

ELECTROCHEMICAL DETECTION AND ADSORPTION OF Pb(II) IONS USING ION-IMPRINTED POLYMERS FUNCTIONALIZED ON MULTI-WALLED CARBON NANOTUBES

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Abstract

The detection and removal of lead (Pb(II)) ions from contaminated water sources is a critical environmental challenge due to the toxic and non-biodegradable nature of lead. This study presents the development of a novel ion-imprinted polymer (IIP) layered on vinyl-functionalized multi-walled carbon nanotubes (MWCNTs) for dual applications in adsorption and electrochemical sensing of Pb(II) ions. The composite material (MWCNT-IIP) was synthesized by polymerizing acrylamide and N,N'-methylenebisacrylamide onto vinylated MWCNTs in the presence of Pb(II) ions, followed by Soxhlet extraction to remove the template ions. Comprehensive characterization (FT-IR, SEM, HR-TEM, EDAX, TGA) confirmed successful functionalization and imprinting. Electrochemical evaluation using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) revealed a highly selective redox response for Pb(II), with a detection limit of $2 \times 10^{-2} \mu\text{M}$ and excellent linearity ($R^2 = 0.9987$). The sensor exhibited strong selectivity against competing metal ions and achieved over 99% recovery in real samples, including mining effluent, lake water, food, and cosmetics. The MWCNT-IIP system demonstrates high sensitivity, environmental compatibility, and potential for real-time water quality monitoring and remediation.

Keywords: Ion-imprinted polymer, Multi-walled carbon nanotubes, Lead detection, Electrochemical sensor, Environmental remediation, Vinyl functionalization, Heavy metal adsorption, Real sample analysis

1. Introduction

The contamination of aquatic ecosystems by heavy metals has emerged as a pressing environmental and public health concern across the globe. Among these pollutants, lead (Pb(II)) ions are particularly notorious due to their high toxicity, non-biodegradability, and tendency to bioaccumulate in living organisms. Exposure to elevated levels of lead can lead to neurological disorders, developmental issues in children, kidney damage, and various chronic illnesses. Industrial discharge, mining activities, improper waste disposal, and urban runoff have significantly contributed to lead ion contamination in water bodies [1]. Consequently, developing efficient, selective, and sensitive methods for the detection and removal of Pb(II) ions is a research imperative. Traditional methods such as atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectrometry (ICP-MS), and UV-visible spectroscopy, while highly accurate, require expensive instrumentation, skilled personnel, and are often not amenable to on-site or real-time monitoring. In contrast, electrochemical sensing techniques offer distinct advantages including rapid response, portability, simplicity, and the potential for in-situ monitoring [2]. However, the selectivity and sensitivity of conventional electrodes are often inadequate, particularly in complex sample matrices where interfering ions may be present. To address these limitations, researchers have increasingly turned toward molecular imprinting technology (MIT), a powerful method that enables the creation of highly selective recognition sites within polymer matrices [3]. Ion-imprinted polymers (IIPs) are a specialized form of molecularly imprinted polymers (MIPs) that exhibit high specificity for target metal ions, owing to the creation of complementary cavities during polymerization in the presence of a template ion. These materials are particularly advantageous for environmental applications due to their stability, reusability, and low cost of production.

Simultaneously, carbon-based nanomaterials have gained substantial interest in the field of sensor and adsorbent development due to their exceptional electrical conductivity, high surface area, chemical stability, and functionalization potential. Among them, multi-walled carbon nanotubes (MWCNTs) have emerged as a versatile platform for designing hybrid nanocomposites. However, pristine MWCNTs tend to aggregate in aqueous environments due to their hydrophobic nature and lack of surface functionality, limiting their direct application in

environmental sensing and remediation. In this study, we report the development of a lead(II) ion-imprinted polymer (IIP) layered on vinyl-functionalized MWCNTs (MWCNT-IIP), designed to function both as a highly selective adsorbent and as an electrochemical sensor [4]. The system was created through the surface polymerization of acrylamide (functional monomer) and N,N'-methylenebisacrylamide (crosslinker) onto vinyl-functionalized MWCNTs in the presence of Pb(II) ions. Post-polymerization, the Pb(II) ions were removed to generate recognition sites within the polymer matrix. The incorporation of MWCNTs into the IIP matrix offers multiple synergistic benefits: it enhances electrical conductivity for sensor applications, increases mechanical and thermal stability, and improves dispersion and surface interaction with water-soluble pollutants [5].

Comprehensive characterization techniques including FT-IR, SEM, HR-TEM, EDAX, and TGA were employed to confirm the successful functionalization of MWCNTs and the integration of imprinted polymer layers. A dispersion test revealed improved aqueous stability of the modified nanomaterials, while swelling studies validated the porosity and cavity formation in IIPs compared to non-imprinted controls. These physicochemical properties are directly linked to the enhanced adsorption and electrochemical detection of lead ions [6].

Electrochemical studies using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed to evaluate the sensing capabilities of the MWCNT-IIP modified platinum electrodes. The modified electrode demonstrated a distinct redox peak for Pb(II) ions in acetate buffer (pH 5.0), unlike the non-imprinted systems which showed weak or no electrochemical response. The limit of detection (LOD) was found to be as low as 2×10^{-2} μ M, with a linear calibration curve and high correlation coefficient ($R^2 = 0.9987$). This highlights the high sensitivity and selectivity of the system. Additionally, selectivity tests using competing metal ions (Cd(II), Fe(II), Zn(II)) confirmed that the imprinted cavities on MWCNT-IIP are highly specific to Pb(II) ions due to the geometric and chemical match. Real-world application potential was demonstrated through successful detection of lead ions in mining effluent, lake water, food, and cosmetic samples, where the MWCNT-IIP-based sensor showed recovery rates above 99%—significantly outperforming the non-imprinted analogues [7].

The novelty of this research lies in the dual-functionality of the MWCNT-IIP nanocomposite as both a sensor and an adsorbent, enabling its use in environmental monitoring and remediation. By combining the selective recognition of ion-imprinted polymers with the conductive nanostructure of MWCNTs, a synergistic enhancement in analytical performance was achieved. The developed system bridges the gap between laboratory-based detection and field-applicable technologies, offering a cost-effective, scalable, and environmentally friendly approach for detecting and removing Pb(II) ions from contaminated water sources.

This work demonstrates the potential of MWCNT-based ion-imprinted polymer composites for environmental sensing and cleanup applications. The study not only contributes to the growing body of knowledge in green nanotechnology and molecular imprinting, but also provides a practical solution for tackling one of the most persistent threats to water safety and public health.

2. Literature Review

2.1. Heavy Metal Contamination and the Need for Advanced Detection

Heavy metal contamination, particularly by lead (Pb(II)) ions, remains a critical environmental and health issue due to its high toxicity, persistence, and non-biodegradable nature. Lead ions are widely discharged into the environment through industrial activities such as battery manufacturing, mining, electroplating, and smelting [8]. Once released, these ions can infiltrate water bodies and food chains, causing severe health complications such as neurotoxicity, renal dysfunction, and developmental issues in children. Conventional methods for Pb(II) detection—such as atomic absorption spectroscopy (AAS), inductively coupled plasma-mass spectrometry (ICP-MS), and UV-visible spectrophotometry—though highly accurate, are often limited by their need for sophisticated equipment, trained personnel, and time-consuming sample preparation procedures [9]. This has led to increased research into simpler, faster, and more cost-effective alternatives, particularly in the form of electrochemical sensors and advanced adsorbent materials capable of both detection and removal of trace heavy metals from aqueous environments [10].

2.2. Ion-Imprinted Polymers (IIPs): Principles and Applications

Ion-imprinted polymers (IIPs) have emerged as a powerful class of materials for the selective recognition of metal ions. These materials are synthesized through a process where target metal ions (templates) are complexed with functional monomers, followed by crosslinking to form a polymer matrix [11]. After the template ions are removed, complementary binding sites with specific size, shape, and functional group orientation remain in the polymer network, enabling highly selective re-binding. IIPs offer numerous advantages over conventional adsorbents, including high selectivity, chemical stability, resistance to microbial degradation, and reusability [12]. They have been successfully applied for the selective removal and sensing of various metal ions, such as Cd(II), Hg(II), and Cu(II), and more recently, Pb(II). However, traditional IIPs often suffer from limitations like low surface area and poor mass transfer properties, which can hinder their adsorption kinetics and sensing sensitivity. As a result, the integration of IIPs with nanostructured supports such as carbon nanotubes has been proposed to overcome these shortcomings and enhance performance [13].

2.3. Carbon Nanotube-Based Composites for Environmental Sensing

Carbon nanotubes (CNTs), particularly multi-walled carbon nanotubes (MWCNTs), are widely studied nanomaterials known for their extraordinary electrical conductivity, high surface area, and mechanical strength. These properties make them ideal candidates for integration into sensor platforms and adsorbent materials [14]. Numerous studies have demonstrated the utility of CNT-based composites in environmental monitoring and remediation. Functionalizing MWCNTs with various chemical groups, including carboxyl, hydroxyl, and vinyl groups, improves their dispersion in aqueous media and facilitates further modification or polymer grafting [15]. In the context of IIP synthesis, MWCNTs serve as robust scaffolds that improve electron transfer in electrochemical applications and provide a large active surface area for binding sites. Recent advancements include the fabrication of CNT-based electrochemical sensors capable of detecting ultra-trace levels of metal ions with high selectivity, rapid response, and low detection limits [16]. Several works (e.g., Luo et al., 2017; Ivori et al., 2017) have highlighted the advantages of integrating IIPs with CNTs to improve signal transduction, reduce interference from co-existing ions, and enhance the mechanical and thermal stability of the sensing platform. However, there remains a need for comprehensive studies that optimize the synergy between CNTs and IIPs, particularly for dual-function systems capable of both sensing and adsorption in real-world samples [17].

3. Methods and Materials

3.1. Materials

All chemicals used were of analytical grade and used as received. Multi-walled carbon nanotubes (MWCNTs) were purchased from a commercial supplier. Lead(II) nitrate ($\text{Pb}(\text{NO}_3)_2$), acrylamide (AAM), N,N'-methylenebisacrylamide (NNMBA), azobisisobutyronitrile (AIBN), and all other reagents were obtained from standard suppliers. Deionized water was used throughout all experiments.

3.2. Functionalization of MWCNTs

MWCNTs were first treated with concentrated nitric acid to introduce carboxylic acid groups, resulting in acid-functionalized MWCNTs (MWCNT-COOH). This process enhanced the dispersion properties and chemical reactivity of the nanotubes. The degree of carboxylation was determined via alkali titration and found to be 1.987 mmol/g.

The acid-functionalized MWCNTs were then converted into acid chlorides using thionyl chloride, facilitating the attachment of vinyl groups through reaction with vinyl-functional silane. The resulting product, vinyl-functionalized MWCNTs (MWCNT-CH=CH₂), showed a vinylation degree of 94%, indicating successful functional group incorporation.

3.3. Synthesis of Ion-Imprinted Polymer (MWCNT-IIP)

A Pb(II) ion-imprinted polymer was synthesized via in-situ polymerization on the surface of vinyl-functionalized MWCNTs.

- Template ion: Pb(II) nitrate
- Functional monomer: Acrylamide
- Crosslinker: N,N'-methylenebisacrylamide (NNMBA)
- Initiator: AIBN

A specific molar ratio of MWCNT-CH=CH₂, Pb(II) nitrate, AAm, and NNMBA was dissolved in water. AIBN was added, and the mixture was purged with nitrogen gas for 15 minutes to remove oxygen, then polymerized at 70°C for 5 hours under continuous stirring.

The resulting MWCNT-IIP was collected by centrifugation, thoroughly washed with water to remove unreacted monomers, and subjected to Soxhlet extraction using water to remove the template Pb(II) ions. The absence of lead was confirmed via atomic absorption spectroscopy (AAS). The final product was dried in a vacuum desiccator for 24 hours.

3.4. Synthesis of Non-Imprinted Polymer (MWCNT-NIP)

The non-imprinted polymer (MWCNT-NIP) was synthesized under identical conditions as MWCNT-IIP but without the addition of Pb(II) ions. This control was used to evaluate the role of template ion imprinting in adsorption and sensing performance.

3.5. Preparation of Conventional IIP and NIP (Without MWCNT)

To understand the role of MWCNTs in polymer performance, conventional IIP and NIP were also synthesized using the same monomer and crosslinker formulations but without the use of MWCNTs. These served as additional control systems.

3.6. Characterization Techniques

- **Fourier Transform Infrared Spectroscopy (FT-IR):** Used to identify functional groups and confirm vinyl and polymer incorporation.
- **Scanning Electron Microscopy (SEM):** Employed to examine surface morphology.
- **High-Resolution Transmission Electron Microscopy (HR-TEM):** Used for detailed structural and morphological analysis.
- **Energy Dispersive X-ray Analysis (EDAX):** Conducted to confirm the presence and removal of Pb(II) ions.
- **Thermogravimetric Analysis (TGA):** Evaluated the thermal stability of the materials.
- **Swelling Test:** Measured water absorption and polymer porosity.
- **Dispersion Test:** Assessed water dispersion and suspension stability.

3.7. Electrochemical Measurements

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were conducted using a standard three-electrode system:

- **Working electrode:** Platinum electrode modified with MWCNT-IIP

- **Reference electrode:** Ag/AgCl
- **Counter electrode:** Platinum wire

Experiments were conducted in **acetate buffer (pH 5.0)**, with variables including scan rate, Pb(II) ion concentration, and pH levels. Redox behavior, selectivity, and sensitivity were systematically analyzed.

3.8. Real Sample Analysis

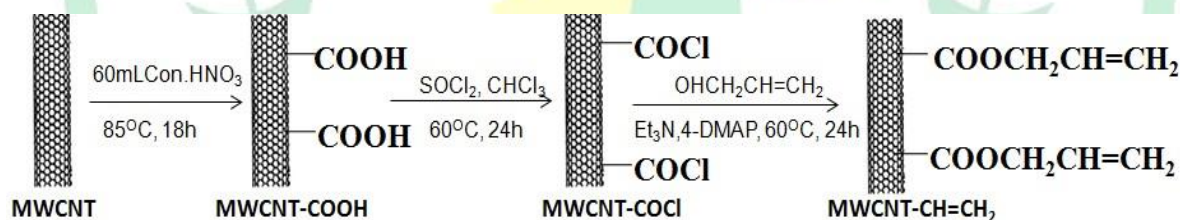
Real samples were collected from:

- Mining effluent
- Lake water
- Food items
- Cosmetic products

Each sample was filtered and spiked with known concentrations of Pb(II) ions before analysis using the MWCNT-IIP-modified platinum electrode. Recovery rates and accuracy were evaluated against standard AAS results.

4. Analysis and Results

Materials with nanostructures that are designed for specific metal ions can be customised through the polymerisation of imprinted polymers onto nanomaterials. In the current investigation, a metal ion imprinted polymer was developed by layering it onto the surface of multiwalled carbon nanotubes (MWCNTs). This was achieved through the polymerisation of a functional monomer combined with a crosslinking agent featuring vinyl groups on the MWCNTs. To facilitate the incorporation of vinyl groups, MWCNTs underwent an initial treatment with concentrated nitric acid, resulting in the formation of acid-functionalized MWCNTs (refer to Scheme 4.1.1). The degree of carboxylation assessed through alkali titration was measured to be 1.987mmol/g. The acid-functionalized multi-walled carbon nanotubes (MWCNTs) were transformed into acid chlorides to facilitate the incorporation of vinyl groups onto the MWCNTs. The degree of vinylation was determined to be 94%.



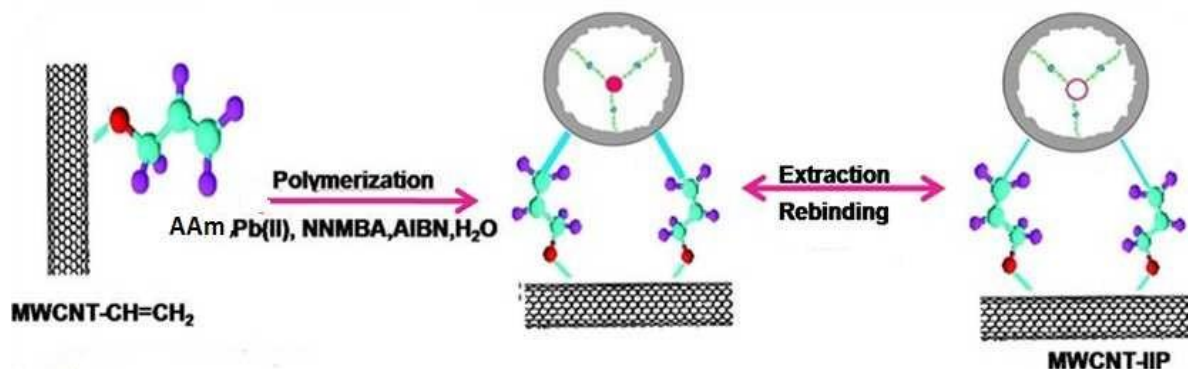
Scheme 4.1.1. Schematic representation of vinyl group functionalization of MWCNT

4.1. Pb(II) ion imprinted polymer layered on MWNCTs as sensor and sorbent for Pb(II) ion

4.1.1. Synthesis of Pb(II) ion imprinted and non-imprinted polymers

A polymer imprinted with ions on multi-walled carbon nanotubes (MWCNT-IIP), utilising lead ions as the template, was created through the polymerisation of the ion-imprinted polymer onto the surface of MWCNT that has vinyl groups integrated. The molar quantities of vinyl-functionalized multi-walled carbon nanotubes (MWCNT-CH=CH₂), lead(II) salt, acrylamide, and N,N'-methylenebisacrylamide (NNMBA) were solubilised in water. The initiator AIBN was incorporated and subjected to heating at 70°C for a duration of 5 hours (refer to Scheme 4.1.2.). The resulting polymer underwent centrifugation and was rinsed with water to eliminate any unreacted monomer and crosslinking agent. The Pb(II) ions were extracted through Soxhlet extraction with water serving as the solvent, continuing the

process until no lead ions were detectable in the eluent via AAS analysis. The polymer that was acquired underwent a drying process in the vacuum desiccator for a duration of 24 hours. To conduct the assessment, a non-imprinted polymer was synthesised in a similar manner, omitting the use of the template lead ion (MWCNT-NIP). In order to understand the influence of MWCNT on the detection and retrieval of the template Pb(II) ions, traditional ion imprinted polymer (IIP) and non-imprinted polymer (NIP) formulations devoid of MWCNT were also synthesised.



Scheme 4.1.2. Schematic representation of the synthesis of lead ion imprinted polymer

4.1.2. Characterization of lead ion imprinted and non-imprinted polymers

4.1.2 (A) Fourier transform infrared spectroscopy (FT-IR)

Figure 4.1.1 illustrates the FTIR spectra for MWCNT, MWCNT-CH=CH₂, and MWCNT-IIP. The unblemished MWCNT exhibits an absence of distinctive peaks within the IR spectrum, thereby affirming that they lack any functional groups. However, following the functionalisation of vinyl, the spectrum reveals a distinctive stretching band of C=C at 1630 cm⁻¹. This indicates the integration of a vinyl group onto MWCNT. In MWCNT-IIP, a prominent broad band observed at 3300 cm⁻¹ is attributed to the N-H stretching vibrations of the amide functional group present in acrylamide. Furthermore, the intensity of the C=O peak at 1630 cm⁻¹ was heightened owing to the presence of an extra –C=N bond originating from the amide group of acrylamide. All of these indicate the integration of the vinyl group and its following copolymerisation with acrylamide and NNMB.

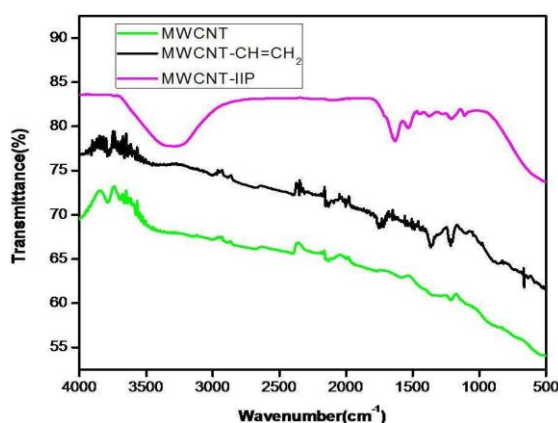


Fig. 4.1.1. FT-IR spectra of MWCNTs, MWCNT-CH=CH₂ and MWCNT-IIP

4.1.2. (B) Scanning electron microscopy (SEM)

The morphological distinctions between MWCNT-IIP and IIP were examined utilising a scanning electron microscope, as illustrated in Fig. 4.1.2. The IIP exhibits a coarse surface due to the clustering of polymers. However, the structure is completely distinct for MWCNT-IIP because of the application of IIP on MWCNT.

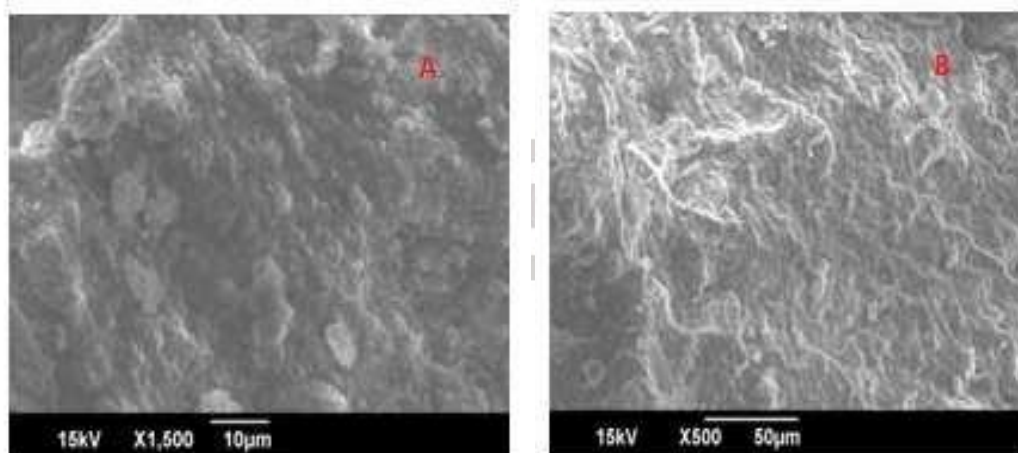


Fig. 4.1.2. SEM images of (A) IIP, and (B) MWCNT-IIP

4.1.2 (C) High-resolution transmission electron microscopy (HR-TEM)

In the context of detailed morphological investigations, HR-TEM was employed (see Fig. 4.1.3). The TEM images distinctly reveal that the unaltered MWCNTs exhibit slender tubular formations characterised by minimal diameters. However, upon functionalisation, the diameter of the nanotube expands to three times greater than that of the unmodified MWCNTs. Conversely, MWCNT-IIP showcased the application of the imprinted polymer onto the surface of vinyl-functionalized MWCNTs.



Fig. 4.1.3. TEM images of (A) MWCNTs, (B) MWCNT-CH=CH₂, and (C) MWCNT-IIP

4.1.2. (D) Energy dispersive X-ray analysis (EDAX)

The presence and elimination of Pb(II) ions within the imprinted polymers have been validated through energy dispersive X-ray analysis [12], as illustrated in Fig. 4.1.4. A distinct, precise signal is evident in the Pb(II) ion imprinted polymer. However, in Figure 4.1.4B, this peak is missing as a result of the lead ion being leached out during the elution procedure.

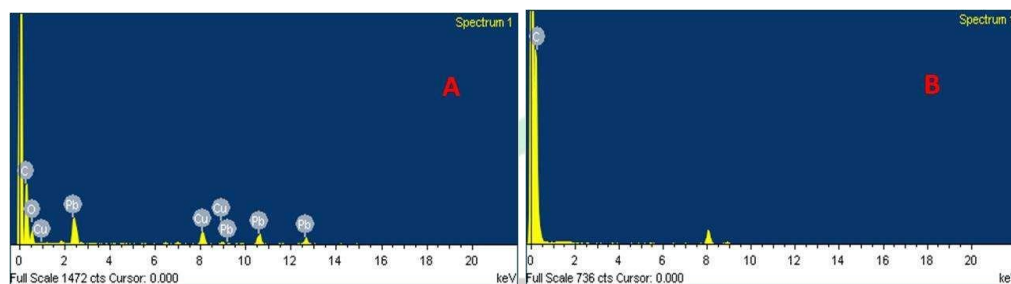


Fig. 4.1.4. EDAX of Pb(II) ion (A) bound, and (B) desorbed polymer

4.1.2 (E) Thermogravimetric analysis (TGA)

The thermal stability characteristics of MWCNT, MWCNT-IIP, and IIP were examined through thermogravimetric analysis, as illustrated in Fig. 4.1.5. The thermogravimetric curve of multi-walled carbon nanotubes (MWCNT) presents a linear profile up to 800°C, exhibiting no significant mass reduction. The findings demonstrated the exceptional thermal stability of MWCNTs. The thermal degradation temperature of MWCNT-IIP surpassed that of IIP. The enhanced thermal stability of MWCNT-IIP suggests that these nanostructures possess the capability to safeguard the materials against abrupt decompositions.

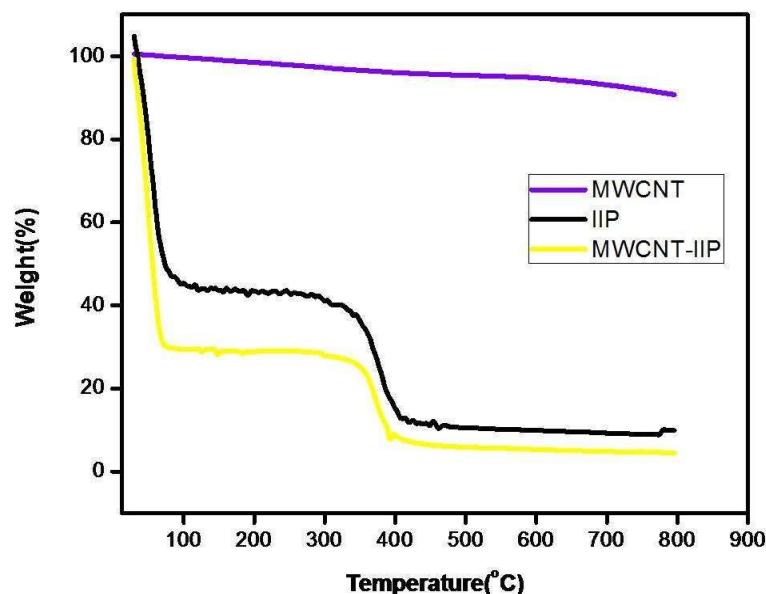


Fig. 4.1.5. TG curves of MWCNT, MWCNT-IIP, and IIP

4.1.3 Dispersion test

All three samples underwent thorough dispersion in water through sonication and were examined after a duration of one day. The MWCNT has fully settled after a duration of 24 hours. The findings indicate that there is an absence of direct interaction between the MWCNT and the selected solvent. However, in the case of functionalised MWCNT, a modest enhancement in dispersion is noted. Conversely, MWCNT-IIP disperses effortlessly in water and remains suspended even after a full day. The chemical alteration of MWCNTs augmented its polarity, leading to improved interaction with the aqueous environment and consequently enhancing its dispersibility. The distribution characteristics of MWCNT, functionalised MWCNT, and MWCNT-IIP are illustrated in Figure 4.1.6.



Fig. 4.1.6. Photographs of (A) MWCNTs, (B) MWCNT-CH=CH₂, and (C) MWCNT-IIP dispersed in water

4.1.4 Swelling study

The swelling characteristics of both metal ion imprinted and non-imprinted polymers in aqueous environments were examined. Investigations into swelling reveal the structural variations among the polymers. The expansion characteristics are influenced by the specific polymer type, its chemical properties, and the extent of crosslinking [13]. The expansions of the ion imprinted polymers (refer to Table 4.1.1) surpass those of the corresponding non-imprinted polymers. In ion imprinted polymers, water infiltrated the cavities formed during the imprinting procedure. The imprinted voids were formed as the lead ions departed during the elution process of the metal ions. The ion imprinted system exhibits significant swelling when the IIP is layered onto MWCNT. The straightforward accessibility of the pore sites within MWCNT-IIP facilitates the entry of water molecules. The compatibility of the NNMB-crosslinked IIP with MWCNT and water promotes efficient swelling. In non-imprinted polymers, there are no voids or recesses created by metal ions. The degree of swelling is lower compared to the ion imprinted system.

The sequence of expansion is as follows: MWCNT-IIP surpasses IIP, which in turn exceeds MWCNT-NIP, while NIP ranks last.

Table 4.1.1 Swelling studies of various lead ion imprinted and non imprinted systems

Polymers	EWC (%)
MWCNT-IIP	95.66%
IIP	87.84%
MWCNT-NIP	79.56%
NIP	65.81%

4.1.5. Sensing of Pb(II) ions by MWCNT-IIP modified platinum electrode

4.1.5 (A) Electrochemical sensing of Pb(II) ion with cyclic voltammetry

Cyclic voltammetry serves as a highly effective method for detecting a range of chemical constituents. Figure 4.1.7 illustrates the recorded cyclic voltammetric experiments of MWCNT-IIP/Pb/PE conducted in an acetate buffer solution (ABS) with a pH of 5.0. Similar to the scenario involving a bare electrode, the cyclic voltammogram exhibits a diminished electrochemical response when analysed in acetate buffer. Furthermore, the cyclic voltammetric response seemingly improved upon the incorporation of the MWCNT-IIP integrated platinum electrode. Furthermore, the MWCNT-IIP/Pb/PE in the buffer containing the template Pb(II) ion exhibits a distinct reduction peak, which is attributed to the internal electrochemical interaction of MWCNT-IIP present on the platinum electrode's surface. However, MWCNT-NIP/Pb/PE, IIP/Pb/PE, and NIP/Pb/PE did not exhibit any redox peaks; nonetheless, they displayed variations in the electrochemical response when compared to the bare electrode. The MWCNT-NIP/Pb/PE,

IIP/Pb/PE, and NIP/Pb/PE configurations were excluded from any additional investigations due to their unsatisfactory electrochemical performance. The findings validate that the metal ions have infiltrated the cavities of the imprinted polymer, which can be detected by a platinum electrode exhibiting a potential range from -400 to +1200 mV.

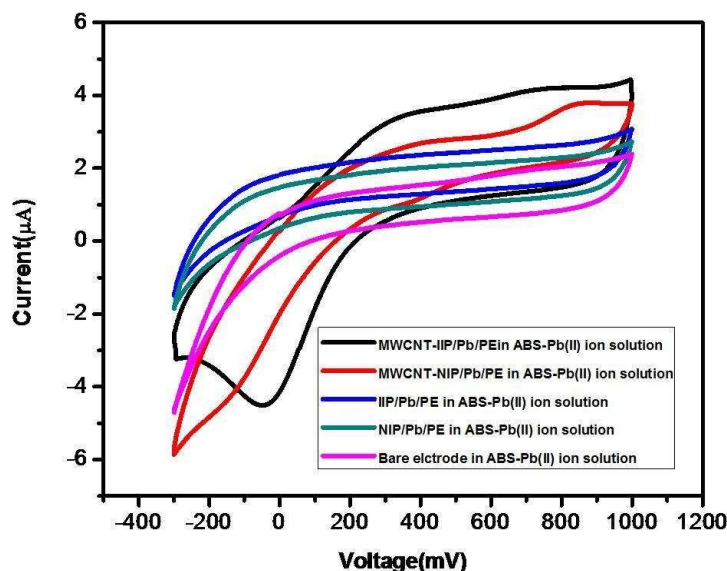


Fig. 4.1.7. CV runs for bare and modified electrodes

4.1.5 (B) Effect of Pb(II) ion concentration

The influence of Pb(II) ion concentration on MWCNT-IIP/Pb/PE within ABS was examined using cyclic voltammetry, as illustrated in Fig. 4.1.8. The peak current associated with the redox reaction rises as the concentration of Pb(II) ions escalates from 1 to 5 ppm, ultimately attaining its highest value at 5 ppm. The concentration effect demonstrates a direct correlation with the current observed at its redox peak.

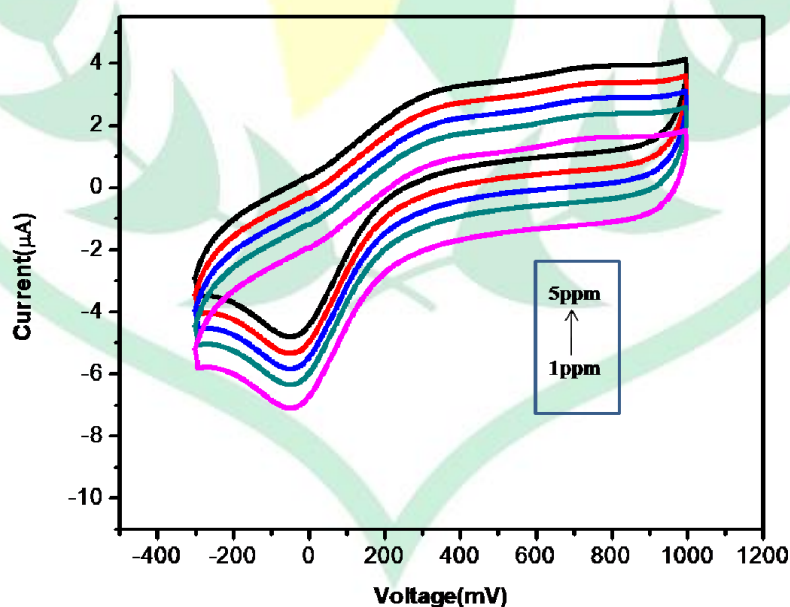


Fig. 4.1.8. CV runs of MWCNT-IIP/Pb/PE with different concentration of Pb(II) ion solution

4.1.5 (C) Effect of pH

The impact of pH on the detection of Pb(II) ions using MWCNT-IIP/Pb/PE was fine-tuned to achieve optimal performance. The capabilities and status of the MWCNT-IIP modified electrode were modified in ABS across varying pH levels, achieving a peak redox current at pH 5.0 (Fig. 4.1.9). Furthermore, with the alteration of pH, the electrochemical characteristics of Pb(II) ions on MWCNT-IIP/Pb/PE exhibited variations as well. Upon elevating the pH beyond 5.0, the free state of the Pb(II) ion within the test solution underwent a transformation, which was not assessed by MWCNT-IIP/Pb/PE, leading to a reduction in the redox current. To conclude, a solution with a pH of 5.0 has been selected as the optimal pH environment for detecting Pb(II) ions.

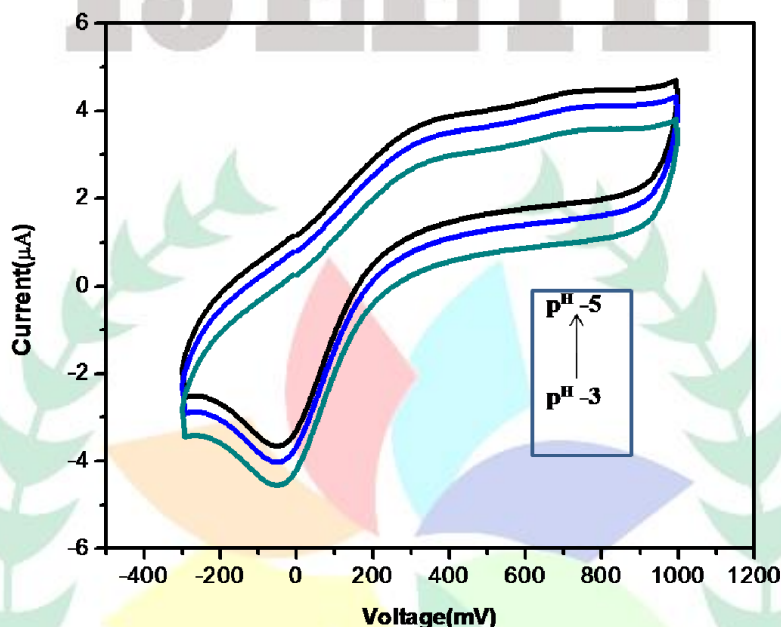


Fig. 4.1.9. Effect of pH on the peak current of Pb(II) ion solution (5ppm) with a scan rate of 100mV/s

4.1.5 (D) Effect of scan rate

The redox current exhibits an upward trend with the scan rate, escalating from 10 mV/s to 100 mV/s, as illustrated in Fig. 4.1.10. Furthermore, the cathodic peak potential experienced a complete shift towards the positive direction as the scan rate was elevated. The relationship between peak current and the square root of the scan rate exhibits a linear trend characterised by a strong correlation coefficient. The findings validate that the electrode mechanism is governed by adsorption control. The consistent linearity was dependable concerning the electrochemical response of Pb(II) ions on the MWCNT-IIP modified platinum electrode.

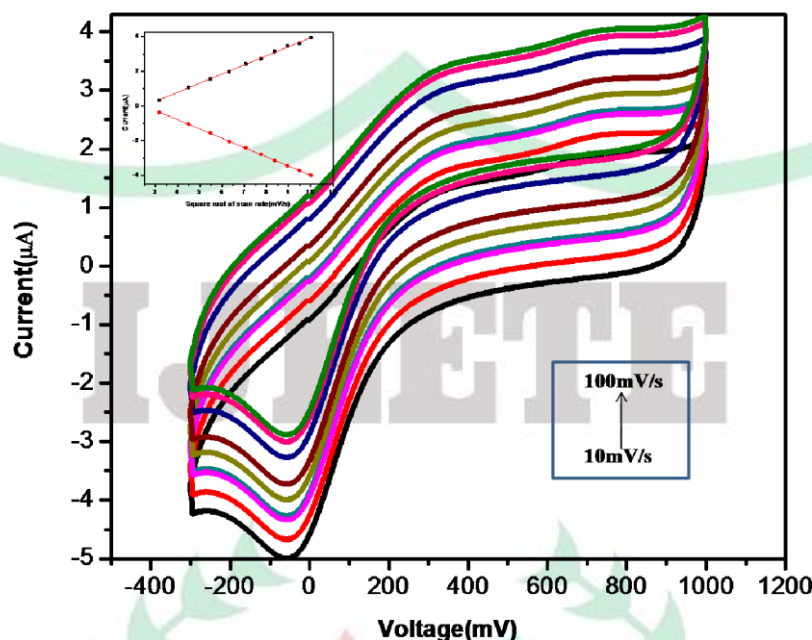


Fig. 4.1.10. CV runs of MWCNT-IIP/Pb/PE with Pb(II) ion solution (5ppm, pH - 5) with a scan rate of 10-100mV/s, inset shows the linear plot of redox current with square root of scan rate

4.1.5 (E) Selectivity study

The investigation into the selectivity of the MWCNT-IIP modified electrode was conducted using various metal ions, including Cd(II), Fe(II), and Zn(II) ions. The electrode modified with MWCNT-IIP demonstrated a pronounced sensitivity to Pb(II) ions, as depicted in Fig. 4.1.11. The Pb(II) ion can effortlessly reside within the voids formed on the surface of MWCNT-IIP. The dimensions of these cavities correspond to those of the Pb(II) ion, allowing for effortless capture by the imprinted sites. However, the dimensions of alternative metal ions and the voids created by lead ions are incompatible, resulting in insufficient detection of other ions. The redox peak was exclusively generated by the particular Pb(II) ion. The findings indicated that the sole metal ion detectable by the altered electrode was the Pb(II) ion. The engineered MWCNT-IIP/Pb/PE exhibits remarkable selectivity for the intended Pb(II) ion.

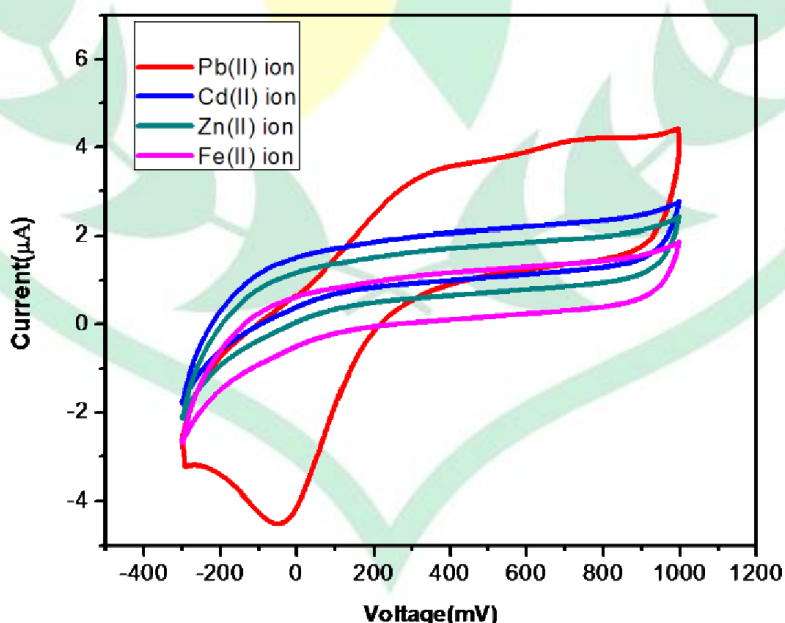
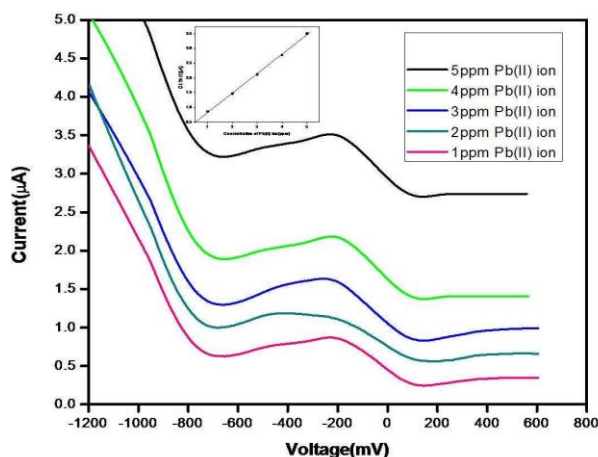


Fig. 4.1.11. Selectivity of MWCNT-IIP/Pb/PE towards Pb(II) ions

4.1.5 (F) Differential pulse voltammetry

The determination of the limit of detection (LOD) for the proposed electrochemical sensor was conducted using differential pulse voltammetry (DPV). DPV was utilised to unravel the detection capabilities of Pb(II) ions through the use of MWCNT-IIP/Pb/PE, as illustrated in Fig. 4.1.12. The impact of Pb(II) ion concentration on the MWCNT-IIP modified electrode was evaluated in an acetate buffer with a pH of 5.0. As the Pb(II) ion was progressively introduced, the current response of MWCNT-IIP/Pb/PE exhibited an increase. A linear calibration curve was established for Pb(II) ion, achieving a detection limit of $2 \times 10^{-2} \mu\text{M}$, accompanied by a correlation coefficient of 0.9987. The findings demonstrate that the engineered MWCNTIIP enhanced electrochemical sensor is capable of identifying Pb(II) ions at remarkably low concentrations.

**Fig. 4.1.12.** DPV runs of different concentrations of Pb(II) ion solution in ABS (pH-5.0), inset plot represents peak current as a function of Pb(II) ion concentration ranging from 1 to 5ppm

4.1.6. Sensing of Pb(II) ion by MWCNT-IIP/Pb/PE in real samples

An evaluation was conducted on the effectiveness of the established system for detecting Pb(II) ion levels in mining wastewater, aquatic environments, food products, and cosmetic items. The findings presented in Table 4.1.2 indicate that the innovative method can be employed for the direct analysis of actual samples utilising this straightforward modified electrode.

Table 4.1.2 Summary of the electrochemical sensing of Pb(II) ions in real samples

Modified electrodes	Real Samples	Found (ppm)	Detected (ppm)	Detected (%)
MWCNT-IIP/Pb/PE	Mining effluent	5.00	4.96 ± 0.002	99.20 ± 0.003
	Lake water	4.30	4.28 ± 0.004	99.50 ± 0.001
	Food	0.57	0.56 ± 0.001	99.10 ± 0.002
	Cosmetics	0.25	0.24 ± 0.003	99.20 ± 0.001

MWCNT-NIP/Pb/PE	Mining effluent	5.00	3.20 ± 0.001	64.00 ± 0.003
	Lake water	4.30	2.90 ± 0.004	67.40 ± 0.001
	Food	0.57	0.36 ± 0.002	63.10 ± 0.004
	Cosmetics	0.25	0.16 ± 0.001	64.00 ± 0.002

5. Discussion

The incorporation of multi-walled carbon nanotubes (MWCNTs) into the ion-imprinted polymer matrix significantly improved both the electrochemical and adsorption performance of the material. This enhancement can be attributed to the increased surface area, improved electron conductivity, and mechanical robustness introduced by the nanotube backbone [18, 19]. The dispersion study clearly illustrated that pristine MWCNTs tend to agglomerate in aqueous environments, but once functionalized with vinyl groups and layered with the IIP matrix, their hydrophilicity improved markedly [20]. The successful grafting of the IIP onto MWCNTs also created a more accessible porous network, enabling better interaction with Pb(II) ions. These modifications not only improved the uniform distribution of the polymer on the nanotube surface but also enhanced the number of effective binding sites available for selective ion uptake and redox interactions [21].

Characterization results provided solid evidence for the successful functionalization and imprinting processes. FTIR spectra confirmed the incorporation of vinyl and amide functionalities, indicating copolymerization of the monomers onto the functionalized MWCNTs [22]. SEM and TEM images further supported the structural transformation, showing a clear coating of the polymer layer on the nanotubes and an increase in the overall diameter after polymerization. EDAX analysis demonstrated the presence and complete removal of Pb(II) from the imprinted material, confirming the effectiveness of the Soxhlet extraction [23]. TGA results showed enhanced thermal stability of the MWCNT-IIP composite compared to the bare IIP, suggesting a stabilizing effect of the MWCNT core. Together, these results validate the successful fabrication of a robust, functional nanocomposite for selective Pb(II) ion recognition [24].

The electrochemical behavior of the MWCNT-IIP modified electrode revealed a strong, specific, and sensitive response toward Pb(II) ions. Among all tested electrodes, only MWCNT-IIP/Pb/PE exhibited a clear and reproducible redox peak in the cyclic voltammetry studies, while non-imprinted and control systems showed negligible or no signals [25]. The electrode displayed a detection limit as low as $2 \times 10^{-2} \mu\text{M}$, with a high correlation coefficient in the calibration curve ($R^2 = 0.9987$), indicating both accuracy and linearity across the tested concentration range [26]. The redox peak current showed direct dependence on both ion concentration and scan rate, affirming an adsorption-controlled mechanism. Notably, the sensor demonstrated optimal performance at pH 5.0, where Pb(II) exists predominantly in its free ionic form [27]. The electrode's selectivity was confirmed through interference studies with Cd(II), Zn(II), and Fe(II), showing minimal response to other ions, proving the high specificity of the imprinted cavities toward Pb(II) [28].

A vital outcome of this study is the real-world applicability of the MWCNT-IIP sensor system. When tested with real samples — including mining effluent, lake water, food products, and cosmetics — the modified electrode delivered high accuracy and recovery rates exceeding 99%. In contrast, the non-imprinted polymer system underperformed significantly, confirming the critical role of imprinting in target ion recognition. These results establish the MWCNT-IIP nanocomposite not only as a laboratory tool but as a practical solution for field deployment in environmental monitoring, especially in scenarios requiring rapid, portable, and low-cost detection methods. The dual functionality as both a sensor and adsorbent also offers promise for remediation, making this system a viable component of integrated water purification technologies.

6. Conclusion

This study successfully demonstrates the synthesis and application of a novel MWCNT-based ion-imprinted polymer

(MWCNT-IIP) as a highly selective and sensitive system for the detection and adsorption of Pb(II) ions. By integrating vinyl-functionalized MWCNTs with an imprinted polymer matrix, the resulting nanocomposite displayed excellent dispersion, thermal stability, and electrochemical performance. The material showed strong selectivity toward Pb(II) ions, with a low detection limit, high sensitivity, and exceptional recovery in real samples. These results confirm the potential of MWCNT-IIP as a dual-function material for real-time sensing and environmental remediation of lead contamination. The scalable synthesis and environmentally friendly approach further support its promise for widespread use in water quality monitoring and purification.

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