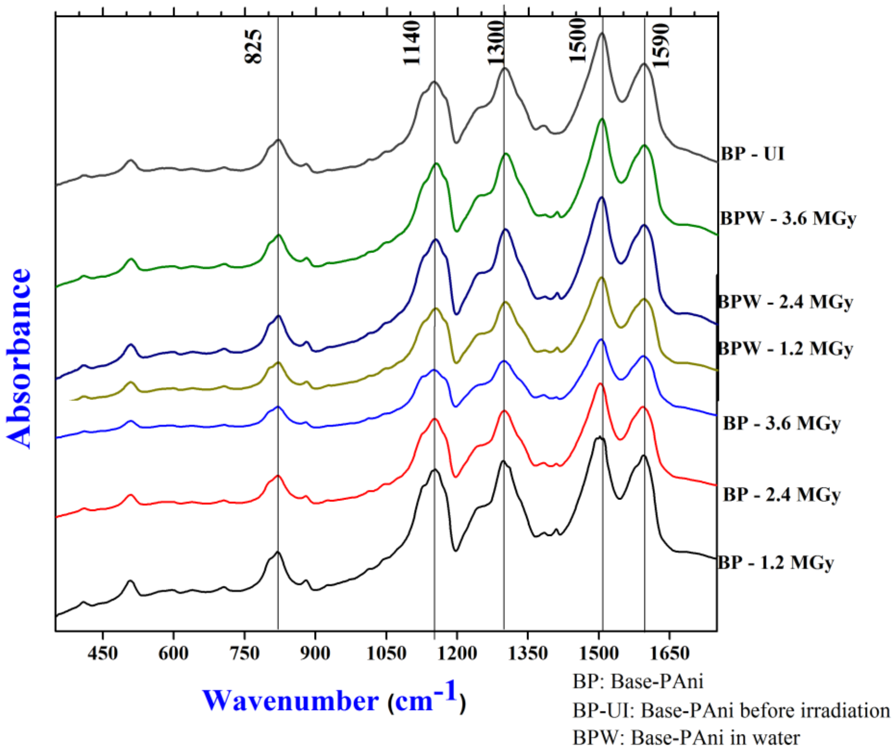
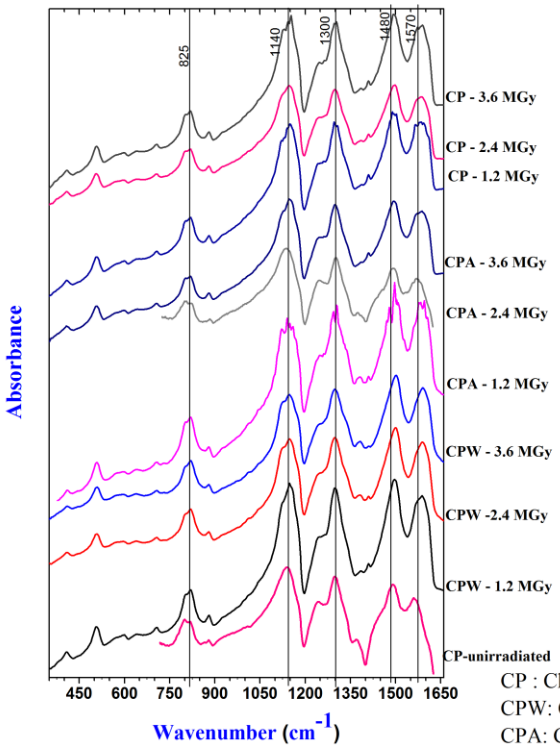


Fig.3.3 FTIR spectra of base-PAni (Unirradiated and irradiated with different gamma radiation doses as mentioned in this Fig.)

Although the structure is apparently intact on gamma irradiation and the FTIR spectra are similar, a closer examination of Fig. 3.3 indicated that the C-N bond strength (band at 825 cm^{-1}) was slightly reduced on irradiation, whereas the N=Q=N bond (1140 cm^{-1}) gained strength. This observation can be explained as the effect of extended conjugation in N=Q=N, where the lone pair of electrons of nitrogen also participates in delocalization. This lone pair participation in delocalization is less probable in the case of amine nitrogens and hence a lowering in the bond strength observed in the case of C-N. The band at 1140 cm^{-1}, referred to as an ‘electronic like’ band is considered as a measure of the degree of delocalization of electrons in PAni [91]. These results suggest a proton doping effect induced by gamma radiation [92]. Fig. 3.4 shows the FTIR spectra of unirradiated and irradiated chloride-PAni.



CP : Chloride-PAni
CPW: Chloride-Pani irradiated in water
CPA: Chloride-PAni irradiated in HCl

Fig. 3.4 FTIR spectra of chloride-PAni (Unirradiated and Irradiated with different radiation doses as mentioned in this Fig.)

Bands corresponding to quinoid and benzenoid ring deformations as well as the out of plane bending of C-N are shifted by ~ 20 cm^{-1} to lower wavenumbers in chloride-PAni, as compared to base-PAni, which is in accordance with the reported data [65, 91]. The extended conjugation over the entire polymer chain is re-emphasized by the comparable bond strengths in both amine and imine nitrogens in chloride-PAni FTIR spectra.

3.3.2 Effect of gamma irradiation on the elemental profile of PAni

Elemental composition of PAni, synthesized during the present work, was compared with that reported [20] and that calculated from formula, as shown in Chapter 2, Table 2.2. Table 3.1 shows the effect of gamma irradiation, in various media, on the elemental composition of PAni. Each value is an average of four independent determinations and the results are rounded off according to the guidelines of ASTM E29-13 [61].

It was observed that there was no significant change in the composition of PAni on irradiation, except for chlorine. The lower precision in the C, H and N values (Table 3.3) may be attributed to the sample inhomogeneity and instrumental noise. C, H and N account for ~ 82% of mass and the remaining could be due to bound water or partial oxidation of PAni [20]. Although PAni samples were vacuum dried for 48 h under room temperature prior to elemental analysis, complete removal of moisture might not have been achieved, as vacuum drying would remove only free water. Chlorine percentage in all PAni samples was found to decrease on gamma irradiation, which was a clear indication of the reduction in anion exchange capacity of PAni upon irradiation.

Table 3.1 Effect of gamma irradiation on the elemental composition of PAni

Sample	Medium	Gamma dose (MGy)	Elemental composition (weight %)			
			C	H	N	Cl
Base PAni		0	69 ± 2.5	5.3 ± 0.31	13.9 ± 0.21	0.30 ± 0.082
	air	1.2	71 ± 2.9	5.8 ± 0.22	14.3 ± 0.21	0.28 ± 0.091
		2.4	72 ± 3.1	5.3 ± 0.22	14.2 ± 0.31	0.23 ± 0.080
		3.6	68 ± 3.3	4.4 ± 0.42	13.8 ± 0.21	0.16 ± 0.061
	water	1.2	72 ± 3.4	5.1 ± 0.21	14.2 ± 0.42	0.24 ± 0.081
		2.4	69 ± 2.6	5.7 ± 0.31	13.6 ± 0.33	0.19 ± 0.090
		3.6	69 ± 2.8	5.5 ± 0.42	13.7 ± 0.33	0.14 ± 0.070
Chloride PAni		0	56 ± 3.2	5.7 ± 0.42	10.9 ± 0.20	11.4 ± 0.62
	air	1.2	59 ± 3.4	5.2 ± 0.21	9.4 ± 0.33	7.3 ± 0.46
		2.4	59 ± 3.3	5.1 ± 0.31	11.6 ± 0.22	7.30 ± 0.13
		3.6	59 ± 3.3	4.4 ± 0.31	11.5 ± 0.22	8.7 ± 0.49
	water	1.2	60 ± 2.9	6.4 ± 0.21	11.7 ± 0.32	8.7 ± 0.51
		2.4	59 ± 3.4	5.8 ± 0.48	12.0 ± 0.11	9.2 ± 1.2
		3.6	62 ± 3.1	4.5 ± 0.21	12.1 ± 0.22	8.5 ± 0.50
	HCl	1.2	58 ± 3.1	5.7 ± 0.56	11.0 ± 0.41	9.4 ± 0.41
		2.4	56 ± 3.7	6.4 ± 0.52	10.9 ± 0.23	10.3 ± 0.66
		3.6	59 ± 2.9	4.3 ± 0.49	11.3 ± 0.29	9.0 ± 0.23

3.3.3 Effect of gamma irradiation on the ion exchange capacity of PAni

The effect of ionizing radiations on ion exchangers is often measured in terms of the exchange capacity of the material, at various doses, and under a variety of environmental conditions. This provides a quantitative measure of the change in functional properties of ion exchangers as a result of radiation-induced chemical and structural changes [78]. Effect of gamma irradiation on the ion exchange capacity can be visualized in Table 3.2.

Table 3.2 Effect of gamma irradiation on the anion exchange capacity of PAni

Sample	Medium	Gamma dose (MGy)	Anion exchange capacity (meq g^{-1})
Base-PAni		0	3.2 ± 0.81
	air	1.2	2.9 ± 0.63
		2.4	2.30 ± 1.0
		3.6	1.6 ± 0.22
	water	1.2	2.7 ± 0.93
		2.4	2.11 ± 0.11
		3.6	1.6 ± 0.23
Chloride-PAni		0	3.2 ± 0.60
	air	1.2	2.11 ± 0.50
		2.4	2. 21 ± 0.12
		3.6	2.5 ± 0.51
	water	1.2	2. 5 ± 0.52
		2.4	2.6 ± 1.2
		3.6	2.4 ± 0.51
	HCl	1.2	2.6 ± 0.44
		2.4	2.9 ± 0.72
		3.6	2.5 ± 0.23

Ion exchange capacity of the un-irradiated chloride-PAni (3.25 ± 0.084 meq g^{-1}) was comparable to the reported value [46, 48]. In the present studies, the ion exchange capacity of base-PAni was found to decrease from 3.2 meq g^{-1} to 1.6 meq g^{-1} upon irradiation, as shown in Fig. 3.5. It is vivid from Fig. 3.5 that the loss in ion exchange capacity of base-PAni was slightly higher in the presence of water at intermediate gamma doses. However, the effect of water medium was negligible at the maximum dosage, namely 3.6 MGy. For samples irradiated in air, the structural changes could be due to the direct effect of irradiation only, whereas for samples irradiated in aqueous solution, additional effects could be expected due to the radiolysis products of water [78, 93], as discussed below.

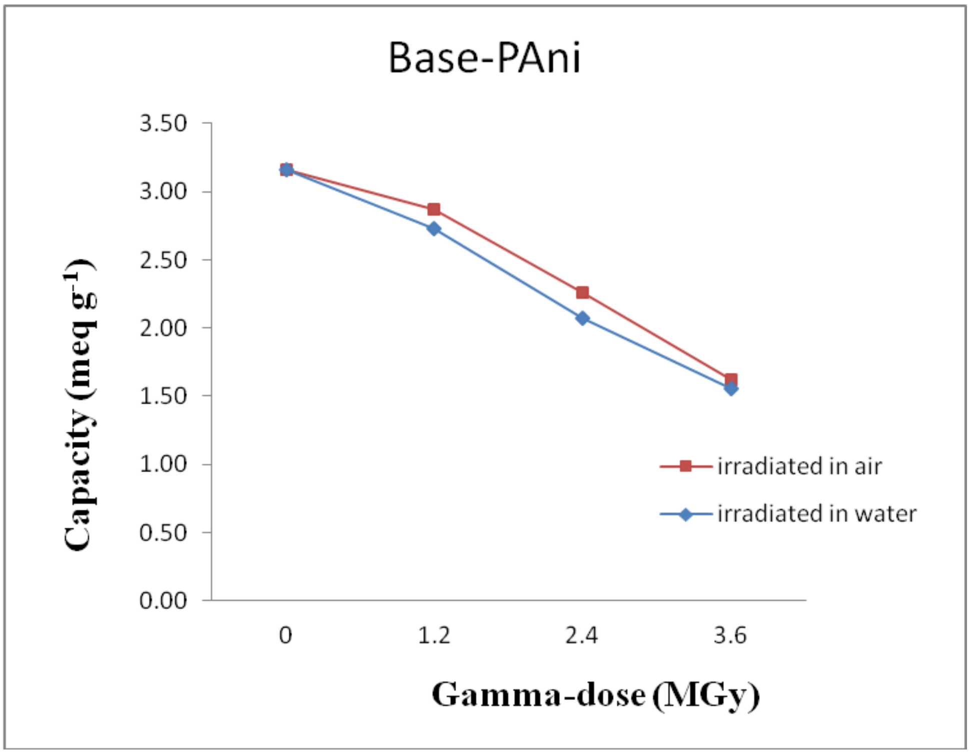


Fig.3.5 Effect of gamma irradiation on the ion exchange capacity of base-PAni

Gamma irradiation of a material leads primarily to radiolytic species like highly oxidizing species OH radical ($^{\bullet}$OH), highly reducing aqueous electron (e_{aq}^{-}) and comparatively weaker reducing species H radical ($H^{\bullet}$). These species further react with the material (solvent, solute or polymer) in their vicinity to cause a whole gamut of radiation chemical effects [93]. Radiolysis of water results in the formation of the strongest reducing species, namely e_{aq}^- and hence leads to significant structural modification of solute molecules in the vicinity. Thus, when PAni is irradiated in water, in addition to the direct effects of radiation on PAni, the radiolysis products of water would also react with PAni to affect its exchange capacity to different extents, depending on the rate as well as the net dose imparted.

As described in Section 3.3.2 above, vacuum dried chloride-PAni had higher bound water content than base-PAni. The reduction in the capacities of chloride-PAni as a function of the absorbed gamma radiation dose is shown in Fig. 3.6.

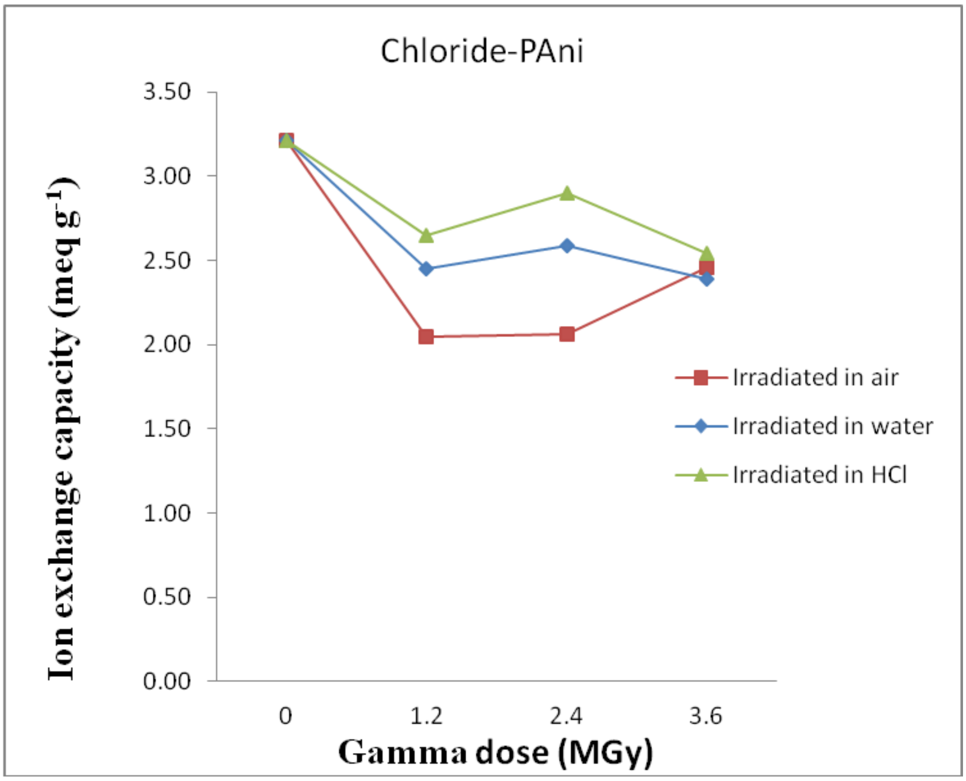


Fig.3.6 Effect of gamma irradiation on the ion exchange capacity of chloride-PAni

Chloride-PAni showed better stability towards gamma irradiation in HCl medium at lower doses, compared to those in water, which in turn, was more stable than those irradiated in air. This higher stability in acidic (HCl) medium may be due to the reaction of e_{aq}^- in accordance with equation (1) to result in $H^\bullet$ which is comparatively much weaker reducing agent than e_{aq}^- [93] and thus leading to lower reduction in capacity of chloride-PAni in HCl.

$$H^+ + e_{aq}^- \rightarrow H^\bullet \quad (\text{Rate} = 2.5\ \text{x}10^7\ \text{m}^3\text{mol}^{-1}\text{s}^{-1}) \qquad \textbf{(3.1)}$$

From the present investigations, it could be established that the effect of medium decreased and finally became negligible, with absorbed dose. At the highest radiation dose of 3.6 MGy, loss in the exchange capacity of chloride-PAni was almost the same (~22-25%), irrespective of the irradiation conditions, as summarized in Table 3.3.

Table 3.3 Reduction in ion exchange capacity of PAni upon gamma irradiation (3.6 MGy)

Sample description	Reduction in capacity (%)
Base-PAni in air	48.7 ± 1.8
Base-PAni in water	50.6 ± 2.6
Chloride-PAni in air	23.4 ± 4.3
Chloride-PAni in water	25.4 ± 4.4
Chloride-PAni in 1 M HCl	20.9 ± 2.0

Table 3.3 summarizes the percentage reduction in exchange capacity for both the forms of PAni. These results clearly indicate that chloride-PAni is more resistant to gamma radiation than base-PAni. Approximately 35-40% reduction in the capacity was reported for anion exchangers subjected to similar gamma radiation dose [80].

The effect of gamma irradiation on commercially available Dowex resins (Dow Chemicals, USA) has been extensively studied and the results are available in the literature. The results from the present studies show that PAni is more resistant to gamma irradiation than Dowex 1x4 resins, which has quaternary ammonium groups as anion exchange sites [87]. The functional nitrogen atoms in PAni are present in the backbone of polymer chain, leading to an extended conjugation and hence the enhanced stability; whereas in Dowex resins, the functional groups are attached as pendant groups to the main chain.

3.4 Conclusion

The effects of gamma irradiation on the elemental composition, chemical structure and ion exchange capacity of PAni in different chemical forms showed that the ion exchange capacity of PAni decreased on irradiation and the decrease was a function of the absorbed dose, chemical form of PAni and irradiation conditions. The decrease in the capacity on irradiation in aqueous medium was attributed mainly to the indirect effects of radiation. Insignificant radiation damage to the structural integrity of PAni on irradiation was revealed by FTIR analysis. Chloride-PAni was found to be more stable to gamma radiation than the base-PAni. In addition to this, chloride-PAni showed superior radiation resistance, compared to literature reported effects on Dowex 1x4 resins, in terms of reduction in ion exchange capacity. It could be concluded that PAni is a potential sorbent for ion exchange separations in radioactive environments.

Chapter 4

Evaluation of thermal stability of polyaniline

Executive summary

Thermal stability of polyaniline was evaluated to assess its use as ion-exchanger at elevated temperature. Thermogravimetric analysis of salt (chloride) and base form of polyaniline revealed the decomposition pattern and volatile products. Structural modifications in PAni upon heating upto 500^oC *were studied using UV-visible spectroscopy, Fourier Transform Infrared spectroscopy, and viscometry. The gaseous decomposition products of polyaniline were identified using high resolution infrared spectroscopy. Anion exchange capacity of polyaniline, in terms of ionizable chlorine, determined using Energy Dispersive X-ray Fluorescence spectrometry, was found to be* 3.25 ± 0.084 *meq* g^{-1}*. Polyaniline was found to retain ~ 90% of the original capacity on heating upto* 200^oC*. These studies evinced the superior thermal stability of polyaniline over conventional anion exchangers.*

4.1 Introduction

Kinetics of sorption in ion exchange chromatographic processes is generally governed by either ion exchange or complex-formation process [5]. Temperature is one of the factors which influence the exchange rates significantly. In certain cases, the separation efficiency could be improved by carrying out the separation at elevated temperatures in the range of 100-150^oC. The exchange rate was reported to increase rapidly at elevated temperatures, during the anion exchange chromatographic separation of ^{235}U and ^{238}U using strong anion exchange resins in HCl medium [5, 95]. Shibukawa et al have reported that the anion exchange selectivity of various anions like IO_3^-, Br^-, NO_3^-, SCN^-, $C_2O_3^{2-}$ and $S_2O_3^{2-}$ could be reversed by using superheated steam, where the rationale has been assigned to the disruption of hydration structure of the ions [94]. However, conventional organic anion exchangers start losing their capacity on heating above 60^oC in air [6, 96]. Hence these exchangers are seldom used at elevated temperatures. Thus there is an increasing need for a thermally stable and efficient sorbent material for elevated temperature ion exchange applications.

Even though Polyaniline (PAni) possesses promising thermal stability, reports are sparse, from the ion exchange application point of view. Stability of PAni, a key factor in most of its applications, has been evaluated by many researchers. Chemical stability of PAni has been established by various researchers [53, 54]. Work carried out on the radiation stability of PAni and the existing literature is discussed in Chapter 3. It was concluded that PAni is stable upto a gamma radiation dose of 3.6 MGy [97]. Effect of heating on the conductivity of PAni has been reported in the literature [40, 41, 77]. However, the effects of heat treatment on the ion exchange capacity of PAni have not been reported in the literature.

In this chapter, effects of heat treatment on the ion exchange capacity of PAni, alongwith the probable structural modifications, studied using various analytical tools are discussed. Thermogravimetric analysis was carried out for both the chloride and base forms of PAni. Thermal stability of PAni was evaluated by subjecting it (chloride as well as base PAni in the powder form) to temperatures upto 400^{o}C in an electrical furnace. Structural modifications in PAni upon heating upto 500^{o}C were studied using UV-visible spectroscopy, Fourier Transform Infrared Spectroscopy and viscometry. Ion exchange capacities were determined using EDXRF spectrometry. Role played by the medium on thermal stability of PAni was evaluated, in order to gain further insight into the thermal behavior of PAni.

4.2 Experimental

4.2.1 Synthesis of PAni

Chemical oxidative polymerization of aniline was carried out using ammonium persulphate in HCl medium below 5^{0}C. The detailed synthesis procedure is reported [52, 97] and discussed in Chapter 2, Section 2.1, of this thesis.

4.2.2 Thermogravimetric analysis

Thermogravimetric (TG) measurements, alongwith evolved gas analysis (EGA), were carried out on 10 mg samples in air as well as nitrogen atmosphere (flow rate: 120 mL min^{-1}) using Netzsch thermal analyzer (Model No.: STA 409 PC Luxx) coupled to Bruker Fourier Transform Infrared (FTIR) system (Model No.: Tensor 27) via a heated Teflon capillary (1 m long, 2 mm internal diameter). Specimen holders, made from recrystallized alumina, were used for thermal measurements. The heating rate of 10^{o}C min^{-1} was maintained in all the measurements. EGA was carried out using FTIR spectroscopy and the evolved gases were identified through their vibrational bands in the mid infrared region (400 - 4000 cm^{-1}). The adapter heads of thermo-balance, transfer line and sample cell were heated to a constant temperature of 200^{o}C to avoid condensation of low volatile compounds. The FTIR compartment was continuously purged with high purity nitrogen and molecular sieves / silica gel were used to minimize the water and carbon dioxide background in the recorded spectra. FTIR data analysis was carried out using Opus software from Bruker.

4.2.3 Thermal treatment of PAni powder

Both chloride and base PAni, in the form of powder (~ 2 g each)**,** were taken in ceramic boats and heated in air, at different temperatures in the range of 50^{o}C to 500^{o}C in an electrical furnace. Holding time was fixed as 1 h at each temperature.

Effect of water and 1 M HCl media, during heat treatment was also studied. The upper limit of temperature was 100^{o}C for these studies, as dictated by the boiling points of these media. Approximately 2 g each of PAni alongwith 100 mL of water / 1 M HCl was taken in a round-bottom glass flask and heated at ~ 100^{o}C for 1 h using a heating mantle. Temperature of the mixture was monitored using a thermometer.

4.2.4 UV-visible spectroscopy

All the heat-treated samples were allowed to attain equilibrium with ambient temperature. Pristine as well as heat-treated samples of base-PAni were dissolved (~ 20 µg mL^{-1}) in 0.5% LiCl - N-Methyl pyrrolidinone (NMP) solvent system. UV-visible spectra of all the solutions were recorded using a JASCO-V-530 spectrophotometer in the wavelength range of 200-800 nm, as discussed in Chapter 2, Section 2.3.3.

4.2.5 FTIR spectroscopy

FTIR spectroscopic analyses of both the solid PAni and the gaseous decomposition products of PAni were carried out, as described below.

4.2.5.1 Solid samples of PAni

Infrared spectroscopic measurements were performed on the pristine as well as heat-treated PAni samples, using FTIR in transmission mode under vacuum. A Bruker IFS 125 high resolution spectrometer was used for these measurements at room temperature and the spectra were recorded in the wave number range of 400-4000 cm^{-1}. Details of the measurements are discussed in Chapter 2, Section 2.3.4, of this thesis.

4.2.5.2 Gaseous decomposition products of PAni

Approximately 100 mg of chloride-PAni was taken in a clean quartz tube (diameter: 12 mm and length: 10 cm) fitted with a high vacuum Teflon stop cock. Sample in the tube was electrically heated at 100^oC for 1 h with continuous evacuation by a diffusion pump (upto ~ 10^{-4} mbar), to remove any trapped O_2, N_2 and condensed H_2O vapour on the sample surface. Next, the degassed sample-tube was connected to a pre-evacuated (vacuum 10^{-5} mbar) gas cell of length 26 cm fitted with KBr window. The tube, containing the sample, was heated at 300^oC for 30 min. All the stable gaseous products, generated from the decomposition of chloride-PAni, were collected in the connected gas cell for IR measurements. The whole set-up for heating and gas collection was devised in-house and is depicted in Fig. 4.1.

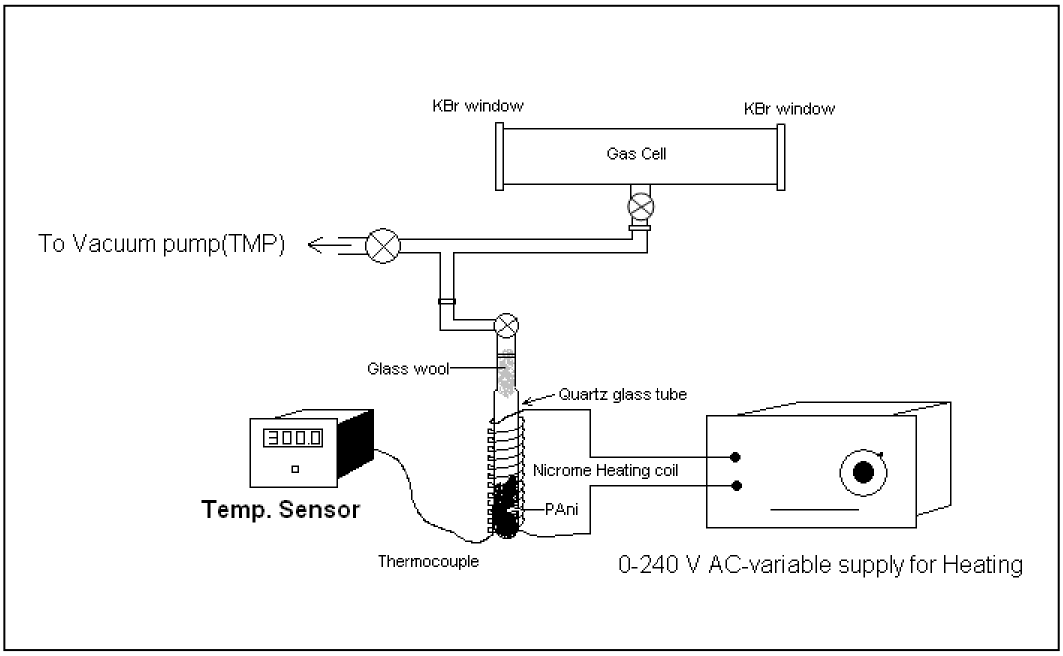


Fig. 4.1 Set-up for heating and collection of gases for vibrational spectroscopic analysis

Instrumentation and measurements for FTIR spectroscopy were the same as those described in Chapter 2, Section 2.3.4. The spectra were recorded in the range of 400-4000 cm^{-1}, at spectral resolutions of 2 and 0.05 cm^{-1} each, in order to get a comprehensive picture of both the broad features and the rotational structures of each gaseous molecule, for their unambiguous identification. A liquid nitrogen cooled MCT (HgCdTe) detector was used to record the high resolution (0.05 cm^{-1}) spectrum.

4.2.6 Molecular weight and viscometric properties

Molecular weight of PAni was determined by dilute solution viscometry, using a calibrated Ostwald viscometer. Solutions for viscometric measurements were prepared by dissolving known amounts of pristine base-PAni (2 - 200 μg mL^{-1}) in 0.5% LiCl-NMP solvent system, at room temperature. Kinematic viscosities, η, of the pure solvent as well as the base-PAni solutions were calculated from the respective measured times of flow. The calculated kinematic viscosities were converted to the reduced viscosities for each of the base-PAni solutions. Intrinsic viscosity of base-PAni solutions was obtained by plotting the reduced viscosities against the corresponding concentration of base-PAni in the solution and using the Huggin's relation, as shown by equation 2.2 in Chapter 2, Section 2.3.5. [71]. Molecular weight of PAni was calculated by employing the Mark-Houwink-Sakurada relation [69, 70] as shown by equation 2.3 and detailed in Chapter 2, Section 2.3.5.

Further, the effect of heating on the viscometric properties of PAni was investigated. Heat-treated base-PAni powder samples were dissolved in 0.5% LiCl-NMP solvent system and the kinematic viscosities were determined through Ostwald viscometry. From these values, reduced viscosities were derived and plotted against the corresponding concentration of base-PAni in solution.

4.2.7 Variation of chlorine-content of PAni upon heat treatment

The chlorine profiling in chloride-PAni as a function of heating was carried out using EDXRF spectrometry, as detailed in Chapter 2, Section 2.3.2.2. All the samples were allowed to attain thermal equilibrium with the ambient temperature (25-30^{o}C), prior to the determination of chlorine. Pelletization of the sample powders was carried out using an automatic KBr press (Technosearch instruments) at a constant pressure of 10 tons. Pellets of chlorine standard were prepared by evaporating standard NaCl solution in microcrystalline cellulose powder, followed by pelletization. All the sample and standard pellets were of identical dimensions (~ 150 mg weight, 13 mm diameter and 0.4 mm thickness).

EDXRF spectra of the pressed pellets were acquired at room temperature, using a Jordan Valley EX-3600M spectrometer under optimized acquisition parameters viz. applied voltage = 35kV, emission current = 1400 µA, Ge-secondary target, counting time = 500 s and air medium. Calibration curves were generated by plotting the net counts for the characteristic X-rays, viz. Cl-K_α (energy = 2.6 keV) versus the corresponding concentration of Cl in the standard pellets. The chlorine content in each of the chloride-PAni samples was calculated from the net counts obtained for Cl using K_α X-ray intensity in the sample pellets and the calibration plot. Variation of Cl-content in chloride-PAni with heating was obtained from the EDXRF analysis.

4.2.8 Ion exchange capacity

Ion exchange capacity of chloride-PAni, in terms of ionizable chlorine, was determined by EDXRF spectrometry, as discussed in Chapter 2, Section 2.3.2.2. Ionizable chlorine content in chloride-PAni was obtained by subtracting the covalent chlorine from the total chlorine. For the determination of total chlorine, both the pristine and heat-treated chloride-PAni samples were equilibrated with 1 M HCl and filtered. Excess HCl was washed with deionized water, till the washings were free of chloride, as confirmed by $AgNO_3$ test. The HCl-treated PAni samples were further air-dried, pelletized and analyzed by EDXRF to obtain the total chlorine. In order to determine covalent chlorine, all the chloride-PAni samples were equilibrated with 1 M NH_4OH, washed with deionized water, air-dried, pelletized and analyzed by EDXRF.

4.3 Results and discussion

PAni was synthesized via the chemical oxidation of aniline in HCl medium and was converted to chloride and base form by appropriate chemical treatment, as discussed in the Chapter 2, Section 2.1.

4.3.1 Thermogravimetric analysis

Fig. 4.2 shows the thermograms for both chloride and base PAni in air as well as nitrogen atmosphere. It can be seen from Fig. 4.2 that a three-stage weight loss occurred in nitrogen atmosphere and two-stage weight loss in air, for both chloride and base PAni.

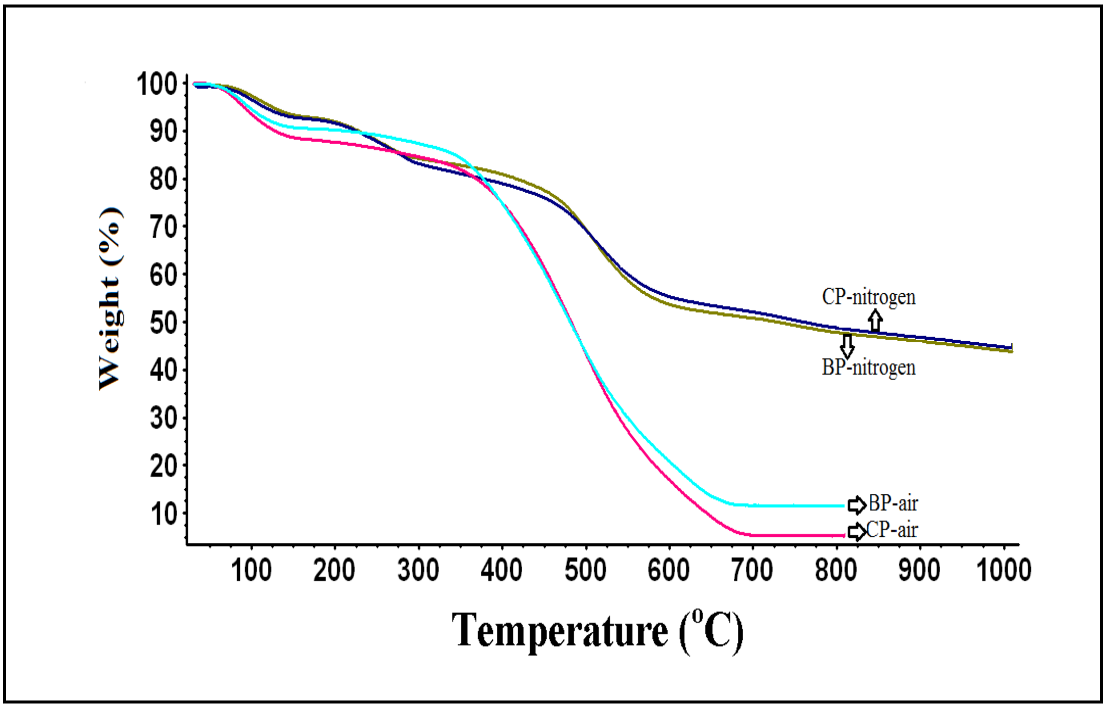


Fig.4.2 Thermograms for chloride (CP) and base PAni (BP) in air as well as nitrogen atmosphere

During the initial phase of heating upto 60^{o}C, all the four thermograms showed no significant weight loss. Above 60^{o}C, chloride-PAni in air showed the highest rate of weight loss, whereas base-PAni in nitrogen showed the least. This initial weight loss upon heating upto 150^{o}C was assigned to the loss of moisture and bound water. In the temperature range of 150-350^{o}C, both chloride and base PAni showed lower rates of loss in air, compared to those in nitrogen. Nitrogen atmosphere was found to induce an additional step of weight loss in this temperature range. In the case of chloride-PAni heated in the air above 150°C, it has been postulated that the total chlorine content remains the same, but the PAni gets transformed to a deprotonated structure, containing chlorine-substituted aromatic rings [41, 77]. Oxidation of benzenoid to quinoid moieties and subsequent chlorination of the aromatic rings of chloride-PAni have been reported as the main ageing mechanism of PAni subjected to heating in air at 140^{o}C for 10 days [75]. Further heating of chloride-PAni beyond 350^{o}C showed the highest rate of weight loss in both the atmospheres. The final weight loss could be attributed to the breakdown of the polymer chain, resulting in volatile products. Presence of oxygen in the air caused a much higher decomposition rate beyond 400^{o}C, compared to that in nitrogen atmosphere. Heating in air led to complete combustion of carbon, whereas ~ 45% of the original weight was left behind in nitrogen atmosphere, which corresponds to unburnt carbon [40, 41, 77].

It could be inferred from the thermograms that the chloride-PAni is more susceptible to thermal agitation, compared to base-PAni. This could be explained on the basis of delocalization of electrons in the two systems. In chloride-PAni, islands of delocalized π-electrons are present in the aromatic rings and these are not extendable to the entire polymer chain. In the case of base-PAni, the conjugation is extended throughout the polymer chain. Thus it exhibited better stability, as observed. Present results are in agreement with previous reported results on the better thermal stability of base-PAni compared to various salt forms of PAni [76]. Kulkarni et. al. reported that the base-PAni is a highly heat-resistant polymer with thermal stability upto 420^{o}C.

EGA, carried out in conjunction with TG, indicated the evolution of H_2O in the temperature range of 60-150^{o}C, followed by HCl in the region of 115-198^{o}C and finally CO_2 in the temperature range of 447-683^{o}C. The gas evolution pattern was in accordance with the thermal decomposition behavior of PAni.

4.3.2 UV-visible spectroscopy

Fig. 4.3 shows the UV-Visible absorption spectra of base-PAni in 0.5% LiCl-NMP, before and after heat-treatment. UV-visible absorption spectrum of base-PAni in 0.5%LiCl-NMP is reported to have two absorption maxima at around 330 nm and 640 nm [64]. Former one is attributed to the π-π* transition and the latter to a charge-transfer exciton-like transition from benzenoid to quinoid rings [64].

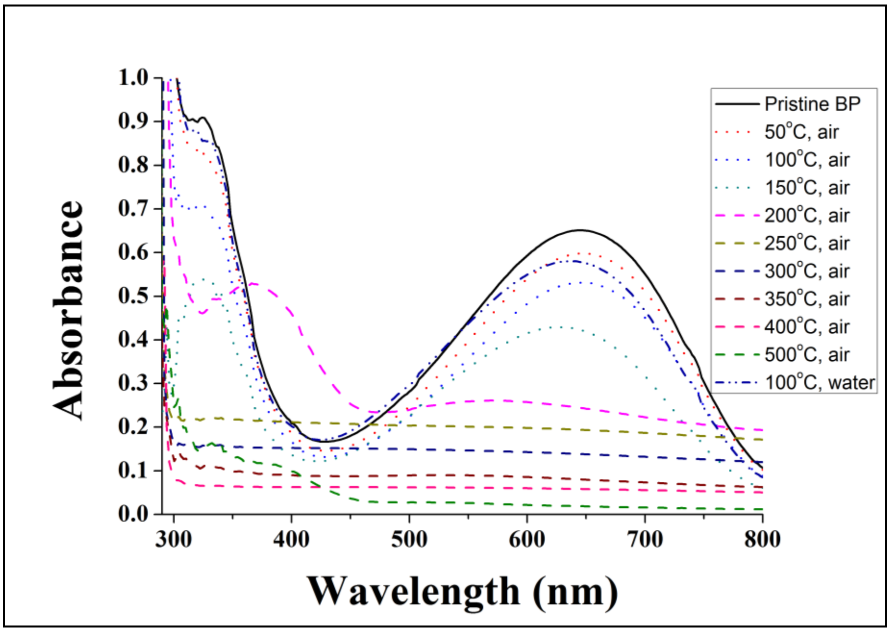


Fig. 4.3 UV-Visible spectra of base-PAni in 0.5% LiCl-NMP solvent system, before and after heat treatment to different temperatures

Presence of benzenoid alongwith quinoid rings could be ascertained in pristine base-PAni, as is evident from the characteristic bands around 324 and 646 nm in Fig. 4.3. Heating of base-PAni, in air upto 150^{o}C, resulted in marginal hypsochromic shift in the band at 646 nm and gradual reduction in intensity of both the characteristic bands. A remarkable change in the UV-visible spectrum was observed upon heating base-PAni at 200^{o}C. Beyond 250^{o}C, both the peaks disappeared. Oxidation, of benzenoid to quinoid units is proposed to be the rationale behind the above observations.

4.3.3 FTIR spectroscopy

4.3.3.1 Solid samples of PAni

FTIR spectroscopy was used as an analytical tool for recognizing the extent of structural changes taking place in PAni, upon heating. Fig. 4.4 is a comparison of the FTIR spectra of heat-treated chloride-PAni samples with that of as-synthesized chloride-PAni.

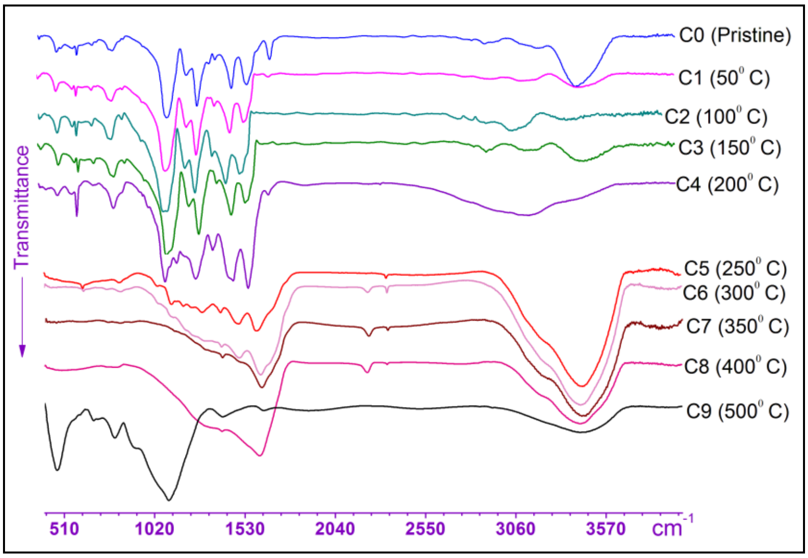


Fig.4.4 Effect of heat treatment (air, 1 h) on the FTIR spectra of solid chloride-PAni

Identity of as-synthesized chloride-PAni was ascertained by the presence of characteristic peaks at 815, 1140, 1290, 1490 and 1590 cm^{-1} as has been reported in the literature [22, 65, 66]. All these peaks were unaltered, with negligible shift, upon heat treatment of PAni upto 200^{o}C. Beyond this temperature, irreversible structural damage was evidenced from the vanishing of characteristic peaks. Appearance of a weak feature at ~2226 cm^{-1} in the FTIR spectra of chloride-PAni subjected to temperatures ≥ 300^{o}C is indicative of the formation of –CN group, resulting from polymer chain cleavage. Beyond 400^{o}C, -CN groups also dissociate, as could be seen from Fig. 4.4.

FTIR spectroscopic measurements could be used to follow the conversion of ionic (Cl^-) to covalent chlorine (-Cl) upon heating of chloride-PAni. Ionic chlorine is the one attached to nitrogen atoms in PAni and is responsible for the ion exchange properties of PAni. Covalent chlorines are attached to carbon atoms of the aromatic rings. The peak at ~ 620 cm^{-1} in the FTIR spectra corresponds to C-Cl stretching [65]. Relative intensity of the C-Cl peak was found to increase on heating till 200°C. Further heating above 250°C led to the loss of covalent chlorine also, as shown in Fig. 4.4. The observed conversion of ionic to covalent chlorine is in accordance with the established relatively higher stability of covalent bonds compared to ionic bonds [98].

4.3.3.2 Gaseous decomposition products of PAni upon heating

As discussed above, chloride-PAni was found to undergo radical changes in the structure, upon heating beyond 250°C. Hence, the chloride-PAni sample was closely examined by subjecting it to a specific temperature of 300°C. The gaseous products were characterized by High Resolution FTIR spectroscopy. The temperature of 300°C was chosen, based on the following two considerations: (i) heating above 250°C is required to generate gaseous decomposition products in sufficient quantity for getting measurable IR signals and (ii) heating beyond 350°C results in the generation of CO and CO_2 in large quantities, which may saturate the spectrum and consequently mask the signals from other decomposition products. Observed spectra of gaseous products formed from chloride-PAni upon heating at 300°C are shown in Fig.4.5.

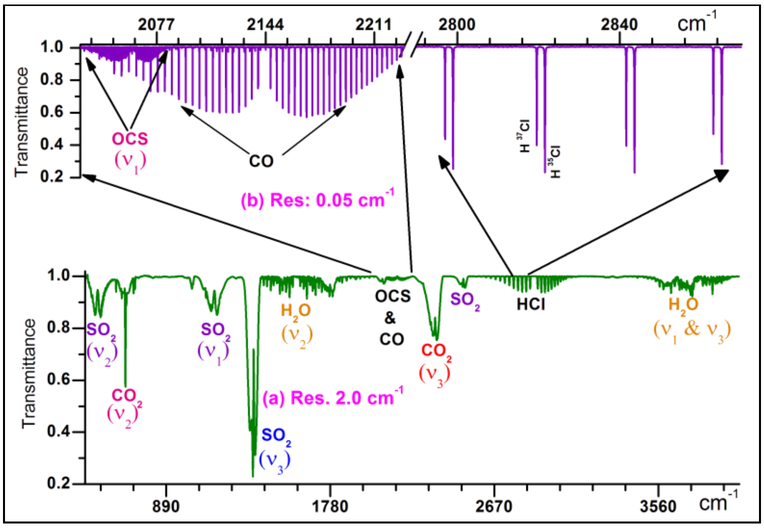


Fig.4.5 Vibrational spectra of gaseous decomposition products of chloride-PAni subjected to heating at 300°C

Fig. 4.5(a) indicates the broad features (Resolution = 2 cm^{-1}) of the spectrum, showing all gaseous products viz. CO, CO_2, OCS, H_2O, HCl and SO_2. Fundamental vibrational modes of OCS, H_2O, CO_2 and SO_2 are also marked in the Figure. Fig. 4.5(b), recorded at a higher resolution of 0.05 cm^{-1}, shows the rotationally resolved characteristic spectra of CO, HCl and OCS. Formation of HCl gas was confirmed by resolving its isotopic species as $H^{35}Cl$ and $H^{37}Cl$ with their respective natural abundances. Signatures of nitrogen-containing gases, namely NO_x and HCN were not observed in the FTIR spectrum, which affirms the promising heat-stability of C-N bonds in chloride-PAni. Sulphonyl groups were reported to get incorporated in PAni during synthesis using ammonium persulphate [20] and hence are proposed to be the genesis for the formation of SO_2 and OCS upon heating of chloride-PAni at 300°C.

4.3.4 Effect of heat treatment on the viscometric properties of PAni

Dilute solution viscometry is one of the techniques used for finding out the molecular weight of polymers. Molecular weights are calculated through Mark-Houwink-Sakuarada equation, as discussed in Chapter 2, Section 2.3.5. Viscometric properties were studied as a function of heating of PAni, in order to gain further insight into the structural modifications during thermal treatment. Fig. 4.6 depicts the effect of heating of PAni on the reduced viscosity.

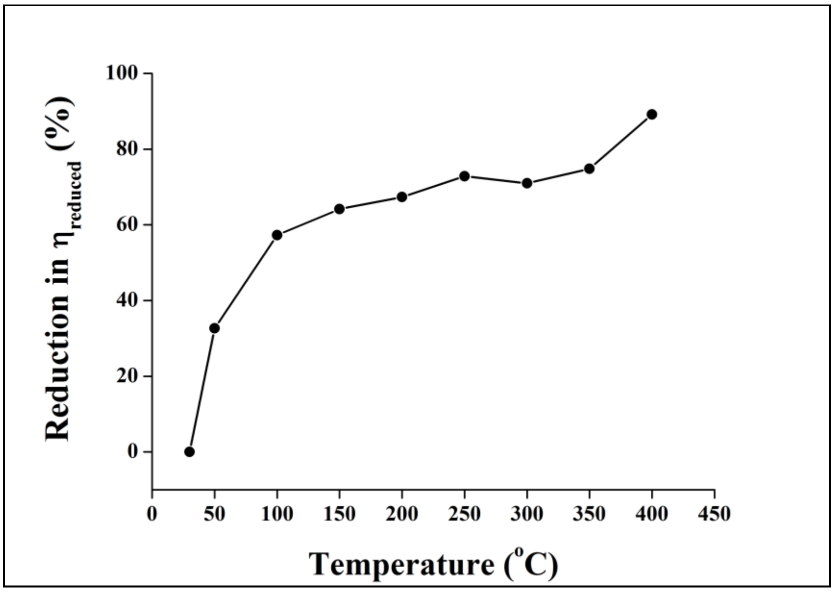


Fig. 4.6 Reduced viscosity of base PAni-0.5% LiCl-NMP system, as a function of temperature

The reduced viscosity of the system decreased gradually as a result of thermal treatment on PAni. Initial heating upto 100^{o}C led to a sharp decrease in viscosity. This could be attributed to (i) the reduced solubility of PAni consequent to the loss of moisture and bound water and (ii) the lowering of inter-chain interactions, namely the hydrogen bonding or cross-linking, since the PAni chain structure was uninterrupted upon heating at 100^{o}C, as confirmed by TG-EGA, UV-visible and FTIR spectrometry. Further heating resulted in a slower rate of reduction.

Viscometric behavior of polymers is indicative of their molecular weight. However, the Mark-Houwink-Sakuarada constants K and α are specific to a particular polymer (or its homologues)-solvent system at a given temperature. As could be seen from the thermogravimetric analysis, thermal decomposition of PAni was not necessarily leading to lower homologues. Hence, the reported Mark-Houwink-Sakurada constants could not be susbstituted for finding out the molecular weight of heat-treated PAni samples. The diminishing trend in reduced viscosity of the heat-treated PAni samples is indicative of the probable lowering of molecular weight of PAni.

4.3.5 Chlorine profile in chloride-PAni upon heating

Loss of chlorine from chloride-PAni upon heating can be visualized from the EDXRF spectra shown in Fig. 4.7. The chlorine content of chloride-PAni was found to decrease upon heat treatment. There was a swift change in chlorine values upon heating above 250°C. Decrease in chlorine content of chloride-PAni, upon heating in an electrical furnace was in concurrence with that obtained from TG and EGA studies. The loss of chlorine could be attributed to the evolution of HCl gas upon heating PAni, as has been reported in the literature [99].

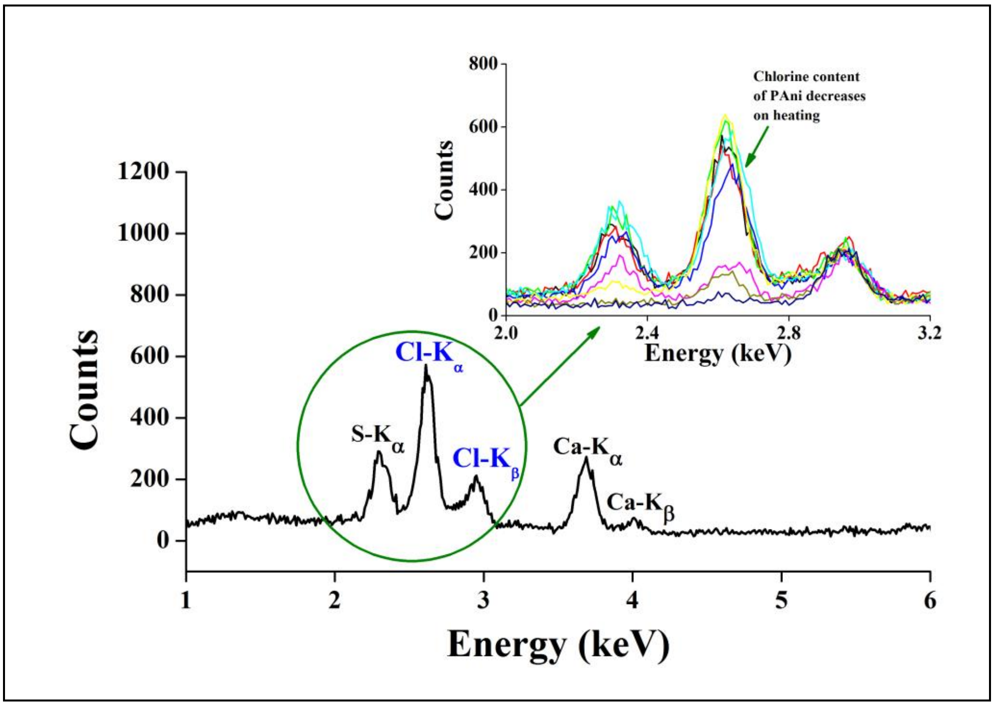


Fig. 4.7 EDXRF spectra of chloride-PAni, before and after heat treatments

A direct correlation was observed between the chlorine profile and self binding ability of chloride-PAni powder. As-synthesized chloride-PAni powder showed excellent self-binding ability and could easily be pelletized for chemical/structural analysis during these studies. However, this self-binding capacity was found to decrease upon heat treatment. This effect was shown to aggravate upon heating to temperatures ≥ 250^{o}C, and the pelletization became increasingly difficult. Even the addition of binding agent, like polyvinyl alcohol (2% aqueous solution, 100-300 µL), could not help improve the integrity /stability of these pellets.

4.3.6 Effect of heat treatment on the ion exchange capacity of PAni

As detailed in Chapter 2, Section 2.3.2, the weak anion exchange property of PAni stems from the labile anions attached with the nitrogen atoms in the salt form of PAni. EDXRF analysis of PAni showed that approximately 2% of the total chlorine in pristine chloride-

PAni was covalent in nature. Formation of covalent chlorine has been reported in the literature, during the synthesis of PAni in the presence of large excess of HCl [20]. The ionic chlorine content in chloride-PAni was calculated from the difference between the total and covalent chlorine values. Ion exchange capacity of as-synthesized chloride-PAni was found to be 3.25 ± 0.084 meq g^{-1}, in conformity with the reported value [48, 49].

Retention of the structural integrity upto 200°C, as was evidenced by the FTIR spectra, encouraged to investigate whether the heat treated chloride-PAni samples can regain the ion exchange capacity on equilibration with HCl. Fig. 4.8 shows the effect of heating on the ion exchange capacity of chloride-PAni.

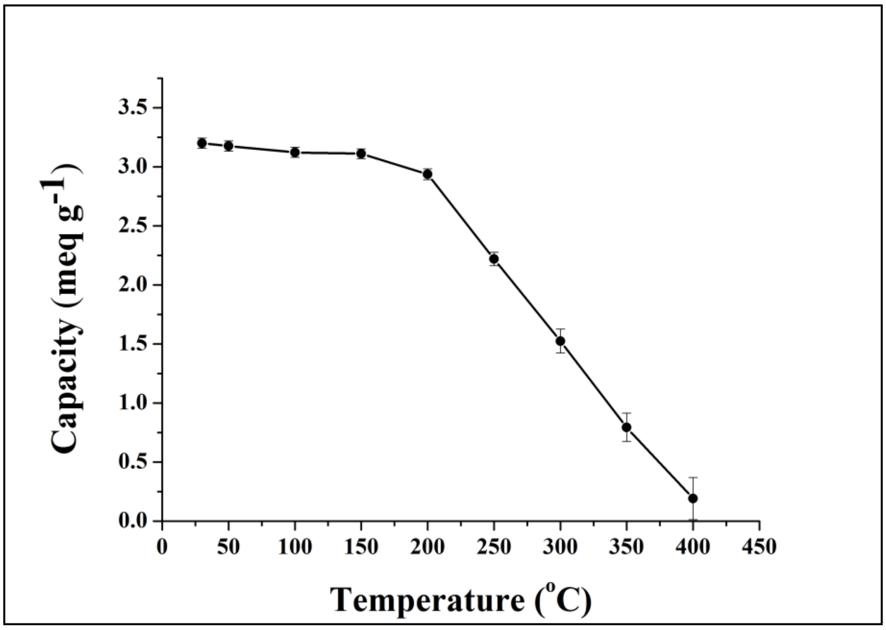


Fig. 4.8 Ion exchange capacity of chloride-PAni[†], as a function of heating in air

([†] Ion exchange capacity of as-synthesized chloride PAni = 3.25 ± 0.084 meq g^{-1})

Chloride-PAni was found to be thermally stable upto 200°C and could regain ~ 90% of the original capacity upon HCl treatment. Heating above 200°C resulted in rapid decrease in the ion exchange capacity and the rate of decrease was linear, as shown in Fig. 4.9. A similar trend has been reported for the conductivity of chloride-PAni, which was subjected to heat ageing at 150°C for long duration [41, 63, 75]. Loss of ionizable chlorine upon heating above 150°C could be attributed to the elimination of HCl from the nitrogen and simultaneous chlorination of the aromatic ring [41, 63, 75]. It was interesting to note that the percentage of covalent chlorine showed an initial rise upon heating, passed through a maximum corresponding to 200°C and showed a rapid reduction on further heating. Most importantly, the sample subjected to 200°C was found to contain covalent chlorine solely. These observations are in close agreement with the TG data shown in Fig.4.2.

As all ion exchange processes are invariably carried out in appropriate solvent media, thermal stability studies were extended to investigate the effects of medium (water and 1 M HCl) during heat treatment. PAni was found to retain the ion exchange capacity, during heat treatment upto 100°C, irrespective of the medium. The retention of the ion exchange capacity is a promising feature, as far as the ion exchange applications are concerned.

Generally, the thermal stability of ion exchange resins depends on the matrix structure, nature of the active groups and the counterion [100]. Anion exchangers are more susceptible to thermal agitation than cation exchangers. The thermal effects are more pronounced in the case of strong anion exchangers, in comparison with weak anion exchangers. Further, the salt forms are reported to have higher thermal stability than the corresponding hydroxide forms [101]. Thermal decomposition of anion exchangers are reported to be due to the Hoffman degradation, deamination and polymer decomposition. Most of the conventional anion exchangers possess the functional (amine /ammonium) groups either in the side-chain or as a pendant to the main chain. These are susceptible to cleavage, even upon slight heating above 60^{o}C, and hence the exchangers start losing their capacity during heating above 60^{o}C. The recommended maximum operating temperature for conventional weak anion exchangers is 100^{o}C [102].

PAni is a weak anion exchanger and was expected to have better thermal stability compared to conventional anion exchangers, since the functional nitrogen atoms are in the main chain/backbone of the polymer. It could be concluded from the present studies that PAni does not undergo deamination upto 200^{o}C and hence is a promising ion exchanger for applications at elevated temperatures.

4.4 Conclusion

Thermal stability of PAni was evaluated to assess its use as ion-exchanger at elevated temperatures. Thermogravimetric analysis showed that the weight loss in air was more pronounced compared to that in nitrogen atmosphere, for both chloride and base PAni. The higher weight loss in air above 350^{o}C was attributed to the oxidation of the polymer to form volatile components. The observed better stability of base-PAni, compared to chloride-PAni, was attributed to the extension of conjugation throughout the polymer chain. Structural modifications in PAni upon heating upto 500^{o}C were studied using UV-visible spectroscopy, Fourier Transform Infrared Spectroscopy and viscometry. FTIR spectroscopic studies clearly indicated the conversion of ionic chlorine to covalent chlorine upon heat treatment. Identity of the gaseous decomposition products of chloride-PAni upon heating at 300^{o}C was established by high resolution infrared spectroscopy. Anion exchange capacity of polyaniline, as determined by Energy Dispersive X-ray Fluorescence spectrometry, was found to be 3.25 ± 0.084 meq g^{-1}. PAni could regain ~ 90% of the original ion exchange capacity upon equilibration with HCl after heat treatment upto 200^{o}C. Hence, it could be concluded that the nitrogen atoms are being retained and the polymer backbone is intact during heat treatment upto 200^oC. Water and HCl media were found to have negligible effect on the ion exchange capacity of PAni at elevated temperatures. These studies evinced the superior thermal stability of polyaniline over conventional anion exchangers, in terms of ion exchange capacity as well as structural stability.

Chapter 5

Sorption of Hg(II) from aqueous solutions using polyaniline and its composites

Executive summary

Hg(II) was sorbed on polyaniline from aqueous solutions, followed by determination using energy dispersive X-ray fluorescence spectrometry. Distribution ratio of Hg(II) was determined in HCl solutions. Rapid kinetics of sorption was evinced by the 80% uptake within the initial 1 min and quantitative sorption within 5 min of equilibration. The sorption was found to follow Langmuir isotherm model and the ability of polyaniline to form stable and homogeneous pellets facilitated the energy dispersive X-ray fluorescence determination without recourse to elution. Detection limit of Hg was 166 ng, as obtained from the calibration plot. The apparent detection limit was 42 pg, as the preconcentration factor of Hg(II) on polyaniline was $4\text{x}10^3$.

5.1 Introduction

Mercury is one of the most significant pollutants due to its high toxicity and widespread industrial applications [103-105]. Most common analytical techniques for the determination of Hg are cold vapor atomic absorption spectrometry (CVAAS), cold vapor atomic fluorescence spectrometry (CVAFS), inductively coupled plasma mass spectrometry (ICPMS), electrochemical methods and neutron activation analysis (NAA) [104-106]. Analytical techniques are compared and qualified in terms of sensitivity, selectivity, precision and detection limit. Determination of mercury demands adequate precautions during sample processing, to address its loss due to volatilization [105], in addition to the above-mentioned analytical figures of merit. A technique requiring minimal sample processing is ideal in such circumstances. The attractive features of energy dispersive X-ray fluorescence (EDXRF) spectrometry are that it is a non-destructive technique, requires minimal sample preparation and solid samples can be directly analyzed [104, 107]. EDXRF, as applied to solid powders, involves the preparation of pressed pellets of both samples and standards, having identical dimensions, in order to ensure reproducibility in quantitative analyses. However, limited sample quantity and the generally low concentration ranges of Hg (mg kg^{-1} or even less) observed in most of the samples may complicate the EDXRF quantification in certain cases [104]. The limitations put forward by sample quantity can be compensated by adding appropriate base materials during the sample preparation, provided that the concentration levels of Hg are sufficient for EDXRF determinations. The most common base materials used in EDXRF sample preparations, are microcrystalline cellulose, boric acid and boron nitride, which help in both sample size management and preparation of sturdy pellets. These base materials are compounds of low-Z elements and thus are nearly transparent to both the probing X-rays from the exciting source as well as signal generating characteristic X-rays of the analytes.

However, determination of very low levels of Hg using EDXRF technique requires a separation or preconcentration step, since the detection limits are of the order of 10 parts per million (ppm) [108]. Preconcentration of Hg on sorbents having suitable X-ray absorption/emission characteristics will improve the detection limits, linear dynamic range and reduce the matrix effects, in EDXRF determinations.

A multitude of sorbents have been reported in the literature for the preconcentration of Hg from aqueous solutions such as polymers [103, 109], activated carbon [107], chitosan [110, 111], natural minerals [112, 113] and biomass such as bacteria [114], to name a few. Most of these materials bind Hg through sulfur, nitrogen or oxygen atoms present in the functional groups [115].

Polyaniline (PAni) contains amine and imine functional groups, and thus is expected to have interactions with metal ions having strong affinity to nitrogen [115]. PAni has been used for the anion exchange separation of platinum group elements as well as Hg from acidic solutions [48, 49, 52]. PAni has also been reported in the literature as a base material for preparing Hg-standard for neutron activation analysis [116]. Homogeneity and long-term stability of PAni-Hg complex is well established [116]. PAni, being constituted with low-Z elements (carbon, hydrogen and nitrogen), has very low X-ray absorption/emission characteristics and hence is an ideal matrix for EDXRF spectrometry. Additionally, PAni powder has excellent self binding ability and forms stable pellets.

In this chapter, studies on the sorption of Hg (II) on PAni and its composites from aqueous solutions are discussed. Distribution ratio, kinetics and isotherm for the sorption

Hg(II) on PAni were investigated. Further, the sorbed Hg was quantified by EDXRF spectrometry using the pressed pellets of PAni via the calibration method. Suitability of PAni as a base material for the preparation of Hg-standard pellets for calibration is discussed, considering the X-ray absorption/emission characteristics. Preconcentration of Hg on PAni and the resultant improvement in the detection limit of EDXRF measurements are discussed.

Two different composites of PAni, discussed in Chapter 2 of this thesis, have been utilized in the present investigations for the sorption and determination of Hg. PAni-alginate beads and PAni-silane discs were investigated for the sorption of Hg, keeping in mind the practical ion exchange column applications as well as reducing the sample preparation steps for EDXRF determinations.

5.2 Experimental

5.2.1 Materials and methods

PAni and its composites namely PAni-alginate beads and PAni-silane discs were synthesized and characterized as discussed in Chapter 2.

5.2.2 Determination of Hg by EDXRF spectrometry

5.2.2.1 Preparation of calibration standards

Calibration standards were prepared in the form of pellets as well as discs for the determination of Hg. For the preparation of standard pellets, varying volumes of Hg(II) standard solution (20 µg mL^{-1}) were added to 100 mg of pristine PAni powder, followed by drying under infrared (I.R.) lamp and homogenization. Pellets of the calibration standards were prepared using a KBr press (AP-15, Technosearch Instruments) at 10 tons pressure. Standards in the form of discs were prepared by in-situ incorporation of $HgCl_2$ in PAni-silane composites, during their synthesis.

In addition, Hg-standard pellets were prepared by direct solid mixing of $HgCl_2$ and PAni powder, followed by serial /stepwise dilution and pelletization. The required 1000-fold dilution was carried out by mixing with PAni powder, stepwise in three stages. For checking the homogeneity, three replicate pellets were prepared for each concentration of Hg. Another set of calibration standard pellets for Hg was prepared by replacing PAni with microcrystalline cellulose (particle size < 75 µm), in order to study the effect of the base material in EDXRF determinations. All pellets had identical dimensions (weight = 100 mg, diameter = 12 mm and thickness = 0.2 mm).

5.2.2.2 EDXRF Instrumentation and measurement procedure

XRF measurements were made using an EDXRF spectrometer (EX-3600 M, Jordan Valley, Israel; Resolution = 145 eV for 5.9 keV X-rays). Characteristic $L_{III}M_V$ (9.988 keV) and $L_{II}M_{IV}$ (11.823 keV) [117] X-rays were used as analytical lines for Hg determination. Triplicate measurements were made on each standard pellet and the X-ray fluorescence intensities of Hg were obtained from EDXRF spectra. Calibration curve for Hg was obtained by plotting the intensity of characteristic X-rays against the concentration of Hg in the standard pellets.

5.2.3 CVAAS determination of Hg(II) in solutions

Hg(II) in solution was determined by CVAAS using a GBC 906 AA atomic absorption spectrometer. Absorbance at 253.7 nm was used for quantification of Hg in the solutions. Calibration standards of Hg (5 to 50 ng mL^{-1}) were prepared by appropriate dilution of the stock standard solution.

5.2.4 Sorption of Hg(II) from aqueous solutions

The kinetics, distribution ratio and equilibrium of sorption of Hg(II) from aqueous solutions in PAni were investigated, as follows. Effect of various metal ions on the sorption of Hg(II) in PAni were also studied.

5.2.4.1 Kinetics of sorption of Hg(II) in PAni and its composites

Sorption kinetics of Hg(II) was investigated on PAni powder as well as its composites namely PAni-alginate and PAni-silane discs. Accurately weighed PAni/PAni-alignate (150 mg each) was equilibrated with 10 mL of 1 M HCl solution containing 200 µg of Hg(II) and filtered after definite time interval. Duration of equilibration was varied between 1 min to 24 h. Hg(II)-sorbed PAni/PAni-alginate composite was dried under I.R. lamp and pelletized (weight = 100 mg, diameter = 12 mm and thickness = 0.2 mm). The pellets were analyzed by EDXRF and the quantification was carried out with the aid of calibration equation. In the case of PAni-silane composite discs, weight of disc taken for equilibration was fixed as ~ 100 mg each and no processing was required after sorption of Hg. The solutions, before and after equilibration, were analyzed by CVAAS.

5.2.4.2 Determination of distribution ratio of Hg(II) in PAni

The distribution ratio, D_m, of Hg(II) in PAni was determined by batch equilibration method. Accurately weighed PAni powder (150 mg) was added to 10 mL HCl solutions having molarities 0 to 10 M, containing 200 µg of Hg(II). Solutions were equilibrated for 1 h on a mechanical shaker at room temperature and filtered using Whatman 540 filter paper. Concentrations of Hg(II) in the solutions, before and after equilibration, were determined by CVAAS. Distribution ratio of Hg(II) in PAni was calculated using equation 5.1.

$$D_m = \frac{(a_0 - a)}{w}\frac{L}{a} \tag{5.1}$$

where a_o and a are the amounts of Hg(II) (µg) in the solution before and after equilibration respectively, L is the volume (mL) of the solution and w is the weight (g) of PAni.

5.2.4.3 Sorption isotherm for Hg(II) in PAni

Equilibrium sorption characteristics were obtained by varying the concentration of Hg(II) in the solution between 50 ng mL^{-1} to 20 mg mL^{-1} while the volume of solution (10 mL), amount of sorbent (150 mg each for PAni and PAni-alginate composite beads, 100 mg for each for PAni-silane disc), acidity (1M HCl) and equilibration time (1 h) were kept constant. The Hg(II)-loaded PAni/alginate composite samples were pelletized (weight = 100 mg) and analyzed by EDXRF spectrometry. Further, Hg(II) in the solutions, before and after equilibration, were determined by CVAAS. Sorption isotherm was obtained using the experimental data.

5.2.4.4 Studies on interferences from other metal ions

Effects of the presence of other metal ions on the sorption of Hg(II) on PAni/composites as well as the EDXRF analysis of Hg(II)-laden sorbents were studied. Accurately weighed PAni powder /composite (150 mg each) was equilibrated with 10 mL 1 M HCl containing Hg(II), along with Pd(II), Pt(IV), Au(III), Fe(III), Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II). Concentration of Hg was fixed at 1 µg mL^{-1} for these studies. Four sets of experiments were carried out by varying the concentration of all other metal ions between 0 to 10 µg mL^{-1}. All these solutions were filtered after equilibration; the metal-laden PAni/composites (~ 100 mg) were analyzed using EDXRF spectrometry, after drying and pelletization. Metal-sorbed PAni-silane discs (~ 100 mg) were removed from the solution, cleaned with tissue paper to remove the surface-adhering solution and analyzed directly by EDXRF spectrometry.

5.2.4.5 Effect of sample volume on the preconcentration of Hg(II) on PAni and its composites

Batch equilibration studies were carried out to study the effect of sample volume on the preconcentration of Hg(II) on PAni and its composites. 2 µg of Hg(II) was added to 0.1 M HCl (10 - 1000 mL) and equilibrated with 150 mg each of PAni/composite on a mechanical shaker at room temperature. After equilibration for 1 h each, the solutions were filtered through Whatman 540 filter paper. The Hg-laden PAni/composite samples were dried under I.R. lamp, pelletized and analyzed by EDXRF spectrometry. Hg sorbed in the sample pellets (weight = 100 mg) as well as discs were quantified with the aid of calibration equation.

5.2.5 PAni powder as base material for the direct determination of Hg in solid samples by EDXRF spectrometry

PAni powder was investigated as a base material for the direct determination of Hg in solid powder samples. Hg-containing plant leaf powder was obtained from NCCCM, Hyderabad. Sample pellets were prepared by mixing plant leaf powder thoroughly with polyaniline (2:3 w/w). All the sample and standard pellets were of identical size (weight = ~ 100 mg, diameter = 12 mm, thickness = 0.2 mm). Concentration of Hg in the plant leaf sample was calculated from the intensity of L_α X-ray of Hg and calibration equation.

5.2.6 Analysis of reference materials and spiked samples

For validation of the present method, two certified reference materials, viz. IAEA-085 (human hair) and IAEA-336 (lichen) were analyzed and the results are shown in Table 1.

The reported concentrations of Hg(II) in these reference materials were 23.2 ± 0.80 and 0.20 ± 0.40 mg kg^{-1} respectively. Additionally, the method was tested by applying to an aqueous solution sample, spiked with 300 ng mL^{-1} of Hg(II).

5.3 Results and discussion

Fig. 5.1 shows a typical EDXRF spectrum of Hg-loaded PAni pellet, acquired using Rh-target under optimized acquisition conditions (Table 5.1).

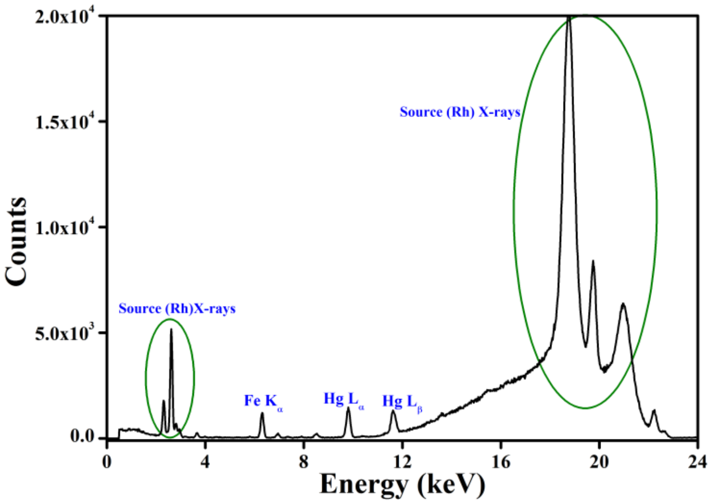


Fig. 5.1 EDXRF spectrum of Hg(II)-loaded PAni pellet

Table 5.1 Optimized acquisition parameters for the EDXRF determination of Hg

Parameter	Value
Filter / Target	Rh
Applied Voltage (kV)	35
Emission Current (µA)	1300
Acquisition time (s)	500
Medium	Air

The most vital step in quantitative XRF analysis is the preparation of calibration standards, due to stringent matrix matching requirements. During these studies, standard pellets of Hg for calibration were prepared using PAni as the base material, in order to overcome the matrix effects. The effective mass attenuation coefficient of PAni (0.285 $cm^2 g^{-1}$) is insignificant, compared to Hg (81.230 $cm^2 g^{-1}$) for the source X-rays (energy = 20 keV) [118, 119]. A linear calibration was obtained in the range of 35 ng to 7 µg of Hg in the pellet, as shown in Fig. 5.2. Similar linear calibration curves were obtained for the discs as well as the standard pellets prepared by both direct solid mixing and cellulose base.

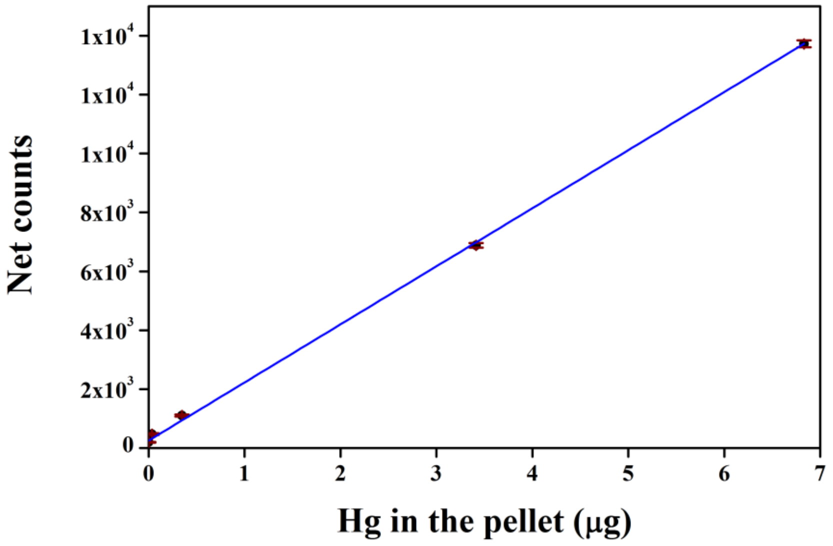


Fig. 5.2 Calibration plot of Hg in the standard pellets prepared using PAni powder by EDXRF spectrometry

All the sample and standard pellets were prepared using approximately 100 mg of PAni powder /composites, in order to maintain identical geometry. In the case of PAni powder and beads, about 150 mg each were used for all batch equilibration experiments, in order that the final pellet weight of 100 mg could be maintained, considering the losses during filtration, drying and pelletization. In the case of PAni-silane discs, since there is no post-sorption processing, 100 mg each of discs were taken for equilibration.

5.3.1 Kinetics of sorption of Hg(II) in PAni /composites

Batch equilibration experiments were carried out to elucidate the kinetics of sorption of Hg(II) on PAni and the results are shown in Fig. 5.3. Rapid sorption of Hg(II) was evinced by the ~ 80% uptake within the initial 1 min of equilibration. For a better visualization of the fast kinetics of sorption, initial part is shown in the inset of Fig. 5.3. Similar observation was reported in the literature for the sorption of Hg on PAni from solutions at pH = 5 [120].

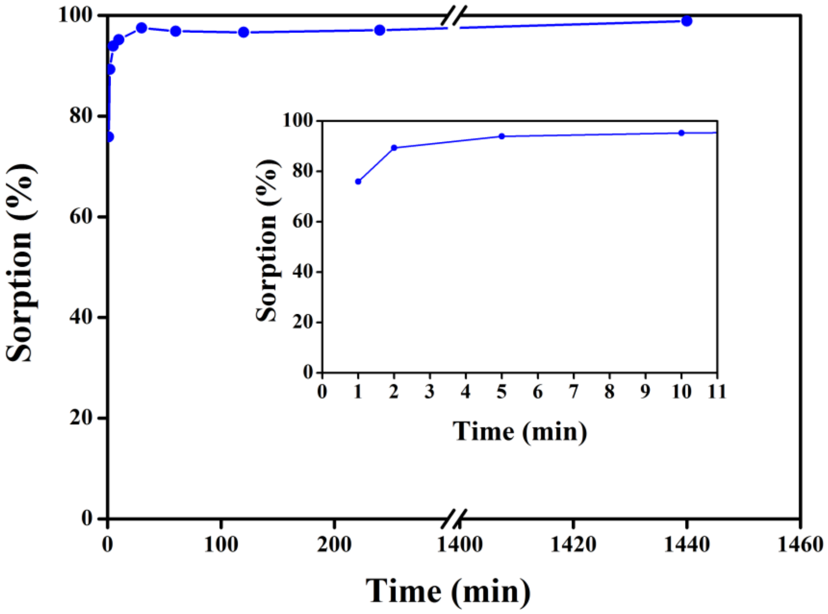


Fig. 5.3 Kinetics of sorption of Hg(II) on PAni powder

Sorption of Hg(II) on the composites of PAni were also found to follow a rapid kinetics. Approximately 80% sorption was observed in the initial 1 min of equilibration.

Quantitative sorption occurred within 5 min of equilibration, reiterating the fast kinetics in all the three sorbents.

There are several reports on the use of kinetic models to describe the experimental data of heavy metals sorption [121-123]. One of the most widely used model for understanding the kinetics of sorption is the Lagergren's equation or the pseudo-first order equation [124]. Equation 5.2 represents the pseudo first-order Lagergren model.

$$\frac{dq}{dt} = k_1(q_e - q) \qquad (5.2)$$

where q (mg g^{-1}) is the amount of Hg(II) sorbed at time t, q_e is the amount sorbed at equilibrium and k_1 (min^{-1}) is the rate constant for first-order sorption.

The Lagergren function was applied to the experimental data obtained for the sorption of Hg(II) on PAni /composites from 0.1 M HCl solutions and it was found that the sorption of Hg(II) on PAni /composites did not follow pseudo first order kinetics, as shown in Fig. 5.4.

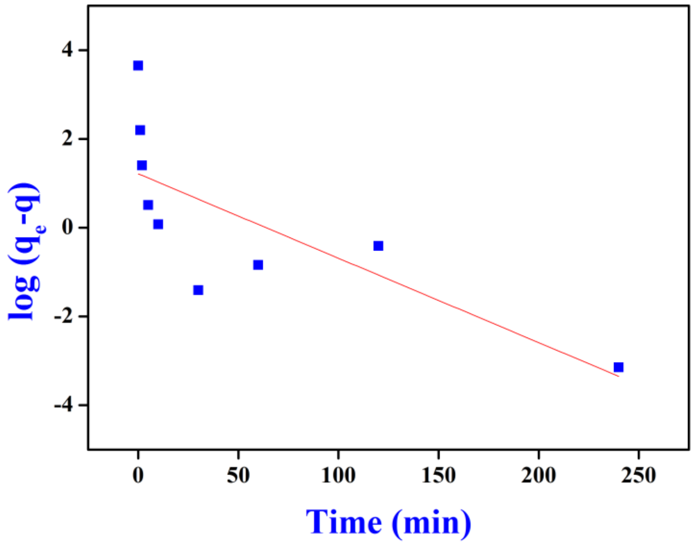


Fig. 5.4 Pseudo first order kinetic model for the sorption of Hg(II) on PAni powder

Subsequently, the pseudo second-order kinetic model (equation 5.3) [125] was applied to the sorption data.

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{5.3}$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant for second order sorption process. The integrated form of equation 5.3 is given by equation 5.4.

$$\frac{1}{q_e - q} = \frac{1}{q_e} + k_2 t \tag{5.4}$$

Equation 4 is rearranged and linearized to obtain equation 5.5.

$$\frac{t}{q} = \frac{1}{k_2 q_e^{\ 2}} + \frac{1}{q_e} t \tag{5.5}$$

A plot of t/q versus t will give a straight line, if second order kinetics is applicable. The values of q_e and k_2 can be obtained from the slope and intercept respectively. In the present sorption studies, a straight line was obtained by plotting t/q against t, as shown in Fig. 5.5. The regression coefficient for the second-order kinetic model was equal to 1 and the value of q_e obtained by this model (19.2 mg g^{-1}) agrees very well with the experimental value (20.9 mg g^{-1}). Hence it was concluded that the sorption of Hg(II) on PAni follows second-order kinetics.

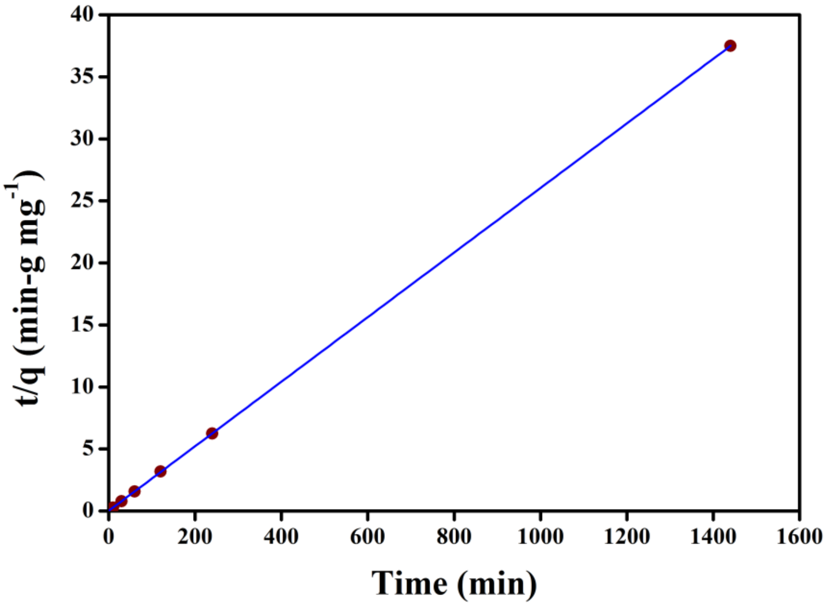


Fig. 5.5 Second order kinetic model for the sorption of Hg(II) on PAni

The initial sorption rate, H, calculated by equation 5.6 [126] was found to be 80.1 mg g^{-1} min^{-1}.

$$H = k_2 q_e^{\ 2} \tag{5.6}$$

5.3.2 Distribution ratio of Hg(II) in PAni

Fig. 5.6 depicts the distribution ratios of Hg(II) in PAni from HCl solutions of varying acidity.

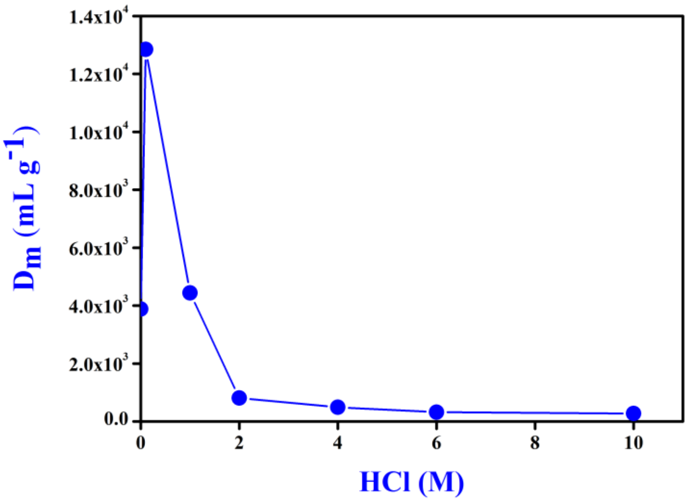


Fig. 5.6 Distribution ratio of Hg(II) in PAni, as a function of molarity of HCl

The distribution ratio values were comparable to those reported earlier [52]. Depending on the species of Hg(II) as well as acidity of the solution, sorption of Hg(II) on PAni can be explained by either complexation or ion exchange phenomenon. In pure water, the sorption proceeds through complex formation between the nitrogen atoms of PAni and Hg(II) species, as has been reported in the literature [115]. Sorption from acidic solutions has been reported to follow an ion exchange phenomenon involving negatively charged species of Hg(II), namely $HgCl_3^-$ and $HgCl_4^{2-}$ [52]. In the present studies, aqueous and 1 M HCl solutions showed a preconcentration factor of 4000 for Hg(II) on PAni.

5.3.3 Isotherm for the sorption of Hg(II) in PAni from HCl medium

Isotherm for the sorption of Hg(II) on PAni powder from aqueous solutions is shown in Fig. 5.7.

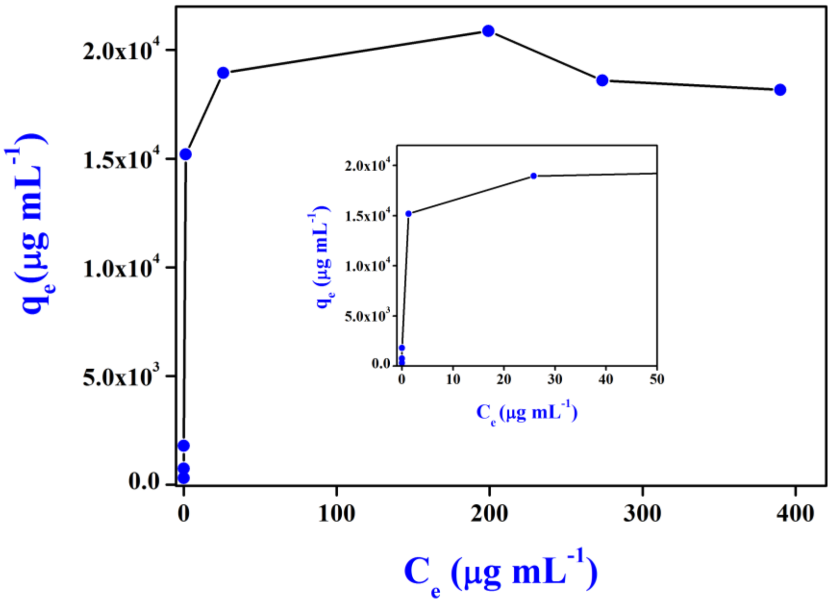


Fig. 5.7 Isotherm for sorption of Hg(II) on PAni powder

Various models have been reported in the literature to describe sorption equilibria [127, 128]. Among all, Langmuir and Freundlich isotherms are the most widely used models. The Langmuir model can be expressed by equation 5.7 [129].

$$q_e = \frac{q_0 b c_e}{1 + b c_e} \tag{5.7}$$

where b is a constant related to energy or net enthalpy of adsorption (L mg^{-1}), and q_0 is the mass of the adsorbed solute required to saturate a unit mass of adsorbent (mg g^{-1}). Linearized form of Langmuir isotherm is shown in equation 5.8.

$$\frac{c_e}{q_e} = \frac{1}{q_0 b} + \frac{c_e}{q_0} \tag{5.8}$$

By plotting (c_e/q_e) versus c_e, q_0 and b can be determined if a straight line is obtained.

The empirical Freundlich equation based on sorption on a heterogeneous surface is shown in equation 5.9 [130].

$$q_e = K_f (c_e)^{1/n} \qquad (5.9)$$

where c_e is the equilibrium concentration (mg L^{-1}) in the supernatant. K_f and n are equilibrium constants indicative of adsorption capacity and adsorption intensity respectively. Equation 5.9 can be linearized in logarithmic form (equation 5.10) and the Freundlich constants can be determined.

$$\ln q_e = \ln K_f + \frac{1}{n} \ln c_e \qquad (5.10)$$

The present experimental sorption data were fitted to both Langmuir and Freundlich isotherm models. It could be seen that the equilibrium sorption data of Hg(II) on PAni fitted better to the Langmuir model than the Freundlich mode, as shown in Figs. 5.8 and 5.9 respectively.

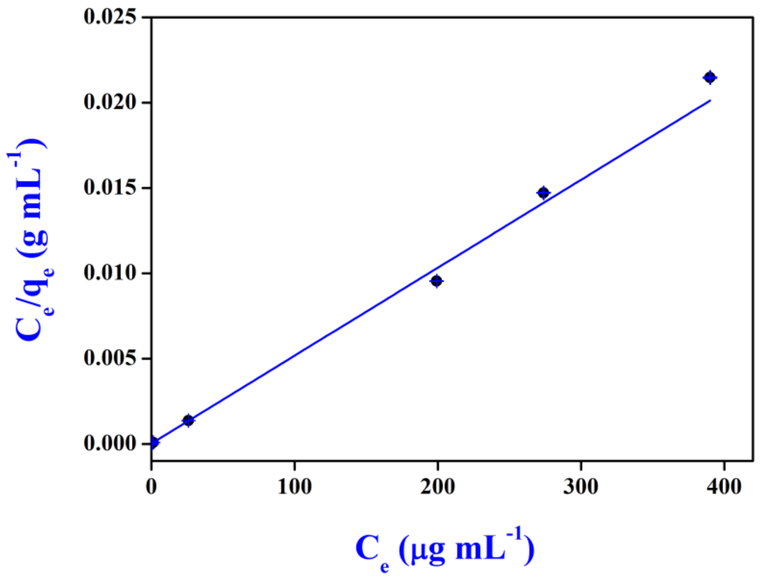


Fig. 5.8 Langmuir isotherm for the equilibrium sorption of Hg(II) on PAni powder

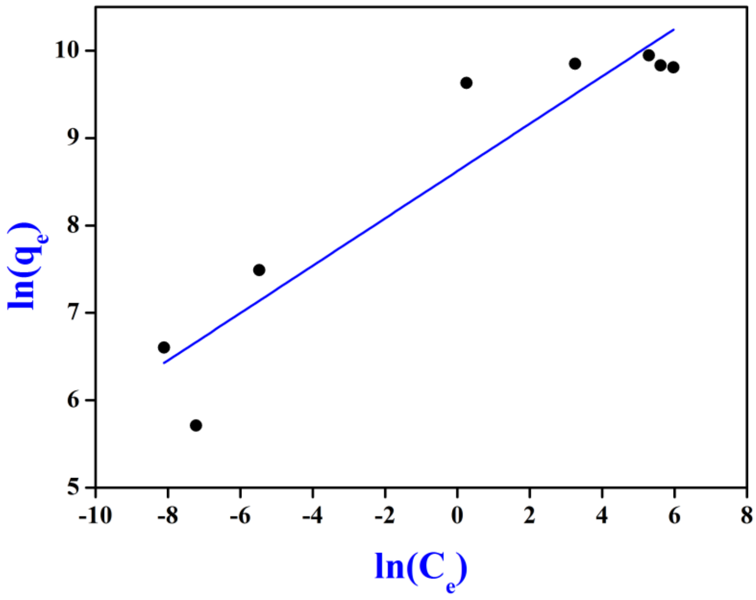


Fig. 5.9 Freundlich isotherm for the equilibrium sorption of Hg(II) on PAni powder

The experimental sorption capacity values were in good agreement with those values obtained from fitting into the Langmuir model, for all the three sorbents. In the case of PAni powder, the experimental capacity was 20.9 mg g^{-1} and the Langmuir capacity was19.7 mg g^{-1}. Langmuir sorption capacities were found to be 2.6 mg g^{-1} and 1.8 mg g^{-1} for PAni-alginate beads and PAni-silane discs respectively.

5.3.4 Studies on tolerance to other metal ions

PAni has been reported in the literature for the sorption of negatively charged species from acidic solutions. In addition to this, nitrogen atoms in PAni can form complexes with metal ions, via the soft base-soft acid interactions. Hence the sorption of Hg(II) on PAni/composites from solutions containing Pd(II), Pt(IV), Au(III), Fe(III), Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II) was studied. Fig. 5.10 depicts the EDXRF spectra of metal-laden PAni pellets, in the absence as well as presence of competing metal ions. Both the beads and discs showed similar sorption behavior, as far as the tolerance to other metal ions, namely Pd(II), Pt(IV), Au(III), Fe(III), Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II), is concerned.

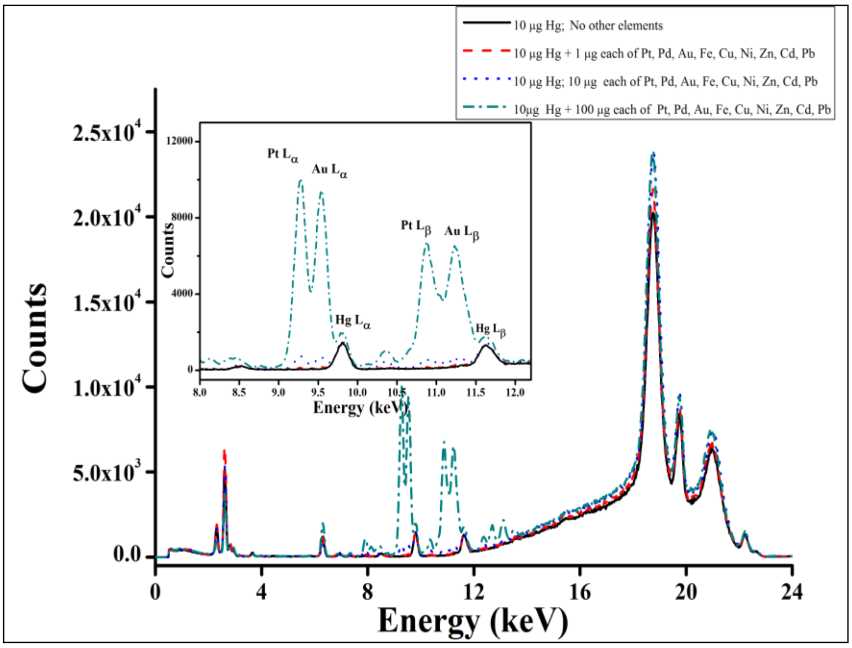


Fig. 5.10 Effect of various metal ions on the sorption of Hg(II) on PAni and EDXRF determination

It is evident from Fig. 5.10 that the EDXRF quantification of Hg was unaffected by the presence of various metal ions except a 10-fold concentration of Au. However, such high concentrations of Au(III) are seldom encountered, alongwith Hg(II). Interference from Au in the EDXRF determination of Hg is due to the proximity of characteristic X-ray energies of Au and Hg.

5.3.5 Preconcentration factor and the effect of sample volume on the sorption of Hg(II) in PAni

Preconcentration factor for Hg(II) on PAni from water was $4x10^3$ and $1.2\ x10^4$ from 0.1 M HCl. A preconcentration factor of $1.7x10^3$ for Hg(II) from drinking water, on Aliquat 336-loaded activated carbon, for EDXRF determinations has been reported in the literature [107]. Effect of sample volume on the preconcentration of Hg(II) on PAni was studied and the results are shown in Fig.5.11.

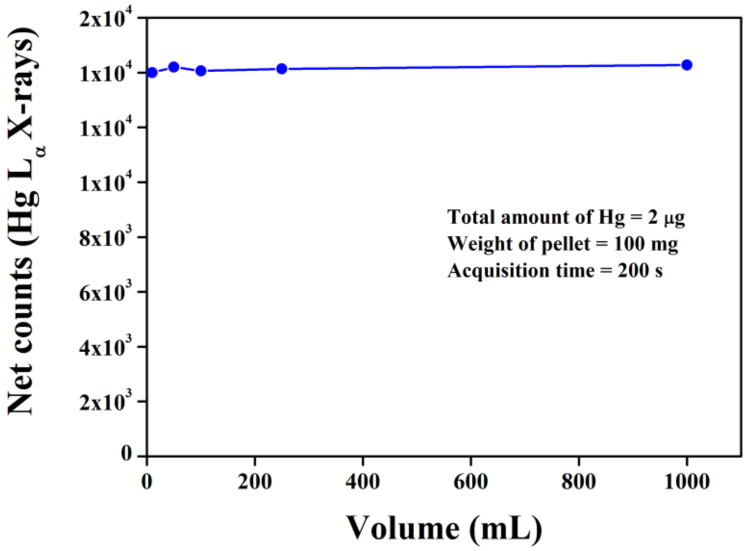


Fig. 5.11 Effect of volume of solution on the preconcentration of Hg on PAni and EDXRF determination

It is vivid from Fig. 5.11 that the sorption and EDXRF determination are unaffected by the sample volume upto 1000 mL. Hence, Hg(II) could be preconcentrated on 100 mg of PAni from a 1000 mL solution containing 2 ng mL^{-1} of Hg and quantified using EDXRF spectrometry. Similar observation has been reported for the ion exchange column sorption of Hg(II) [120, 131].

5.3.6 Detection limit for Hg by EDXRF spectrometry

One of the most significant figures of merit for an analytical technique is the detection limit. Detection limit in EDXRF spectrometry depends not only on the instrumental sensitivity but also on the matrix characteristics namely X-ray mass attenuation coefficients, scattering and fluorescence. PAni, being constituted by low-Z elements, is nearly transparent to both the source and characteristic X-rays, and hence is an ideal matrix for EDXRF analyses. Detection limit of EDXRF spectrometry for Hg in the present studies was 166 ng, as obtained from the calibration equation [132]. The reported detection limit for Hg by the CVAAS technique is 2 ng mL^{-1} [133]. During the present studies, Hg(II) was preconcentrated on 100 mg of PAni from a 1000 mL of 1 ng mL^{-1} solution and quantified by EDXRF spectrometry. Preconcentration (factor = 4×10^3) of Hg(II) on PAni could improve the apparent detection limit to 42 pg, which is better than that obtained by CVAAS technique.

5.3.6 Validation of the method

For validation of the present method, two certified reference materials, viz. IAEA-085 (human hair) and IAEA-336 (lichen) were analyzed and the results are shown in Table 5.2. The reported concentrations of Hg(II) in these reference materials were 23.2 ± 0.80 and 0.20 ± 0.40 mg kg^{-1} respectively. Additionally, the method was tested by applying to an aqueous solution sample, spiked with 300 ng mL^{-1} of Hg(II) and the results are shown in Table 5.3. Accuracy of the proposed method was established by these results.

Table 5.2 Results of analysis of certified reference materials

Reference material	Concentration of Hg (µg g^{-1})		
	Reference value	Present method	% error
IAEA-085	23.2 ± 0.80	22.8 ± 0.23 (n = 3)	-1.60
IAEA-336	0.20 ± 0.040	0.198 ± 0.0045 (n = 3)	-1.02

Table 5.3 Results of analysis of Hg(II)-spiked aqueous solution sample

Sample description	Concentration of Hg (µg mL^{-1})		
	Added	Obtained	% error
Hg(II)-spiked sample	300	295.9	-0.96

5.4 Conclusion

PAni and its composites were used for preconcentration of Hg(II) from water and HCl media and analyzed directly by EDXRF spectrometry. Distribution ratio of Hg(II) on PAni decreases with HCl concentration. Kinetics of sorption of Hg(II) was rapid, attaining 80% of the uptake in the initial 1 min of equilibration. Sorption of Hg(II) on PAni follows Langmuir isotherm model and the sorption capacity was 19.7 mg g^{-1} for PAni powder. Except Au(III), the presence Pd(II), Pt(IV), Fe(III), Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II) had no effect on the sorption of Hg(II) on PAni, and EDXRF analysis. Detection limit of Hg was 166 ng, as obtained from the calibration equation and the apparent detection limit was 42 pg, considering a preconcentration factor of $4x10^3$. Accuracy of the present method was ascertained by the analysis of IAEA reference materials, namely hair and lichen, for Hg(II). PAni powder can be easily pelletized and possesses low X-ray absorption/emission characteristics; hence trace levels of mercury could be directly determined by EDXRF spectrometry. PAni-loaded alginate beads can be used in the form of ion exchange columns for practical sorption/separation of Hg(II). Since PAni-silane composite discs are ready-to use and do not require any post-sorption processing, could be potential sorbents for preconcentration and determination (by EDXRF) of trace levels of Hg (II) from aqueous solutions. Obviation of the elution step reduces the chemical inventory, minimizes sample handling and the associated losses of Hg. Hg-loaded PAni pellets may be preserved carefully and used repeatedly as laboratory-made secondary standards for quantitative EDXRF analyses.

Chapter 6

Determination of distribution ratios of Zr(IV), Co(II), Sb(V) and Nb(V) in polyaniline

Executive summary

Distribution ratios of Zr(IV), Co(II), Sb(V) and Nb(V) were determined in PAni from HCl, HF, oxalic acid HCl-HF mixed media. Further, the separation factors and %-uptake of each metal ion in PAni were calculated and compared. Among the media studied, 1 M HCl was found to be the most promising, in terms of separation efficiency with respect to Zr. The highest separation factors were obtained at 1 M HCl and the values were 52, 108 and 404 for Sb, Co and Nb respectively. The results obtained in these investigations can be utilized for designing a separation strategy for the decontamination of used pressure tube materials in solution, from Indian Pressurized Heavy Water Reactors for the reuse of Zr as structural materials in the nuclear reactors.

6.1 Introduction

Zirconium alloys (Zr-Sn and Zr-Nb) are used in the fabrication of pressure tubes and cladding materials for Indian Pressurized Heavy Water Reactors. Pressure tubes are replaced either after 10 effective full power years or upon failure, whichever is earlier. Used pressure tubes are expected to be radioactive, since their constituents get neutron activated, resulting in the formation of radioactive products. The used Zr-Sn pressure tubes contain two long-lived radioisotopes of cobalt (^{60}Co, $t_{1/2}$ = 5.27 y) and antimony (^{125}Sb, $t_{1/2}$ = 2.77y). Need for the separation of radioisotopes of Co and Sb arises from the decontamination requirements of used pressure tube zircaloy [134, 135]. Presently, zircaloy is being replaced by Zr-2.5%Nb for fabrication of pressure tubes, due to its better mechanical strength and greater resistance to hydride attack. In the case of Zr-Nb alloy, the long-lived ^{94}Nb ($t_{1/2}$ = 24000 y) is the isotope of concern from the radioactive waste management as well as recycling points of view [134]. Very large separation factors (10^6 to 10^7) with respect to these radioactive elements (isotopes) are needed to achieve decontamination so that purified zirconium can be recycled. Several sequential steps are required to achieve the desired purity and reduction in radiation levels, to facilitate the reuse of these pressure tube materials. Among the processes reported in the literature, ion exchange chromatography shows promising separation factors for adopting in large/plant scale operations. Various ion exchangers have been evaluated for the separation of Co and Sb from Zr [1, 135]. Ion exchange separation strategies are reported for the decontamination of zircaloy with respect to ^{60}Co and ^{125}Sb using commercially available ion exchange resins. Since these separations are to be carried out in a radiation environment, radiation stability of the ion exchange resin is of prime importance.

The established gamma irradiation stability of polyaniline (PAni) [97], as detailed in Chapter 3 of this thesis, suggests its possible application towards separation of metal ions of radioisotopes in acidic solutions. Anion exchange properties of PAni in acidic media have been reported in the literature [46, 49].

In the present studies, distribution ratios of Zr(IV), Co(II), Sb(V) and Nb(V) in PAni from various acid media viz. HCl, HF, oxalic acid and mixture of HCl-HF were determined by batch equilibration method. Quantification of all the metal ions in solutions, before and after equilibration, was carried out using the respective radiotracers and the results were compared with those obtained using ICPOES. Distribution ratio as well as the separation factor data, thus obtained, could be useful in designing a separation strategy for these metal ions in solution.

6.2 Experimental

6.2.1 Materials and methods

A.R. grade HCl, HF and oxalic acid were obtained from Qualigens India Ltd. Chemical synthesis and characterization of PAni are described in Chapter 2, Section 2.1, of this thesis. As-synthesized PAni samples were air-dried and stored in desiccator, prior to use.

6.2.2 Radio-tracer solutions

Two sets of radio-tracer solutions were prepared by dissolving small pieces weighing ~ 30 mg each of the replaced pressure tube materials (i) zircaloy and (ii) Zr-Nb from nuclear reactors.

(i) For the preparation of radio-tracer solution containing ^{95}Zr, ^{60}Co and ^{125}Sb, approximately 30 mg of the used pressure-tube zircaloy was dissolved in 1:4 mixture of HNO_3 and HF. The solution was evaporated to near-dryness to remove HF. Residue was dissolved by adding concentrated HNO_3 dropwise, and the solution was evaporated to dryness. This cycle was repeated thrice, in order to ensure complete removal of HF. Finally, the solution was made up to 50 mL using 10 % HNO_3, in a volumetric flask and stored in a plastic container.

(ii) Radio-tracer solution containing ^{95}Zr and ^{94}Nb was prepared by dissolving 30 mg of reactor used pressure tube Zr-Nb via the dissolution procedure discussed in the previous paragraph.

6.2.3 Determination of D_m of Zr(IV), Co(II), Sb(V) and Nb(V) in PAni

Distribution ratios of Zr(IV), Co(II), Sb(V) and Nb(V) in PAni from various acids were calculated from the measured concentrations before and after equilibration with PAni. Radiotracers were used for quantification of all the metal ions. Concentrations were also obtained using inductively coupled plasma optical emission spectrometry (ICPOES) technique and used to calculate distribution ratios. Results obtained by both the techniques were compared.

6.2.3.1 Determination of D_m using radiotracers

For the determination of distribution ratios, 100 µL of each radiotracer solutions, prepared from zircaloy and Zr-Nb, were pipetted into 10 mL solutions of various acids in polypropylene vials. Effect of acidity was studied by varying the acids' concentration. For HCl, the concentration was varied from 0.1 to 10 M; for HF, it was from 0.01 to 10 M and that of oxalic acid was from 0.001 to 0.75 M. Count rates of the solutions were measured by gamma ray spectrometry using an HPGe detector (Relative efficiency = 30 %, Resolution = 1.9 keV at 1332 keV) coupled with an 8k-channel analyzer. Relevant nuclear data of the radioisotopes used in this work are summarized in Table 6.1 [60].

Table 6.1 Relevant nuclear data of the radioisotopes used in this work

Isotope	Half-life ($t_{½}$)	Gamma ray energy (keV)	Gamma ray abundance (%)
^{95}Zr	65.5 d	724 756	44 56
^{60}Co	5.27 y	1173 1332	9.99 10
^{125}Sb	2.77 y	428	10
^{94}Nb	2.4 x10^{4} y	703 872	0.2 20

Approximately 100 mg of PAni was added to these solutions and equilibrated for 1 h at room temperature on a mechanical shaker. Solutions were filtered using Whatman 540 filter paper and the count rates of the filtrates were measured using gamma ray spectrometry. Distribution ratios, D_m, of Zr(IV), Co(II), Sb(V) and Nb(V) in PAni were calculated using equation 6.1.

$$D_m = \frac{(a_0 - a)}{w} \text{ x } \frac{L}{a} \qquad (6.1)$$

where a_o and a are the count rates for each metal ion in solution, before and after equilibration respectively, L is the volume (mL) of the solution and w is the weight (g) of PAni used.

Distribution ratios of Zr(IV), Co(II), Sb(V) and Nb(V) in PAni were plotted against the acidity of each solution.

6.2.3.2 Determination of D_m using ICPOES

Solutions were prepared by dissolving inactive pieces of zircaloy and Zr-Nb alloy and the dissolution procedure was the same as described in Section 6.2.2. Weights of PAni, concentration and volume of solutions, and equilibration time were the same as those described in the radiotracer experiments described in Section 6.2.3.1. ICPOES analyses were carried out using an iCAP 6500 (Thermo scientific, UK) instrument.

Calibration standards, in the range of 1 to 10 µg mL^{-1}, were prepared by dissolution of the respective metals, followed by serial dilution. A 2% aqueous HNO_3 solution, prepared by dilution of suprapure HNO_3 with de-ionized water, was used as the calibration blank for all the metal ions. Quantification of the metal ions in solution, before and after equilibration was carried out using the measured intensity of the selected interference-free emission lines (Table 6.2) [136] and the calibration at their respective wavelengths.

Table 6.2 Elements and their emission wavelengths used for ICPOES quantification [136]

Element	Wavelength (nm)
Zr	339.1 343.8
Co	241.4
Sb	217.5 231.6
Nb	313.0 316.3

6.2.4 Determination of separation factors of Co(II), Sb(V) and Nb(V) with respect to Zr(IV)

Separation factors of Co(II), Sb(V) and Nb(V) with respect to Zr(IV) were calculated from the distribution ratio data, using equation 6.2.

$$\alpha_{(i,Zr)} = \frac{D_{m(i)}}{D_{m(Zr)}} \qquad (6.2)$$

where $\alpha_{(i,\ Zr)}$ is the separation factor of the element i with respect to Zr, D_m is the distribution ratio and i represents one of the elements Co, Sb or Nb to which the specific separation factor is being referred.

6.2.5 Percentage uptake of metal ions on PAni

Percentage uptake of Zr(IV), Co(II), Sb(V) and Nb(V) on PAni was calculated from these experimental data using equation 6.3.

$$\text{Uptake}(\%) = \frac{(a_0 - a)}{a_0} \text{ x } 100 \qquad (6.3)$$

where a_o and a are the count rates of the solutions, before and after equilibration with PAni.

6.3 Results and discussion

6.3.1 Effect of media on the D_m of Zr(IV), Co(II), Sb(V) and Nb(V) in PAni

Distribution ratios were used to compare the selectivity of PAni towards Zr(IV), Co(II), Sb(V) and Nb(V) in acidic media. Fig. 6.1 shows the distribution ratios of all the four metal ions in PAni from HCl media. Among these metal ions, Nb(V) showed the highest and Zr(IV) showed the smallest distribution ratio values in the range of HCl studied (0.1 to 10 M).

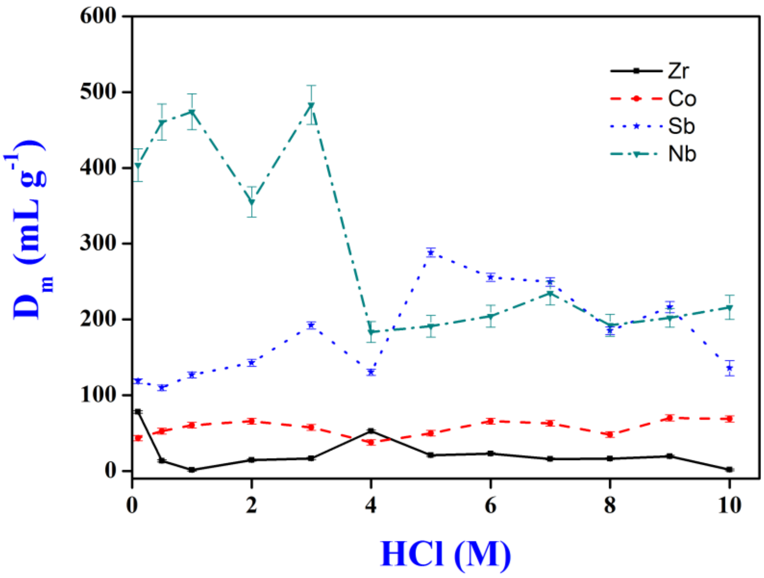


Fig. 6.1 Distribution ratios of Zr, Co, Sb and Nb in PAni from **HCl media**

Zr(IV) has been reported to exist in the following forms in HCl media: cations in 0.1- 2 M HCl, neutral complexes in 6 M HCl and increasing amounts of anions in 3-12 M HCl [137]. Sato et. al. [138] have reported the distribution of Co(II) species in aqueous chloride solutions. The major cobalt species in 0 -1 M HCl are Co^{2+}, $CoCl^{+}$ and $CoCl_2$. Above 1 M HCl, negatively charged species, namely $CoCl_3^-$ and $CoCl_4^{2-}$ exist, and their concentrations increase with acidity. In the case of Sb, $Sb(OH)Cl_5^-$ ion is the predominant species in 8 M HCl and $Sb(OH)_2Cl_4^-$ in 6 M HCl [139]. Below 5 M HCl, $Sb(OH)_3Cl_3^-$ and the more hydrolysed species exist [139]. Nb(V) is reported to exist largely as the six co-ordinated ion in various HCl solutions [140]. Above 6 M HCl, negatively charged $Nb(OH)_2Cl_4^-$ exists and the following reaction equilibrium is reported in the literature for the formation of this species [140, 141].

$$Nb(OH)_{2+m}Cl_{4-n}^{-1+n-m} + mH^{+} + nCl^{-} \rightarrow Nb(OH)_2Cl_4^{-} + mH_2O. \qquad (6.4)$$

Above 5M HCl, chloride ions are preferentially sorbed, which hinder the sorption of negatively charged metallic species [52] and hence the observed lowering of Dm values.

Fig. 6.2 shows the distribution ratios of Zr(IV), Co(II), Sb(V) and Nb(V) in HF media. Even though HF is a corrosive medium, distribution ratio data in HF media were essential, as necessitated by the dissolution requirements of both Zr and Nb.

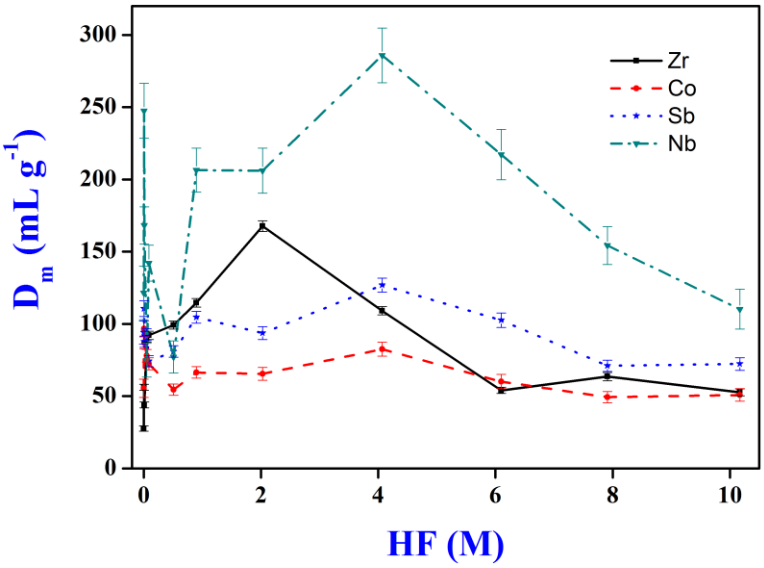


Fig. 6.2 Distribution ratios of Zr, Co, Sb and Nb in PAni from **HF media**

Nb(V) was preferentially sorbed by PAni in HF media also. Co(II) was sorbed the least. Co(II) does not form anionic complexes with HF and thus has low D_m values. Distribution ratios of anionic metal fluorides were reported to decrease with increasing HF concentration [142, 143]. Caletka and Krivan [143] attribute the following reasons for the reduction in sorbability of metal ions with increase in HF concentration: (i) formation of highly coordinated multi-charged anion complexes with lower distribution ratios, (ii) association of the complex anions with protons to the species $H_mMF_n^{-x}$ (M = metal ion) or even neutral complex acids, and (iii) the concurrent displacement of metal complexes in the exchanger phase through F^- and /or HF_2^-. The anion exchange sorption behavior of Zr(IV) and Nb(IV) in HF has been illustrated in the literature [144], due to the repartition of various ionic species of both the metals, namely $[ZrF_5]^-$, $[ZrF_6]^{2-}$, $[ZrF_7]^{3-}$and $[ZrF_8]^{4-}$, $[NbOF_4]^-$ and $[NbOF_5]^{2-}$.

Fig. 6.3 shows the distribution ratios of all the four metal ions in oxalic acid media. Oxalic acid, being a complex medium, prevents the hydrolysis and precipitation of all the metal ions studied. Tri and quadrivalent species such as Au(III), Fe(III), Ti(IV), Zr(IV) and Sn(IV) are known to form very stable oxalate complexes, having stabilities several orders of magnitude higher than those of many bivalent metal oxalate complexes [145]. Hence, several anion exchange procedures have been reported in the literature for separation of bivalent metal ions from multivalent metal ions [145].

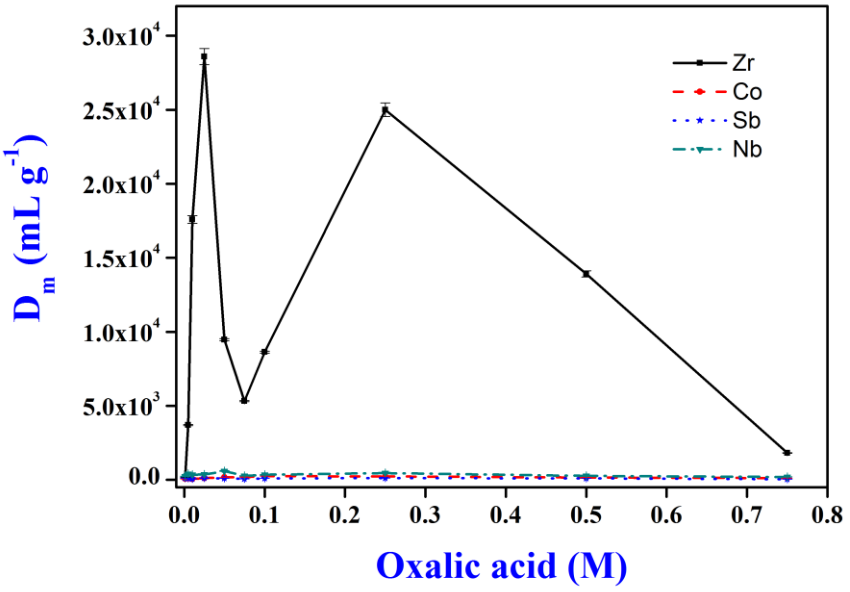


Fig. 6.3 Distribution ratios of Zr, Co, Sb and Nb in PAni from **oxalic acid media**

In the present studies, Zr(IV) and Nb(V) show expectedly high D_m values in PAni from oxalic acid media. Co(II) and Sb(V) show consistently low D_m values in oxalic acid and the results are comparable with those reported for commercially available anion exchangers [1]. Similar behavior has been reported for Co by De Corte [146]. There are several reports on the anion exchange separation of metal ions in HCl-HF mixtures [137, 147-150]. Elution chromatographic separation of Zr was achieved by Kraus and Moore [148], by utilizing the higher elution constant of Zr in HCl-HF combined media, with higher HCl and lower HF molarities, compared to that of Nb. Figs. 6.4-6.7 show the distribution ratios of Zr(IV), Co(II), Sb(V) and Nb(V) in HCl-HF combined media. The data are represented as 3D-images, in order to get a better visualization of the distribution ratios. Another way of representation is through the 2D-contour plots with the acid concentrations on both the axes and the corresponding D_m values indicated numerically on each contour. However, such kind of representation does not allow the exact estimation of the respective distribution ratio at each point of the system [149]. Hence, in the present studies, 3D-representations were adopted and the D_m values for each element are depicted separately.

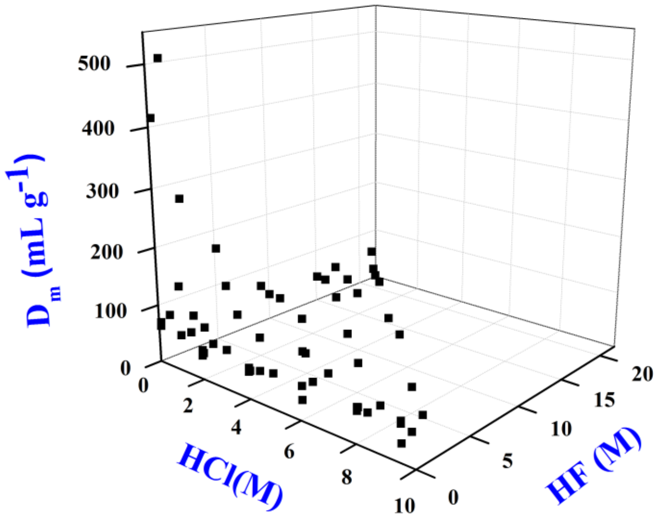


Fig. 6.4 Distribution ratios of **Zr(IV)** in PAni from HCl-HF mixtures

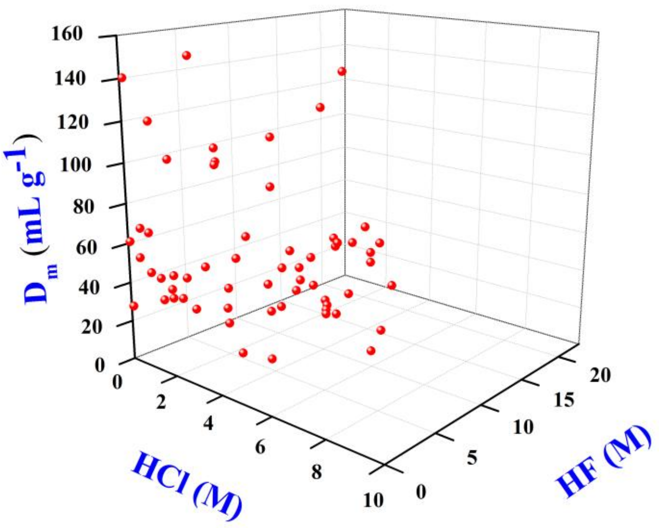


Fig. 6.5 Distribution ratio of **Co(II)** in PAni from HCl-HF mixtures

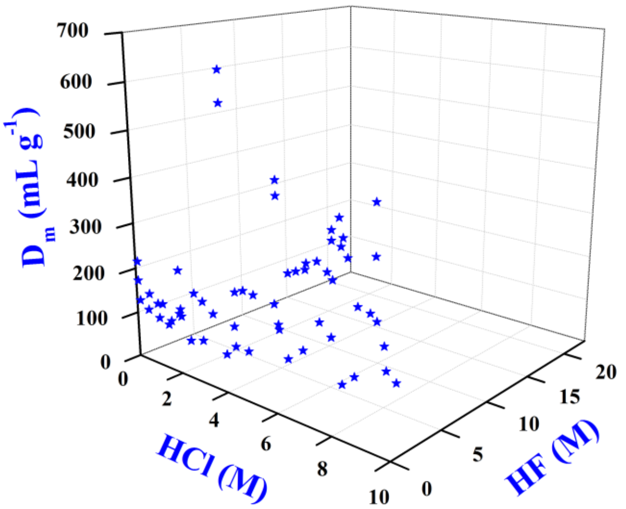


Fig. 6.6 Distribution ratio of **Sb(V)** in PAni from HCl-HF mixtures

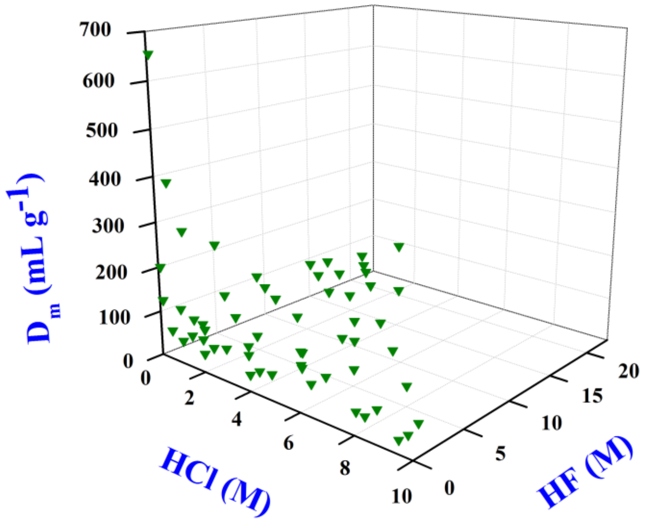


Fig. 6.7 Distribution ratio of **Nb(V)** in PAni from HCl-HF mixtures

It is vivid from the distribution ratios of all the four metal ions in HCl-HF mixed media, that the maximal values of distribution ratios were comparable for Zr (500), Sb (600) and Nb (650), whereas that of Co (150) was slightly inferior. This is due to the fact that Co(II) does not form sorbable anionic fluoro complexes, whereas the other metal ions do. Both Zr(IV) and Nb(V) showed similar trends in the D_m values with acidities. Distribution ratio of Sb(V) increased initially upto 6-7 M HF, followed by a gradual decline upto 22 M HF. As the HF ion concentration increases, F^- and HF_2^- ions start competing with the anionic metal complexes, resulting in the reduction of D_m values [143].

6.3.2 Effect of media on the separation factors of Co(II), Sb(V) and Nb(V) from Zr(IV)

Distribution ratio values are indicative of the affinity of metal ions to either the solid or the liquid phase. Higher the affinity of metal ions to the solid phase, higher will be the distribution ratio. However, the separation between two or more species becomes increasingly difficult in either of the cases where all species have uniformly high distribution ratio values, or all have consistently small distribution ratios. It is the relative distribution of two or more species between the solid and liquid phases, which dictates the efficiency of the separation. Separation efficiency in ion exchange chromatographic processes is described in terms of separation factor, rather than the distribution ratio value. Separation factor is defined as the ratio of distribution ratio of a particular metal ion to that of the reference metal ion, under identical conditions. Higher the separation factor, more efficient will be the separation.

Separation factors for Co(II), Sb(V) and Nb(V) with respect to Zr(IV) were calculated from the distribution ratio values in various media and are shown in Tables 6.3 to 6.6.

Table 6.3 Separation factors for Co(II), Sb(V) and Nb(V) from Zr(IV) in **HCl media** using PAni

Molarity of HCl (M)	Separation factor (α) with respect to Zr (IV)		
	Co(II)	Sb(V)	Nb(V)
0.1	0.55	1.52	5.18
0.5	3.99	8.31	34.84
1	51.5	108.2	404.0
2	4.52	9.84	24.49
3	3.47	11.58	29.10
4	0.72	2.48	3.50
5	2.42	13.95	9.25
6	2.85	11.11	8.89
7	3.96	15.69	14.76
8	2.95	11.36	11.81
9	3.60	11.12	10.39
10	43.1	85.0	135.3

Table 6.4 Separation factors for Co(II), Sb(V) and Nb(V) from Zr(IV) in **HF media** using PAni

Molarity of HF (M)	Separation factor (α) with respect to Zr (IV)		
	Co(II)	Sb(V)	Nb(V)
1.0×10^{-3}	1.98	3.36	4.34
5.0×10^{-3}	1.72	1.98	4.42
0.01	1.98	1.99	3.82
0.05	0.87	1.03	0.83
0.09	0.43	0.44	0.85
0.51	0.42	0.62	0.59
0.90	0.58	0.91	1.80
2.0	0.58	0.84	1.84
4.1	0.76	1.16	2.62
6.1	1.14	1.90	4.02
7.9	0.77	1.11	2.41
10.2	0.96	1.36	2.08

Table 6.5 Separation factors for Co(II), Sb(V) and Nb(V) from Zr(IV) in **oxalic acid media** using PAni

Molarity of oxalic acid (M)	Separation factor (α) with respect to Zr (IV)		
	Co(II)	Sb(V)	Nb(V)
1.0×10^{-3}	0.49	0.745	1.45
5.0×10^{-3}	0.03	0.028	0.11
1.0×10^{-2}	0.004	0.004	0.020
2.5×10^{-2}	0.045	0.040	0.13
5.0×10^{-2}	0.019	0.010	0.064
7.5×10^{-2}	0.034	0.013	0.052
0.1	0.029	0.011	0.039
0.25	0.096	0.047	0.18
0.50	0.012	0.007	0.020
0.75	0.063	0.030	0.11

Table 6.6 Separation factors for Co(II), Sb(V) and Nb(V) from Zr(IV) in **HCl-HF mixed acid media** using PAni

[HCl] = 9.5 M	Separation factor (α) with respect to Zr (IV)		
Molarity of HF (M)	Co(II)	Sb(V)	Nb(V)
1.95	1.32	2.19	0.70
0.98	1.45	4.06	0.68
9.7 x 10^{-2}	1.65	8.89	0.94
9.7 x 10^{-4}	1.38	7.35	6.12
9.7 x 10^{-6}	1.42	6.27	5.24
[HCl] = 8.03 M	Separation factor (α) with respect to Zr (IV)		
Molarity of HF (M)	Co(II)	Sb(V)	Nb(V)
4.972	1.79	2.95	1.03
2.034	1.49	2.37	0.72
0.904	1.34	2.31	0.69
9.0 x 10^{-2}	1.06	5.34	0.84
9.0 x 10^{-4}	1.08	7.61	3.60
9.0 x 10^{-6}	1.00	6.15	3.90
[HCl] = 6.05 M	Separation factor (α) with respect to Zr (IV)		
Molarity of HF (M)	Co(II)	Sb(V)	Nb(V)
9.04	1.10	1.85	0.57
4.97	0.88	2.15	0.75
2.26	0.96	1.91	0.89
0.904	0.900	1.89	0.93
9.04 x 10^{-2}	0.94	1.66	0.84
9.04 x 10^{-4}	0.87	7.64	2.24
9.04 x 10^{-6}	0.81	13.53	2.92
[HCl] = 3.96 M	Separation factor (α) with respect to Zr (IV)		
Molarity of HF (M)	Co(II)	Sb(V)	Nb(V)
13.334	1.58	1.90	0.62
9.04	0.99	1.77	0.70
4.97	3.36	2.51	0.96
2.03	0.66	2.74	0.60
0.904	0.86	2.30	0.86

9.04 x 10^{-2}	2.39	1.75	0.75
9.04 x 10^{-4}	2.39	12.91	1.71
9.04 x 10^{-6}	2.24	12.56	1.87
[HCl] = 1.98 M	Separation factor (α) with respect to Zr (IV)		
Molarity of HF (M)	Co(II)	Sb(V)	Nb(V)
17.402	2.87	2.89	0.91
14.916	2.83	2.73	0.93
9.04	0.83	2.04	1.09
4.972	0.76	1.74	0.99
2.034	0.89	1.55	0.95
0.904	0.70	1.18	0.84
9.04 x 10^{-2}	0.89	3.18	0.90
9.04 x 10^{-4}	0.88	4.51	1.13
9.04 x 10^{-6}	2.58	3.20	1.77
[HCl] = 0.99 M	Separation factor (α) with respect to Zr (IV)		
Molarity of HF (M)	Co(II)	Sb(V)	Nb(V)
19.436	0.93	4.22	1.34
14.916	0.85	5.56	1.57
9.04	0.86	1.26	1.08
4.972	0.71	1.13	0.97
2.034	0.73	1.51	0.86
0.904	0.75	1.38	0.91
9.04 x 10^{-2}	0.80	1.72	0.81
[HCl] = 0.495 M	Separation factor (α) with respect to Zr (IV)		
Molarity of HF (M)	Co(II)	Sb(V)	Nb(V)
20.453	0.75	2.97	1.36
17.402	0.73	2.63	1.52
14.916	0.65	1.59	1.34
9.04	0.62	1.28	1.39
4.972	1.40	0.83	0.95
2.034	0.39	0.95	0.97
0.904	0.49	0.90	0.79
9.04 x 10^{-2}	0.61	1.28	0.71

[HCl] = 0.099 M	Separation factor (α) with respect to Zr (IV)		
Molarity of HF (M)	Co(II)	Sb(V)	Nb(V)
21.266	0.45	2.79	0.98
16.95	0.30	1.06	1.41
14.916	0.40	1.32	1.76
9.04	0.27	0.95	1.46
4.972	0.20	0.59	1.27
2.034	0.43	0.37	0.98
0.904	0.13	0.27	0.75
9.04×10^{-2}	0.34	0.31	0.30
9.04×10^{-4}	0.44	2.71	3.14
9.04×10^{-6}	0.86	3.04	9.19

Separation factors obtained for PAni towards Co(II), Sb(V) and Nb(V) were found to be lower compared to those reported in the literature for commercial ion exchange resins [1]. Among all the media studies, better separation factors were achieved in HCl medium, though concentration is varied for all the three elements with respect to Zr. The highest separation factors were obtained in 1 M HCl, namely 52 for Co(II), 108 for Sb(V) and 404 for Nb(V). Even though the D_m values of both Zr and Nb were high in oxalic acid media, separation factors were lower. In the combined media, selectivity of PAni for Sb with respect to Zr showed an increasing trend with HF molarities, for HCl concentrations ≥ 2 M. It was interesting to note that PAni showed a reversal in the selectivity between Zr and Nb when the HF concentration was reduced from 9.04×10^{-2} to 9.4×10^{-4} M and HCl concentrations were above 2 M in the combined media. Below 2 M HCl, PAni did not show any particular trend in selectivity for Zr and Nb, as a function of HF concentration.

6.3.3 Percentage uptake of Zr (IV), Co(II), Sb(V) and Nb(V) on PAni

Tables 6.7 to 6.10 show the percentage uptake of Zr (IV), Co(II), Sb(V) and Nb(V) on PAni in different acid media.

Table 6.7 Percentage uptake of Zr(IV), co(II), Sb(V) and Nb on PAni from **HCl media**

Molarity of HCl (M)	Uptake (%)			
	Zr(IV)	Co(II)	Sb(V)	Nb(V)
0.1	43.38	18.16	37.84	67.43
0.5	11.90	20.09	34.42	68.76
1	1.22	23.53	39.26	70.70
2	12.76	25.13	42.22	64.52
3	14.67	22.03	48.55	70.35
4	34.80	16.12	39.83	48.23
5	17.14	19.75	58.69	48.50
6	18.73	23.89	55.00	49.40
7	13.66	24.50	56.24	54.73
8	13.98	19.64	48.46	49.42
9	16.32	26.81	53.09	51.39
10	1.64	25.07	39.77	51.22

Table 6.8 Percentage uptake of Co(II), Sb(V) and Nb(V) from Zr(IV) in **HF media** using PAni

Molarity of HF (M)	Uptake (%)			
	Zr(IV)	Co(II)	Sb(V)	Nb(V)
0.001	34.73	20.59	26.94	36.00
0.005	39.64	21.95	28.82	46.80
0.01	24.88	21.46	31.76	49.65
0.05	51.98	28.46	37.95	57.94
0.09	46.12	24.98	32.28	51.20
0.51	53.28	27.50	37.39	54.11
0.90	56.33	23.33	31.12	31.00
2.03	63.23	28.67	29.19	44.10
4.07	47.92	29.57	32.23	28.72
6.1	30.20	32.25	32.43	47.92
7.91	35.44	33.64	36.74	56.51
10.17	22.21	24.06	34.95	40.95

Table 6.9 Percentage uptake of Co(II), Sb(V) and Nb(V) from Zr(IV) in **oxalic acid media** using PAni

Molarity of oxalic acid (M)	Uptake (%)			
	Zr(IV)	Co(II)	Sb(V)	Nb(V)
0.001	89.73	37.21	21.93	51.16
0.005	99.31	46.41	33.30	58.96
0.01	99.57	5373	36.21	68.61
0.025	97.06	55.33	32.78	62.70
0.05	94.48	48.22	26.70	58.51
0.075	96.69	46.95	33.00	74.98
0.1	99.65	39.31	36.44	65.13
0.25	99.46	25.47	25.78	64.82
0.50	97.36	31.77	33.44	66.17
0.75	60.55	28.40	37.75	54.07

Table 6.10 Percentage uptake of Co(II), Sb(V) and Nb(V) from Zr(IV) in **HCl-HF mixed acid** media using PAni

[HCl] = 9.5 M	Uptake (%)			
Molarity of HF (M)	Zr(IV)	Co(II)	Sb(V)	Nb(V)
1.95	36.97	41.79	93.03	27.63
0.98	29.15	35.16	93.93	20.43
9.7×10^{-2}	25.83	35.01	95.96	22.83
9.7×10^{-4}	41.71	48.13	97.42	80.41
9.7×10^{-6}	39.81	46.69	96.86	76.41
[HCl] = 8.03 M	Uptake (%)			
Molarity of HF (M)	Zr(IV)	Co(II)	Sb(V)	Nb(V)
4.972	33.17	44.96	93.48	32.03
2.034	31.75	38.90	92.40	23.63
0.904	31.75	36.31	92.29	23.83
9.04×10^{-2}	38.39	38.04	92.27	32.83
9.04×10^{-4}	36.73	36.89	97.00	66.01
9.04×10^{-6}	38.63	31.18	96.83	69.61

[HCl] = 6.05 M	Uptake (%)			
Molarity of HF (M)	Zr(IV)	Co(II)	Sb(V)	Nb(V)
9.04	43.61	44.38	93.48	29.23
4.97	37.44	32.85	93.03	29.63
2.26	38.63	36.02	92.78	34.43
0.904	38.63	34.58	92.75	35.23
9.04 x 10^{-2}	54.27	51.58	94.67	48.82
9.04 x 10^{-4}	39.34	34.58	97.28	57.62
9.04 x 10^{-6}	27.73	21.90	97.32	50.42
[HCl] = 3.96 M	Uptake (%)			
Molarity of HF (M)	Zr(IV)	Co(II)	Sb(V)	Nb(V)
13.334	26.54	34.01	90.55	16.83
9.04	29.15	27.09	90.79	20.83
4.97	27.96	54.18	91.88	25.23
2.03	22.75	14.70	91.07	16.63
0.904	31.28	26.51	92.19	26.43
9.04 x 10^{-2}	34.12	53.31	91.67	26.44
9.04 x 10^{-4}	34.60	53.89	97.91	45.62
9.04 x 10^{-6}	36.49	54.47	98.01	50.02
[HCl] = 1.98 M	Uptake (%)			
Molarity of HF (M)	Zr(IV)	Co(II)	Sb(V)	Nb(V)
17.402	33.41	57.06	92.89	29.63
14.916	31.28	54.18	92.40	28.03
9.04	28.20	22.77	91.14	28.04
4.972	26.54	19.88	90.24	24.43
2.034	27.72	23.63	90.06	24.83
0.904	37.20	27.95	90.73	31.63
9.04 x 10^{-2}	36.02	31.70	94.25	32.03
9.04 x 10^{-4}	37.20	32.56	99.61	54.02
9.04 x 10^{-6}	32.23	53.03	93.62	43.62
[HCl] = 0.99 M	Uptake (%)			
Molarity of HF (M)	Zr(IV)	Co(II)	Sb(V)	Nb(V)
19.436	26.54	23.34	93.55	30.43

14.916	18.96	14.70	92.78	24.03
9.04	39.81	34.58	91.39	40.02
4.972	39.10	29.97	90.87	36.83
2.034	39.11	30.55	91.95	36.43
0.904	40.28	31.99	91.81	36.44
9.04 x 10^{-2}	39.57	32.85	92.54	33.23
[HCl] = 0.495 M	Uptake (%)			
Molarity of HF (M)	Zr(IV)	Co(II)	Sb(V)	Nb(V)
20.453	27.25	20.17	92.36	31.63
17.402	26.30	19.02	91.70	32.83
14.916	34.60	24.21	91.39	39.62
9.04	40.05	27.95	91.50	46.42
4.972	52.84	59.94	91.88	50.42
2.034	46.68	24.49	91.42	44.42
0.904	59.24	40.63	93.20	52.42
9.04 x 10^{-2}	48.82	35.45	92.89	39.22
[HCl] = 0.099 M	Uptake (%)			
Molarity of HF (M)	Zr(IV)	Co(II)	Sb(V)	Nb(V)
21.266	42.42	23.92	94.77	40.42
16.95	38.86	14.99	90.59	45.62
14.916	35.78	17.29	90.90	47.62
9.04	42.89	16.14	90.83	50.82
4.972	63.98	25.07	92.40	68.41
2.034	73.91	54.18	92.42	72.81
0.904	83.89	39.77	93.48	79.21
9.04 x 10^{-2}	80.97	58.21	93.27	55.62
9.04 x 10^{-4}	41.47	22.48	94.53	67.61
9.04 x 10^{-6}	44.08	38.90	95.29	87.21

PAni showed the highest %-uptake for Nb(V) from all the HCl concentrations studied. Zr(IV) was taken up to the largest extent from oxalic acid media, whereas Sb(V) was sorbed highest from HCl-HF combined media. The %-uptake of Zr(IV) and Nb(V) were comparable from HF media.

Based on the separation factors and %-uptake of all the four metal ions, it could be concluded that among all the media studied, 1 M HCl was the most suitable medium for anion exchange separation of Co(II), Sb(V) and Nb(V) from Zr(IV) using PAni.

6.4 Conclusion

PAni showed the highest distribution ratio for Nb(V) and the lowest for Co(II) in both HCl and HF media. Distribution ratios of both Zr(IV) and Nb(V) were higher in oxalic acid media, whereas those of Co(II) and Sb(II) were negligible. Separation factors for Co(II), Sb(V) and Nb(V) with respect to Zr(IV) were higher in HCl; compared to those in HF, oxalic acid and HCl-HF combined media. Among all the media studied, 1 M HCl was the most suitable medium for anion exchange separation of Co(II), Sb(V) and Nb(V) from Zr(IV) using PAni. Separation factors for Sb(V), Co(II) and Nb(V) with respect to Zr(IV) were 52, 108 and 404 respectively, from 1 M HCl medium. The obtained distribution ratios, separation factors and %-uptake data are useful for designing an ion exchange separation process using PAni in acidic media.

Chapter 7

Summary, conclusions and future perspectives

7.1 Summary

Synthetic polymeric sorbents are extensively used as ion exchangers in analytical separations, effluents treatment, recovery of valuables, catalysis and other applications. It is possible to design and tailor these polymers to meet specific end-use, provided that the structure-property relations are well-understood. Polymerization /immobilization of organic compounds on inorganic/organic support not only provides better mechanical, thermal and radiation stability but also may result in materials with different properties. The main objective of the thesis was to synthesize and characterize polymers that are suitable for separation of metal ions, particularly Zr, Co, Sb and Nb that are relevant to reprocessing and radioactive waste management studies and environmentally important metal ions like Hg(II). Based on a thorough literature survey and past experience, it was decided to synthesize conducting polymers like Polyaniline (PAni) and its composites, characterize them and investigate their possible applications in separation science. PAni works as an anion exchanger in acidic media and hence is a candidate sorbent for metal ions which form anionic species in these media. These materials while used in chemical separations get exposed to varying chemical environment, heat and ionizing radiation, which might influence the performance of these sorbents. In order to evaluate the influence of the above parameters on the efficacy of the synthesized materials, investigations were carried out by simulating these conditions and applied to real samples. PAni and its derivatives were used to (i) preconcentrate and determine Hg(II) from aqueous media, and (ii) separation of Co, Sb and Nb from Zr in solution. Results of these studies are summarized in what follows.

Polyaniline (PAni) and its composites with XAD, silica gel, calcium alginate and tetraethoxy silane (TEOS) were synthesized from acidic media by chemical route, using aniline as the starting material. PAni, in the form of powder was obtained by chemical oxidative polymerization of aniline using ammonium persulphate in HCl medium. PAni-coated XAD and silica gel beads were obtained by in-situ polymerization in the presence of the bare beads. Composites of PAni with calcium alginate and TEOS-discs were prepared by incorporating PAni during their synthesis. Characterization of PAni and its composites were carried out using elemental analysis, FTIR spectroscopy, ion exchange capacity determinations, viscometry, UV-visible spectroscopy and TG-DSC-EGA. EDXRF and NAA were used for the determination of chlorine in PAni, which, in turn could be converted to equivalent ionizable chlorine and hence the ion exchange capacity. Ion exchange capacity of PAni was studied in detail for its application in the sorption/separation/ preconcentration of anionic (metal) species in acidic media.

Radiation stability of PAni was evaluated by subjecting PAni powder to gamma radiation from a ^{60}Co source upto a dose of 3.6 MGy @ 5 kGy h^{-1}. Chloride as well as base form of PAni was irradiated in air, water and HCl media and the stability. From these studies, it was concluded that PAni was stable upto a dose of 3.6 MGy. Radiation stability studies showed that the ion exchange capacity of PAni decreased on irradiation and the decrease was a function of the absorbed dose, chemical form of PAni and irradiation conditions. The decrease in the capacity on irradiation in aqueous medium was attributed mainly to the indirect effects of radiation. FTIR analysis revealed minor radiation damage to the structural integrity of PAni on irradiation. Chloride-PAni was found to be more stable than the base-PAni when exposed to γ-radiation. Further, chloride-PAni showed superior radiation resistance, compared to the literature reported values for Dowex 1x4 resins, in terms of less reduction in ion exchange capacity. It could be concluded that PAni is a suitable candidate material for anion exchange separations in radiation environments.

Studies on thermal stability of PAni were carried out to examine its suitability for applications at elevated temperatures. Thermogravimetric analysis showed that the weight loss in air was more pronounced compared to that in nitrogen atmosphere, for both chloride and base PAni. The observed better stability of base-PAni, compared to chloride-PAni, was attributed to the extension of conjugation throughout the polymer chain. Structural modifications in PAni upon heating upto 500°C were studied using UV-visible spectroscopy, Fourier Transform Infrared (FTIR) spectroscopy and viscometry. FTIR spectroscopic studies clearly indicated the conversion of ionic chlorine to covalent chlorine upon heat treatment. Identity of the gaseous decomposition products of chloride-PAni upon heating at 300°C was established by high resolution infrared spectroscopy. Anion exchange capacity of polyaniline, as determined by Energy Dispersive X-ray Fluorescence (EDXRF) spectrometry, was found to be 3.25 meq g^{-1}. PAni could regain ~ 90% of the original ion exchange capacity upon equilibration with HCl after heat treatment upto 200°C. Hence, it could be concluded that the nitrogen atoms are being retained and the polymer backbone is intact during heat treatment upto 200°C. Water and HCl media were found to have negligible effect on the ion exchange capacity of PAni at elevated temperature (100°C). These studies proved that PAni has superior thermal stability over conventional anion exchangers like Dowex 1x8, in terms of ion exchange capacity as well as structural stability.

PAni and its composites were used for preconcentration of Hg(II) from water and HCl media and analyzed directly by EDXRF spectrometry. PAni powder can easily be pelletized and it comprises of low Z elements. Hence it possesses low X-ray absorption /transmission characteristics and trace levels of mercury could be directly determined by EDXRF spectrometry. Distribution ratio of Hg(II) on PAni decreases with increasing HCl concentration. Kinetics of sorption of Hg(II) was rapid, attaining 80% of the uptake in the initial 1 min of equilibration. Sorption of Hg(II) on PAni follows Langmuir isotherm model and the sorption capacity was 19.7 mg g^{-1}. Except Au(III), the presence of higher concentrations of Pd(II), Pt(IV), Fe(III), Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II) had no effect on the sorption of Hg(II) on PAni. By EDXRF analysis, detection limit of 166 ng was obtained for Hg from the calibration equation and the apparent detection limit obtained was 42 pg, considering a preconcentration factor of $4x10^3$. PAni-loaded alginate beads were used in the form of ion exchange columns for practical sorption/separation of Hg(II). Since PAni-silane composite discs are ready-to use and do not require any post-sorption processing, these discs could be potential sorbents for preconcentration of trace levels of Hg(II) from aqueous solutions, followed by EDXRF determination. Obviation of the elution step reduced the chemical inventory, minimized the sample handling and the associated losses of Hg. One of the additional contributions is that Hg-loaded PAni pellets could be preserved carefully for the repeated use as laboratory-made secondary standards for quantitative EDXRF analyses.

PAni was studied for anion exchange sorption/separation of Zr(IV), Co(II), Sb(V) and Nb(V) in acidic media, for decontamination of used pressure tube materials (Zr-Sn and Zr-Nb), containing the respective radioisotopes and facilitate the reuse of these pressure tube materials. Distribution ratios, separation factors and %-uptake of Zr(IV), Co(II), Sb(V) and Nb(V) in PAni from various acidic media were measured. PAni showed the highest distribution ratio for Nb(V) and the lowest for Co(II) in both HCl and HF media. Distribution ratios of both Zr(IV) and Nb(V) were higher in oxalic acid media, whereas those of Co(II) and Sb(II) were negligible. Separation factors for Co(II), Sb(V) and Nb(V) with respect to Zr(IV) were higher in HCl; compared to those in HF, oxalic acid and HCl-HF combined media. Among all the media studied, 1 M HCl is the most suitable medium for anion exchange separation of Co(II), Sb(V) and Nb(V) from Zr(IV) using

PAni. Distribution ratio, separation factor and %-uptake data are useful for designing an ion exchange separation process using PAni in acidic media.

7.2 Conclusions

Following conclusions were drawn from the present work:

(i) PAni is stable towards gamma irradiation upto a dose of 3.6 MGy and retains ~ 80% of the ion exchange capacity.

(ii) Thermal stability studies could establish the structural stability and retention of ion exchange capacity (~ 90%) of PAni upto 200^{o}C, whereas the base-PAni is thermally stable upto 600^{o}C.

(iii) PAni as well as its composites shows sorption of Hg(II) ions from aqueous/acidic solutions and the sorption capacity was ~ 20 mg g^{-1}. Preconcentration of Hg from aqueous solutions, on PAni could improve the detection limits upto 42 pg in EDXRF determinations.

(iv) The highest separation factors were obtained at 1 M HCl for Sb, Co and Nb with respect to Zr in PAni and the values were 52, 108 and 404 respectively.

7.3 Future perspectives

Future perspectives of the work are listed below:

(iii) In view of proven stability of PAni in radiation fields and at elevated temperatures, it can be used in radiochemical separations of metal ions. It appears that this conducting polymer and its derivatives may profitably be used for preconcentration and determination of various environmentally important metals like As(V), Sb(V) and Nb(V).

(iv) Anion exchange property of PAni can also be used for separation and preconcentration of platinum group metals like Au(III), Pt(IV) and Pd(II), which form anionic species in acidic media.

(v) The present data on distribution ratio and separation factor of Zr(IV), Co(II), Sb(V) and Nb(V) can be used to design a separation process.

This work resulted in three peer reviewed journal publications and five symposia presentations as listed in Annexure 1 at the end of this chapter.

Annexure 1

List of publications:

Journal

1. Effect of gamma irradiation on the ion exchange capacity of polyaniline. **P.S. Remya Devi**, H. Bhatt, M.N. Deo, R. Verma and A.V.R. Reddy, *Radiation Physics and Chemistry,* **2014**, *96*, 75-80.

2. Evaluation of the effect of heating on the ion exchange capacity of polyaniline. **P.S. Remya Devi**, M.N. Deo, S. Kawadiya, N. Raje, S.R. Vishwakarma, R. Verma and A.V.R. Reddy, *Synthetic Metals,* **2015**, *210 /B*, 297-303.

3. Preconcentration of Hg on polyaniline expands the horizon for energy dispersive X-ray fluorescence determination. **P.S. Remya Devi**, S. Suvarna, M. Ghosh, G. Kiran Kumar, R. Verma and A.V.R. Reddy, *X-ray spectrometry. DOI 10.1002/xrs.2682*.

Symposia

1. Effect of gamma irradiation on the ion exchange capacity of polyaniline. **Remya Devi P.S**, H. Bhatt, M.N. Deo, Y.K. Bhardwaj, Rakesh Verma and A.V.R. Reddy, 4th Interdisciplinary Symposium on Materials Chemistry (ISMC-2012), 11-15 December 2012.
2. Evaluation of the thermal stability of ion exchange capacity of polyaniline. **P.S. Remya Devi**, S.R. Vishwakarma, M.N. Deo, R. Verma and A.V.R. Reddy, 5th Interdisciplinary Symposium on Materials Chemistry (ISMC-2014), 9-13 December 2014.
3. Polyaniline: A base material for the direct determination of mercury in solids using EDXRF spectrometry. **P.S. Remya Devi**, S. Suvarna, M. Ghosh, G. Kiran Kumar,

D.N. Wagh, R. Verma, A.V.R. Reddy, Symposium on Current Trends in Analytical Chemistry (CTAC-2015), 26-29 May 2015.

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