

SYNOPSIS

Metal ion contamination in surface and ground water is a major threat as it has a direct implication on the health of terrestrial and aquatic flora and fauna. Lead (Pb^{2+}), mercury (Hg^{2+}), cadmium (Cd^{2+}), nickel (Ni^{2+}), copper (Cu^{2+}) and cobalt (Co^{2+}) are few of these metal ions which are classified under the high risk category. Of these, lead and mercury are of greater concern, as even nanomolar concentrations can be lethal, as they can be bio-accumulated and result in physiological as well as neurological disorders. In Asian countries like India and China, heavy metal pollution is more prevalent, as a consequence of poor governmental policies or ineffective or inadequate measures to combat this problem. In recent times, the monitoring and assessment of water pollution is a critical area of study, as it has a direct implication for its prevention and control. The major techniques used for metal ion detection are atomic absorption spectroscopy (AAS), X-ray fluorescence, ion chromatography, neutron activation, etc. Alternatively, the electrochemical, optical and electrical methods provide a platform for the fabrication of portable devices, which can facilitate the on-site analysis of samples in a rapid and cost-effective manner. This has led to a new field of research called chemical sensors or chemo sensory devices.

The main aim of this study is to develop various chemosensory materials and test their response towards metal ion sensing. In this study, electroactive polymers have been synthesized for various sensor applications. The focus has been to design synthesize and test various functionalized electroactive polymers (FEAP) for the development of electrochemical, optical and chemoresistive sensors. Electroactive polymers like polyaniline, polypyrrole, polypyrrole grafted to exfoliated graphite oxide and dipyrromethene conjugated with p-(phenylene vinylene) have been synthesized and evaluated after functionalizing with metal coordinating ligands. These metal coordinating ligands were selected, in order to enhance their metal uptake capacity. Various metal ligands like imidazole, tertiary amine group, iminodiacetic acid, and dipyrromethene incorporated either in the polymer backbone or as a part of the backbone have been chosen for the metal binding. These functionalized electroactive polymers (FEAP) served as active material for metal ion sensing.

The present investigation is subdivided into three sections. The first part includes design and chemical synthesis of the functionalized polymers by a series of organic reactions. The synthesis has been followed up by characterization using spectroscopic methods including NMR, FTIR, GCMS and Mass spectrometry. In the second part of the investigation, the synthesized polymer has been characterized for the changes in electronic, electric and optical

properties after interaction with the selected metal ions. For this, the FEAP is allowed to interact with various metal ions and the changes in the relevant properties have been measured. This includes the study of changes in the conductivity, electronic properties like absorption or emission of the polymer, changes in the redox properties, etc. The third phase of investigation deals with the fabrication of the devices using the active FEAP. The sensor devices comprised of either films, or electrode modified with FEAP or solution of the FEAP, in combination with an appropriate technique has been used for the sensing.

The major objectives are enumerated below

1. Functionalization of polyaniline with imidazole functional group to get imidazole functionalized polyaniline (IMPANI) and study of the electronic, electrical and optical properties of the same.
2. Preparation of films of IMPANI and study of the change in conductivity of the film upon interaction with various metal ions, namely Cu^{2+} , Co^{2+} and Ni^{2+} in their chloride form.
3. Synthesis of amine functionalized aniline monomer and chemical graft polymerization onto exfoliated graphite oxide as a substrate to synthesise the amine functionalised polyaniline grafted to exfoliated graphite oxide (EGAMPANI). Modification of the carbon paste electrode (CPE) with EGAMPANI and study of the electrode characteristic.
4. Study of the electrode properties of EGAMPANI modified carbon paste electrode.
5. Evaluation of the EGAMPANI modified carbon paste electrode as a multi-elemental voltammetric sensor for Pb^{2+} , Hg^{2+} and Cd^{2+} in aqueous system.
6. Functionalization of polypyrrole with iminodiacetic acid and characterization of the polymer to synthesis iminodiacetic acid functionalized polypyrrole (IDA-PPy).
7. Modification of the CPE with IDA-PPy by drop casting method and evaluation of the Pb^{2+} sensing properties.
8. Study of the effect of other metal ions say Hg^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+} and Cd^{2+} on the anodic stripping current of Pb^{2+} using EGAMPANI modified CPE.
9. Synthesis of dipyrromethene-p-(phenylene vinylene) conjugated polymer for heavy metal ion sensing.
10. Study of the changes in the optical absorption and emission properties of the polymer in THF and evaluation of the change in these optical properties upon interaction with the metal ions as analyte.

The salient findings of the research work are highlighted as follows,

In the first synthesis, aniline has been functionalized with imidazole group and this monomer has been chemical oxidatively polymerized to obtain imidazole functionalized polyaniline (IMPANI). The synthesized polymer possesses a nano-spherical structure, as confirmed from the morphological characterisation using scanning electron microscopy. The IMPANI has been interacted with a representative metal ion, copper (II) chloride, and the copper complexed polymer (Cu-IMPANI) has been subjected to various studies. The coordination of copper with IMPANI results in an increase of molecular weight of the polymer as a result of aggregation, as observed from dynamic light scattering measurements. Apart from this, a significant finding is the decrease of the pH of the system after copper ion coordination attesting to the generation of a secondary hydrochloride ion during the coordination of the copper to the imidazole side chain. This is further confirmed by an increase in conductivity of the Cu-IMPANI compared to IMPANI, measured using the four-probe technique. The increase of conductivity due to copper coordination is one order of magnitude higher. The films which have been prepared from IMPANI and Cu-IMPANI exhibit different morphology. The Cu-IMPANI film prepared by prior co-ordination of Cu ion with IMPANI powder shows a flaky structure, which is not preferable for the conductivity measurements, as a consequence of discontinuity in the medium. To overcome this problem, IMPANI films were initially prepared and then interacted with copper ions for a desired duration, before measurement of the conductivity. This latter procedure enabled the preparation of smooth films for the development of chemoresistive sensors.

In continuation of the initial study highlighted above, IMPANI films of thickness 0.02 ± 0.001 mm have been prepared using IMPANI and PANI in DMPU in the ratio of 7:3 by mass. After exposure of the films with respective metal chlorides, such as Ni^{2+} , Co^{2+} and Cu^{2+} , a change in conductivity is observed in the concentration range of 10^{-2} to 1 M of metal chlorides. The sensor response may be arranged in the sequence: $\text{Ni}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+}$ at 1M concentration. On the contrary, films prepared from PANI-EB under identical conditions do not exhibit any appreciable change in conductivity. The optimum exposure time is determined to be 10 min for a maximum change in conductivity, after exposure to the chosen metal ions.

In the second system taken up for investigation, a tertiary amine containing polyaniline (AMPANI) has been grafted to exfoliated graphite oxide. The amine containing polyaniline grafted to exfoliated graphite oxide (EGAMPANI) has been characterised for structural,

morphological and elemental composition. The grafting percentage has been determined to be 7 % by weight of AMPANI on the EGO surface. The synthesized EGAMPANI (5 weight %) has been used to modify carbon paste electrode (CPE) for electrochemical sensor studies. Based on the differential pulse anodic stripping voltammetric studies, the electrochemical response may be arranged in the following sequence: $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Hg}^{2+}$. The minimum detection levels obtained are 5×10^{-6} , 5×10^{-7} , and 1.0×10^{-7} M for Hg^{2+} , Cd^{2+} and Pb^{2+} ions respectively.

In the next study, an iminodiacetic acid functionalized polypyrrole (IDA-PPy) has been synthesized and characterised for its elemental and structural properties. This has been further used to modify the CPE by drop casting method and used for the specific detection of Pb^{2+} in acetate buffer. Various parameters governing the electrode performance such as concentration of depositing solution, pH of depositing solution, deposition potential, deposition time, and scan rate, have been optimized to achieve maximum performance and found to be 20 μl , 4.5, -1.3 V, 11 min, 8 mV s^{-1} respectively for the chosen parameters. Additionally, the influence of other heavy metal ions on the lead response has been studied and it is observed that Co, Cu and Cd ions are found to be interfering. Further, the response of Cd, Co, Cu, Hg, Ni and Zn on IDA-PPy functionalized electrode has been evaluated. The selectivity of IDA-PPy modified electrode for Pb^{2+} is observed in the concentration range of 1×10^{-7} M and below. The IDA-PPy modified CPE shows a linear correlation for Pb^{2+} concentration in the range from 1×10^{-6} to 5×10^{-9} M and with a lowest limit of detection (LLOD) of 9.6×10^{-9} M concentration. The efficacy of the electrode for lead sensing has also been evaluated with an industrial effluent sample obtained from a lead battery manufacturing unit.

The fourth synthesis pertained to the development of an optical sensor for Fe^{2+} , and Co^{2+} ions. For this, dipyrromethene as a metal coordinating ligand in conjugation with p-phenylenevinylene has been synthesized and tested for its structural as well as optical properties. It is observed that the polymer shows three absorptions, namely at 294 nm, 357 nm and a major absorption observed as a broad band ranging from 484 to 670 nm. The emission spectrum of the polymer excited at 357 nm shows a characteristic blue emission with a maximum intensity centered at 425 nm. The emission quenching in the presence of various metal ions have been tested and are found to be quenched in presence of Fe^{2+} and Co^{2+} ions. All the other metal ions tested namely, Cr^{3+} , Cu^{2+} , and Zn^{2+} are not found to exhibit any change in the emission spectra below the concentration of 1×10^{-4} M. The linear correlation of the emission intensity with the concentration of the Co^{2+} and Fe^{2+} ions has been determined using

Stern-Volmer plot. For Co^{2+} the Stern-Volmer regime is observed from 1×10^{-4} to 9×10^{-4} M concentration and the quenching constant K_{sv} is determined to be $8.67 \times 10^3 \text{ M}^{-1}$. For Fe^{2+} , the linearity is found to be in the regime of 1×10^{-5} to 9×10^{-5} M and the quenching constant K_{sv} is determined to be $7.90 \times 10^3 \text{ M}^{-1}$.

In conclusion, different electroactive polymers functionalized with metal coordinating ligands have been synthesized, characterised and evaluated for metal sensing applications. Techniques like electrochemical, optical and conductivity have been used to characterise the response of these FEAP towards metal sensing. It can be concluded that the electrochemical sensors are more reliable for sensing especially at very low concentrations of metal ions such as Pb, Cd and other techniques like optical and conductimetric are good for detecting metal ions namely Fe, Co, Ni, Cu. The selectivity towards the metal ions is a function of the metal chelating ligand and the extent of sensitivity is dependent upon the technique employed.