



ADVANCED NANO-SORBENTS FOR HEAVY METAL ION REMOVAL IN CONTAMINATED WATER: A NANOTECHNOLOGY BASED SOLUTION

¹Mr. Vikas Nain, ²Dr. Ranjeet Kaur

¹Research Scholar, ²Supervisor (Assistant Professor)

¹⁻²Department of Chemistry, IEC School of Basic & Applied Sciences, IEC University, Baddi, (HP), India

Abstract

High levels of heavy metals in water, specifically, zinc (Zn^{2+}) are of great environmental and health concern, because standard purification procedures are often not effective at low concentrations. This study discusses a novel approach that uses multiwalled carbon nanotube-derived ion imprinted polymer (MWCNT-IIPs) to accomplish a specific task of selectively removing Zn ions of polluted water resources. Generation Acid- functionalised MWCNTs Productability MWCNTs functionalised by acrylic acid and zinc salt were polymerised and used as the template. The polymerisation process produced a nanocomposite with a high adsorption capacity and a high selectivity to the Zn^{2+} ions. MWCNT-IIPs were synthesised and characterised using Fourier-transform infrared spectroscopy (FT-IR), scanning electron (SEM), transmission electron (TEM), and energy dispersive X-ray (EDAX), thus confirming successful synthesis of the polymer and Zn^{2+} ion imprintation. Studies into adsorption showed that MWCNT-IIPs were highly effective in the extraction of Zn^{2+} ions with the highest adsorption variables and values at a concentration of 5 ppm. The kinetics study found that the adsorption followed pseudo-second-order kinetics, however, the adsorption data also resulted in the best fit to the Langmuir isotherm. Moreover, the electrochemical detection of the Zn^{2+} ions on the electrodes that have been modified by MWCNT-IIP was simply amazing in its sensitivity and specificity. The experimental appraisal of actual samples showed a remarkable desire to remove Zn^{2+} in industrial wastewater of the amount of 99.60, which demonstrates the constructive effectiveness of MWCNT-IIPs. By combining unprecedented selectivity, large capacity, reusability, and high-level electrochemical detection characteristics, MWCNT-IIPs promise to be a very promising solution to the challenge of the heavy metals pollution problem in water.

Keywords: Zinc, Heavy metals, Ion-imprinted polymers, MWCNT, Adsorption, Electrochemical sensing, Water purification, Nanotechnology

1. Introduction

Integration of heavy metals in aquatic ecosystems has become a growing environmental challenge across the world with many factors contributing to the problem rendering such industrial activities, mining activities and agricultural activities as the major contributors of the problem. Amid the vast number of these pollutants, heavy metals such as zinc (Zn^{2+}), lead (Pb^{2+}), mercury (Hg^{2+}), cadmium (Cd^{2+}), among others pose a high risk to human health and the environment by the fact that they are highly toxic chemicals. The existence of the heavy metal pollutants is threatening because they are persistent since the metals are non-degradable and may stay in the bodies of the living organisms [1]. The build up would lead to adverse effects, including severity to vital organs, cancer, and developmental difficulties among both human beings and wildlife. Hypothetically, zinc, which is an industrial wastewater pollutant, can cause many health complications including impaired renal functioning, respiratory problems and skin irritation in case it is available in large concentration in drinking water. It has, therefore, turned into the order of the day to address the issue of heavy metals pollution to ensure the protection of the health of the population and environmental sustainability. The traditional methods that are used in extracting the heavy metals such as precipitation, adsorption, filtration and the ion exchange are very often ineffective in extracting the low quantities of the heavy metals and most especially when any other ions or complex matrices are in the contaminated water body [2]. However, it is possible that even though using substances like activated carbon and clays, which can be adsorbed use, may be of usefulness, some results are always disadvantaged in application in terms of selectivity, loading capacity classes, and the potential to be recycled. Moreover, the high costs and inefficiency of these methods in the work under real-life conditions indicates the importance of advanced and more effective methods of purifying water.

The past years have witnessed the emergence of nanotechnology as a promising area of addressing numerous environmental issues particularly through the use of nano-sorbents which can take hold of malicious metalions in



water bodies selectively [3]. Due to their outstanding physical and chemical properties, such as a large surface area, surface functionalities sought after through adjustment, and easy functionalisation, nanomaterials have shown a level of promise in the removal of heavy metal ions. Among the various types of nanomaterials, nanomaterials based on carbon, i.e. multiwalled carbon nanotubes (MWCNTs) have been of significant complexity, due to their large surface area, excellent conductivity, and strong structural design suitability [4]. One of the most radical approaches towards the production of very selective sorbents is the use of ion-imprinted polymers (IIPs). IIPs are synthetic polymers that are engineered, and are unique in the sense of their cavities that are available during the polymerisation process. These cavities have been made to suit the size, shape, and frailty sets of an individual target ion, and the exact and successful removal of a target ion. IIPs have been successfully used to remove various metal ionic concentrations but their use in regard to zinc (Zn^{2+}) ionic concentrations has been somewhat limited. The use of MWCNTs as the basis of ion-imprinted polymerisation can help in enhancing the structural stability, durability and adsorption capacity of the sorbent substantially, which makes the sorbent an ideal way of creating the next generation materials that can be utilized to purify water.

This paper explores the insight of the synthesis and characterisation of Zn (ii)-imprinted polymers (IIPs) functionalised onto the surfaces of the multi-walled carbon nanotubes (MWCNTs), their adsorption properties, selectivity and electrochemical sensing capabilities. This study also evaluates the potential of using this nanocomposite in the effective extraction of Zn(II) ions in contaminated water bodies. The study tries to develop a sorbent with the properties of nanostructural properties and have dedicated ion recognition sites attached on to it in an attempt to introduce an accurate and effective strategy in the treatment of heavy metal pollution of water. Moreover, the research of electrochemical detection of Zn(II) ions is done to research on the effectiveness of the material in the real practices, including wastewater treatment and environmental monitoring.

2. Literature Review

2.1 Heavy Metal Contamination in Water and Its Environmental Impact

Pollution of the water bodies with metals cannot be mentioned and rated as the most urgent environmental problem in the world, because in most areas which have become industrialized the water bodies or the aquatic environments are in most cases a dumping point of the factory wastes. These metals are zinc (Zn^{2+}) lead (Pb^{2+}), mercury (Hg^{2+}), and cadmium (Cd^{2+}) and have very long lifespan with a very high toxicity to natural degradation indicating long term stay by the metals in the environment. Elements of the heavy metals may get into the water bodies in different forms as part of mining activities, industrial effluents, agricultural runs, and even poor waste management activities [1]. Zinc is the example of a product that can be quite prevalent in the effluent of the metal plating process; as well as, battery manufacture, or agricultural drainage. In a biological system although present, in low concentrations, Zn^{2+} may result into serious health disorder including abnormal skeletal structure, lack of immune response, and kidney malfunction in man and animals when it appears in large amounts [2]. What is even more is that the metals are able to build up in the aquatic organisms, thus causing a derailment within their ecosystem and may even end up in the human food chain. The conventional procedures of dealing with the issue of metal pollution like precipitation, ion exchange, and filtration process usually encounter the challenge of extracting the metals in the water, particularly at the low concentrations [3]. The necessity to possess high, specific, and green technologies and the ability of nan-technology has led to increased technological advancement, which provides excellent adsorption properties in latex heavy metal ions removal [4].

2.2 Traditional and Emerging Water Treatment Technologies

The typical techniques such as precipitation are usually limited by factors that must encompass: the inability to extract metal ions at minimal low concentrations, high expense of reagents and secondary wastes. As an example, in the chemical precipitation process, some very high volumes of samples are needed to result in the isolation of insoluble particles that may be later sucked into the water by them [5]. Nevertheless, they tend not to work well with trace level amounts and removing of heavy metals may also be inadequate and even ecological risks of the sludge left behind. Alternatively, ion exchange and adsorption have become more effective however their high levels of operation besides of its limited capacity has been very deterrent [6]. These drawbacks have made it clear that nanotechnology based solution has become some of the potential solutions to water treatment. Nanocomposites, nanoparticles, and nanotubes are amongst the nanomaterials having important benefits due to their high reactivity because of their large surface area, high reactivity, and control over the targeting of surfaces [7]. The carbon-based ones with the carbon nanotube (CNTs) in particular has been a central subject in the new research due to the high-



mechanical strengths and the extraordinary chemical stability coupled with the adsorption properties. The surface area of carbon nanotubes is very high with immense flexibility with broad properties of various chemical uses in usage and hence its choice amidst numerous choices in their usage is limitless and diverse e.g. harvested to remove heavy metals in polluted water sources [8].

2.3 Ion-Imprinted Polymers (IIPs) for Metal Ion Removal

The track of the changing technology is the ion-imprinted polymers (IIPs), which has become a potential treatment of the selective extraction of the heavy metal ions using an aqueous solution. IIPs are complicated polymers which get elaborated by addition of a particular metal ion (the template), which causes the formation of definite punches in the polymer structure and these are wooden designed in terms of area, form as well as charge to suit exclusively the designated metal ion [9]. Ultimately, these cavities explain why it is likely that the IIPs can be so selective and able to select and bind with the target metal ions in more complex mixtures. Their extraction of various metal ions of Pb^{2+} , Cu^{2+} , Cd^{2+} and Zn^{2+} has been studied extensively using IIPs and promising results have been obtained in both laboratory and real life QIS. The recent times have also involved innovations that have seen the introduction of IIPs using carbon nanotubes (CNTs) to increase the efficiency of the mentioned substances in extracting the heavy metal ions [10]. The multiwalled carbon nanotubes (MWCNTs) are uniquely superior due to the successful straightening of the area of the near the surface to be serviced, an un-akinness functionalisation, but still striking mechanical action that enables it to be awarded aptly a substrate to imprinted polymers (IIPs). MWCNTs will serve as a universal platform of IIPs that will yield superior adsorption propensities and kinetics, as opposed to conventional adsorbents [11]. It has been discovered that MWCNT-IIPs are amazingly selective towards individual metal ions, and may be utilized repeatedly with the only small loss of performance. Nanostructured multi-walled carbon nanotube + ion- imprinted polymer gives elicitation of a synergonic effect resulting in an incredibly efficient and economical activity of leeching the heavy metal ions in water.

2.4 Electrochemical Sensing of Heavy Metals Using Nanocomposites

Besides the conventional approaches of adsorption, electrochemical sensing communication initiatives have gained critical value in monitoring and detection of heavy metal ions in the environment in sample. The electrochemical sensors are linked with a number of positive issues like high sensitivity, specificity and a very high rate of response. Cyclic voltammetry (CV) and difference pulse voltammetry (DPV) are recent examples of the many types of electrochemical reaction that have gained popularity in electrochemical methods of metal ions determination [12]. Even the traces of the heavy metals can be detected with the help of the mentioned techniques that allow observing the redox dynamics of the heavy metals and this is highly important concerning the issue of environmental surveillance. Attachment of imprinted polymers onto the electrochemical sensing platforms by a large extent boosts the selectivity of the sensor in identifying a particular metal ion. The latter is achieved due to the existence of cavities of the IIPs, which helps them to capture and focus the desirable ions [13]. The multi-walled carbon nanotubes (MWCNTs) have been integrated with ionic imprinted polymers (IIPs) within in the past few years to enhance the aspects of the electrode material used to create highly sensitive and selective zinc ions ($Zn(II)$) sensor besides a variety of other heavy metal ions. These sensors have demonstrated outstanding colors in the actual world application particularly to identify the existence of $Zn(II)$ in industrial wastewater which is not only a highly selective sensor, but also a very vigorous one, in terms of detectivity [14]. The electrochemical working capabilities of such MWCNT-IIP-improved electrodes under varying conditions have been examined proving the capability to determine $Zn(II)$ ions at low detection limits suitable making it an efficient electrochemical analyzer as an alternative to monitor and test polluted water bodies by lead and other chemicals.

2.5 Real-World Applications of Nano-Sorbents in Heavy Metal Ion Removal

Recent researches that have been carried out have revealed tremendous potentials in the application of the nano-sorbents as the extraction reagent of heavy metals in industrial effluents and also in contaminated water catchments. Operation performance MWCNT-IIPs prove to be able to extract metal ion of $Zn(II)$, $Pb(II)$, $Cu(II)$ and $Cd(II)$ in mixtures of mixtures of ions as far as water samples contaminated with mixtures of ion are concerned. Their ease of selectivity by the metal ions of MWCNT-IIPs renders them to be advantageous in destroying these metal ions despite the existence of the other competent ones individually and with the wastewater treatment, this is a very great challenge. As an example, it was shown that MWCNT-IIPs are applicable in the recovery of $Zn(II)$ ions in wastewater by paint industry had a high recovery rate of 99.60. This makes clear their practical use in a real life scenario, that is, in the treatment of real industrial effluents [15]. It is interesting that these nano-sorbents could be employed to

appear in the harsh real life situations as a testimony to the fact that these nano-sorbents would be employed in the large scale applications in the water purification industry and also contamination of the environment. The ability to reuse MWCNT-IIPs is also a significant contribution to the cost-reduction of the operations. The impending result along with the endurance of raising these sorbents makes them large prospects to the employment in water purification techniques in the context of ecological encompassment. With the global population and strain up on clean water, we may revamp our modes of cleaning up the environment and manage the industrial wastes with the excellent nanomaterials.

Current investigations allowing the innovation of advanced nano-sorbents like MWCNT-IIPs can also be regarded as an effective breakthrough on the arena of reclaiming polluted water sources on heavy metal ions. Such material will be very useful in environmental clean up since it is a combination of selectivity, capacity, reusability, and electrochemical sensors. With improved optimisation and practice in real world scenario, these innovations will go a long way in developing sustainability and water treatment process in the world.

3. Methods and Materials

3.1 Materials

- **Multiwalled Carbon Nanotubes (MWCNTs):** Purchased from [Supplier Name].
- **Vinyl-functionalized MWCNTs (MWCNT-CH=CH₂):** Prepared by treating MWCNTs with concentrated nitric acid followed by vinyl group incorporation.
- **Acrylic Acid:** Used as the monomer for polymerization.
- **Zinc Salt (Zn(NO₃)₂):** Used as the template metal ion for the synthesis of ion-imprinted polymers.
- **NNMBA (N,N'-Methylenebisacrylamide):** Used as the crosslinking agent for the polymerization.
- **AIBN (Azobisisobutyronitrile):** Radical initiator for the polymerization reaction.
- **Solvents:** Deionized water was used for the polymerization process.

3.2 Preparation of Ion-Imprinted Polymers (IIPs)

- **Step 1:** Preparation of vinyl-functionalized MWCNTs
 - MWCNTs were treated with concentrated nitric acid to introduce **carboxyl groups**, followed by conversion to **acid chlorides** to allow for vinyl group incorporation.
 - The extent of carboxylation was confirmed by **alkali titration**, yielding a carboxyl content of **1.987 mmol/g**.
 - Vinyl groups were incorporated on the MWCNT surface by reaction with **vinyl-functionalized groups**.
- **Step 2:** Synthesis of Zn(II)-ion imprinted polymers (IIPs)
 - A mixture of **vinyl-functionalized MWCNTs (MWCNT-CH=CH₂)**, **acrylic acid**, **zinc salt (Zn(NO₃)₂)**, and **NNMBA** was prepared in water.
 - The mixture was stirred and then treated with **AIBN** as the radical initiator.
 - The reaction was carried out at **70°C** for 5 hours to allow the polymerization to occur.
 - After polymerization, the resulting **Zn(II) IIPs** were collected by **centrifugation** and washed

multiple times to remove any unreacted monomers and crosslinkers.

- The polymer was dried in a **vacuum desiccator** for **24 hours** to obtain the final **Zn(II)-imprinted polymer (MWCNT-IIP)**.
- **Step 3: Preparation of Non-Imprinted Polymers (NIPs)**
 - Non-imprinted polymers (NIPs) were synthesized following the same procedure as the IIPs, but without the inclusion of the **Zn(II) template**.
 - This allowed for the preparation of **MWCNT-NIP** and **bulk NIP** (without MWCNTs) for comparative studies.

3.3 Characterization Techniques

- **Fourier Transform Infrared Spectroscopy (FT-IR):**
 - The chemical structure and functional groups of **MWCNTs**, **MWCNT-CH=CH₂**, and **MWCNT-IIPs** were analyzed using **FT-IR** spectroscopy.
 - FT-IR spectra were recorded in the range of **4000-400 cm⁻¹** to identify the characteristic functional groups, such as **C=C** and **C=O** bonds in the vinyl functionalized MWCNTs, and the **O-H stretching** from acrylic acid.
- **Scanning Electron Microscopy (SEM):**
 - The morphology and surface characteristics of **MWCNT-IIPs** and **bulk IIPs** were examined using **SEM**.
 - SEM images were captured at different magnifications to observe the structural differences and the impact of MWCNT incorporation on the **rigidity** and **texture** of the polymer matrix.
- **Transmission Electron Microscopy (TEM):**
 - High-resolution **TEM** was used to observe the internal morphology and coating of the **polymer** on the surface of **MWCNTs**.
 - TEM images confirmed the presence of the polymer coating on the MWCNTs and the tubular structure of the pristine MWCNTs.
- **Energy Dispersive X-ray Analysis (EDAX):**
 - **EDAX** was performed to confirm the **binding of Zn(II) ions** in **MWCNT-IIPs** and to track the desorption process of the metal ion during the extraction phase.
 - The presence of a strong **Zn(II)** peak in the **bound polymer** and its absence in the **desorbed polymer** confirmed the successful imprinted ion capture.
- **Thermogravimetric Analysis (TGA):**
 - **TGA** was used to analyze the **thermal stability** of **MWCNTs**, **MWCNT-IIPs**, and **IIPs**.
 - The TGA curves provided information on the **degradation temperature** and **thermal stability** of the materials, with **MWCNT-IIPs** showing improved thermal stability compared to bulk IIPs.

3.4 Dispersion Study



- The **dispersion** behavior of **MWCNTs**, **MWCNT-CH=CH₂**, and **MWCNT-IIPs** in water was evaluated.
 - Samples were mixed with deionized water and sonicated for **1 hour**, then allowed to settle for **24 hours**.
 - The dispersion efficiency of **MWCNT-IIP** was compared to that of **MWCNTs** and **MWCNT-CH=CH₂**. **MWCNT-IIP** showed the best **dispersion** in water, indicating enhanced interaction with the aqueous medium due to the polymerization process.

3.5 Swelling Study

- The **swelling behavior** of all the prepared sorbents in **water** was measured by determining the **equilibrium water content (EWC)**.
 - The swelling tests were conducted by immersing the sorbents in water and measuring the increase in weight after reaching equilibrium.
 - The **EWC (%)** values were compared for **MWCNT-IIP**, **IIP**, **MWCNT-NIP**, and **NIP**, revealing that **MWCNT-IIP** exhibited the highest swelling due to the presence of imprinted sites and the porous structure of **MWCNTs**.

3.6 Electrochemical Sensing of Zn(II) Ions

- **Cyclic Voltammetry (CV)** was employed to study the **electrochemical behavior** of **MWCNT-IIP/Zn/PE** modified electrodes.
 - The electrode was modified by coating it with the **MWCNT-IIP** material to test its **sensitivity** to **Zn(II) ions**.
 - The electrochemical measurements were conducted in **acetate buffer solution (ABS)**, and the redox peaks were analyzed to determine the **concentration dependence** of **Zn(II)** ion detection.

3.7 Adsorption Studies

- **Effect of Zn(II) Ion Concentration:** The adsorption capacity of **MWCNT-IIPs**, **IIPs**, **MWCNT-NIPs**, and **NIPs** was studied by varying the concentration of **Zn(II) ions** in solution (1-5 ppm).
 - The results helped to determine the **adsorption isotherms** and identify the optimal concentration for **maximum adsorption**.
- **Kinetic Study:** Adsorption kinetics were studied by measuring the **rate of Zn(II) ion binding** over time (up to **90 minutes**).
 - The **pseudo-second-order kinetics model** was applied to fit the adsorption data.
- **Effect of pH:** The influence of **pH** on **Zn(II)** ion binding by the sorbents was studied by adjusting the pH of the solution from **4 to 7**.
- **Effect of Adsorbent Dosage:** Various amounts of the sorbents (from **10 to 50 mg**) were tested to investigate the effect of **adsorbent dosage** on **Zn(II)** ion removal.
- **Effect of Binding Medium:** Different solvents, including **water**, **DMSO**, and **THF**, were tested to determine the best medium for **Zn(II) ion adsorption**.

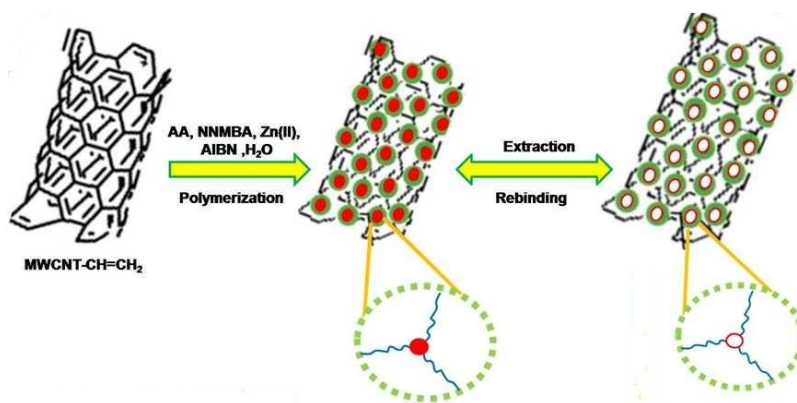
3.8 Real Sample Testing

- The efficiency of the **MWCNT-IIP** sorbent was tested for **Zn(II) ion removal** from **real industrial wastewater**, such as from the **paint industry**.
 - The **Zn(II) concentration** in the sample was measured using **atomic absorption spectroscopy (AAS)** before and after the adsorption process to determine the removal efficiency.

4. Results and Discussion

4.1 Synthesis of Zn(II) ion imprinted and non-imprinted polymers

To create a Zn(II) ion imprinted polymer on the MWCNT surface, a specific molar quantity of vinyl group-modified MWCNT, acrylic acid, zinc salt, and NNMBA were combined in water and agitated thoroughly. The initiator AIBN was incorporated and subjected to heating at 70°C while being stirred. The polymer that was generated was gathered through centrifugation and thoroughly rinsed multiple times to eliminate any unreacted elements from the polymerisation mixture. The resulting polymer underwent vacuum drying for a duration of 24 hours. In the assessment, a sorbent devoid of the template Zn(II) ion was additionally synthesised. To assess the importance of MWCNTs, sorbents lacking MWCNTs were also produced (IIP and NIP).



Scheme 4.1. Schematic representation of the synthesis of zinc ion imprinted polymer

4.2 Characterization techniques

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

Presented in Fig. 4.1 are the FT-IR spectra for MWCNTs, MWCNT-CH=CH₂, and MWCNT-IIP. For MWCNT-CH=CH₂, novel peaks emerged at 1635 cm⁻¹ and 1300 cm⁻¹, attributed to the presence of C=O and C=C groups resulting from vinyl functionalisation. The extensive peak observed at 3300 cm⁻¹ signifies the presence of the O-H group in acrylic acid. All the FT-IR findings corroborate the creation of MWCNT-CH=CH₂ and MWCNT-IIP.

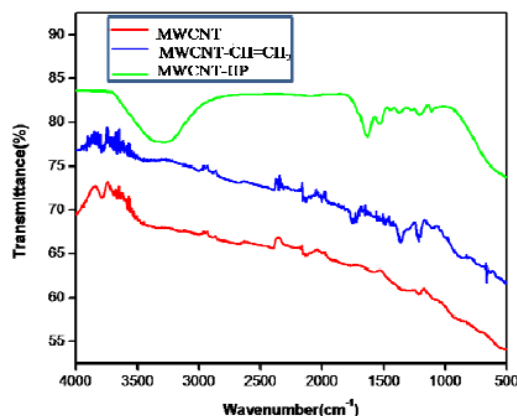


Fig. 4.1. FT-IR spectra of MWCNT, MWCNT-CH=CH₂ and MWCNT-IIP

(B) Scanning electron microscopy (SEM)

The morphological distinctions between MWCNT-IIP and IIP were examined utilising a scanning electron microscope (Fig. 4.2). The MWCNT-IIP exhibited a greater rigidity compared to the bulk IIP, attributed to the incorporation of MWCNTs within the imprinted polymer matrix.

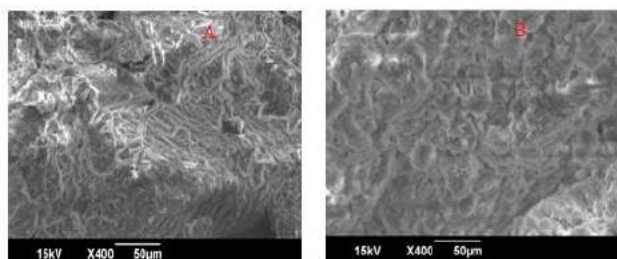


Fig. 4.2. SEM images of (A) MWCNT-IIP, and (B) IIP

(C) Transmission electron microscopy (TEM)

The detailed morphological examination of the different imprinted systems was conducted using HR-TEM (Fig. 4.3). The TEM images distinctly reveal that the unaltered MWCNTs exhibit slender tubular formations characterised by minimal diameters. A layer was established on the exterior of vinyl functionalised MWCNTs in the scenario of MWCNT-IIP.

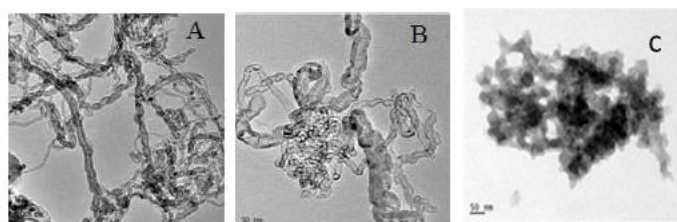


Fig. 4.3. TEM images of (A) MWCNTs, (B) MWCNT-CH=CH₂ and (C) MWCNT-IIP

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

The presence and elimination of Zn(II) ions within the ion imprinted polymers were validated through energy dispersive X-ray analysis (see Fig. 4.4). A distinct and precise signal is observed in the Zn(II) ion associated with MWCNT-IIP. However, in the polymers from which Zn(II) ions have been desorbed, this peak is not present. The findings validate the creation of polymers imprinted with Zn(II) ions

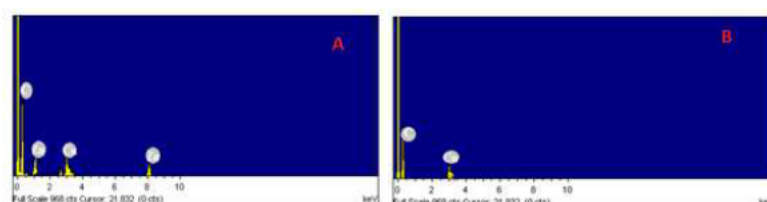


Fig. 4.4. EDAX spectra of Zn (II) ion (A) bound, and (B) desorbed polymers

Thermogravimetric analysis (TGA)

Thermogravimetric assessments were performed to investigate the thermal stability characteristics of MWCNT, IIP,

and the composite MWCNT-IIP (refer to Fig. 4.5). The TG curve of MWCNT displays a straight-line graph up to 800°C, showing no mass reduction. The findings demonstrate the exceptional thermal stability of MWCNTs. The thermal degradation temperature of MWCNT-IIP surpassed that of IIP. The elevated thermal stability of MWCNT-IIP suggests that the nanostructures possess the ability to protect the materials from rapid degradation.

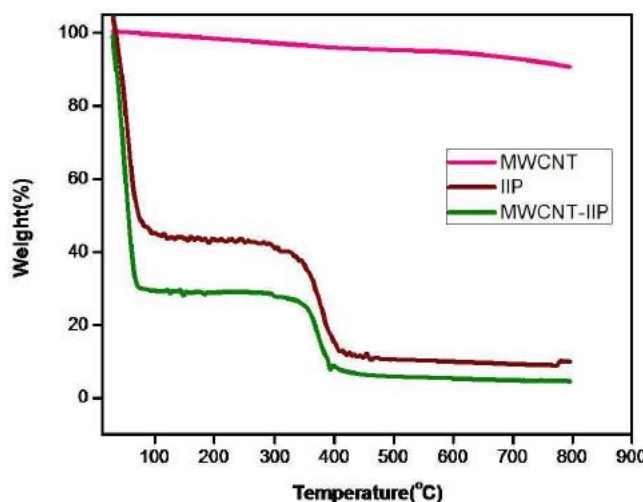


Fig. 4.5. TG curves of MWCNT, IIP, and MWCNT-IIP

4.3 Dispersion test

The distribution of MWCNTs, MWCNT-CH=CH₂, and MWCNT-IIP in water was examined (Fig. 4.6). The test specimens were combined with water and subjected to sonication for one hour, then left undisturbed for a full day. MWCNTs completely settled after a duration of one day. With the incorporation of vinyl groups, the MWCNT exhibits enhanced compatibility with water and demonstrates a noticeable reduction. However, during the polymerisation process involving acrylic acid and NNMB, the system exhibits a significant degree of dispersion within the aqueous medium. Consequently, the alteration of MWCNTs enhances their capacity to interact with water-based environments.

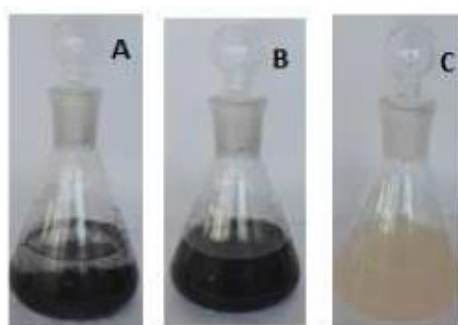


Fig.4.6. Dispersion images of (A) MWCNT, (B) MWCNT-CH=CH₂, and (C) MWCNT-IIP

4.4 Swelling study

The examination of the swelling characteristics of all the synthesised sorbents was conducted using water, as detailed in Table 4.1. The analysis reveals that MWCNT-IIP exhibits significant swelling behaviour attributed to the presence of imprinted sites in conjunction with the porous nanostructure of MWCNTs. Water molecules become ensnared within these locations, which enhances the equilibrium water content. However, the outcomes for non-imprinted polymers were insufficient because of the lack of nanostructure. The overarching pattern observed in the swelling

behaviour of the sorbents is as follows: MWCNT-IIP surpasses IIP, which in turn exceeds MWCNT-NIP, followed by NIP.

Table. 4.1 Swelling studies of various zinc ion imprinted non-imprinted polymers

Polymers	EWC (%)
MWCNT-IIP	98.99
IIP	81.23
MWCNT-NIP	72.54
NIP	62.31

4.5. Sensing of Zn(II) ions by MWCNT-IIP modified platinum electrode

(A) Electrochemical sensing of Zn(II) ion by cyclic voltammetry

Cyclic voltammetry serves as a distinguished method for detecting Zn(II) ions in ABS. In order to draw a comparison, every synthesised sorbent system was employed for the modification of electrodes. Figure 4.7 demonstrates that the MWCNT-IIP/Zn/PE displays superior sensing characteristics, as evidenced by the graph revealing a pronounced redox peak. However, MWCNT-NIP/Zn/PE, IIP/Zn/PE, and NIP/Zn/PE failed to exhibit any electrochemical response, which restricts the ability to detect Zn(II) ions using the MWCNT-IIP modified electrode. The electrodes that were altered with various polymers failed to enhance the interaction efficiency of the platinum electrode, and as a result, they do not demonstrate any electrochemical characteristics. Owing to its inadequate electrochemical reaction, additional investigations were conducted solely with MWCNT-IIP/Zn/PE.

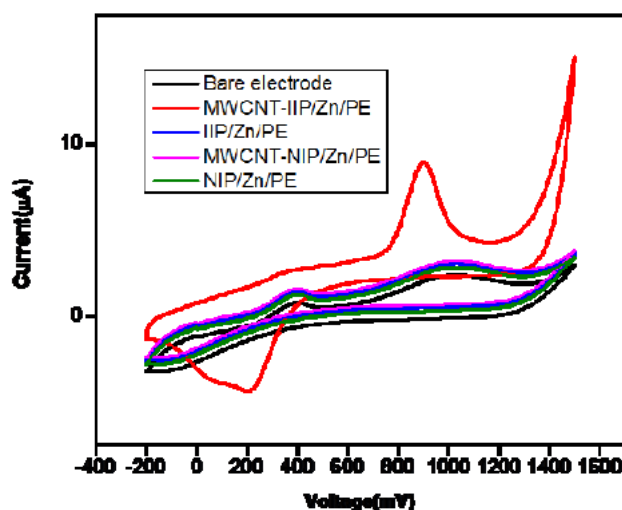


Figure 4.7. CV runs of bare and modified electrodes

(B) Effect of Zn(II) ion concentration

The dependence of concentration on the electrochemical response of MWCNT-IIP/Zn/PE was evaluated using a Zn(II) ion solution with concentrations varying from 1 to 5 ppm, as illustrated in Fig. 4.8. The magnitude of the redox peak amplifies as the concentration of Zn(II) ions rises, attaining its peak at 5ppm. Consequently, the ideal concentration for the electrochemical assessment was determined to be 5ppm. The examination was conducted in ABS at a pH of 6.0 with a scanning velocity of 100 mV/s.

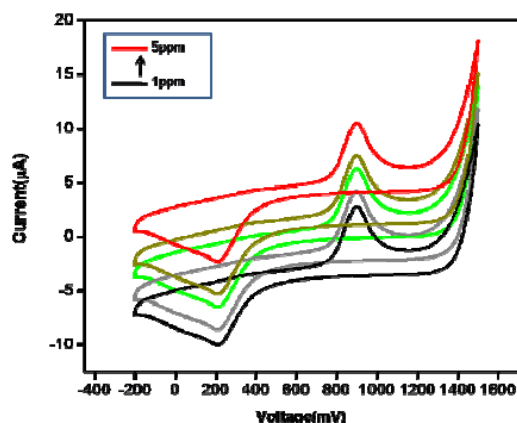


Figure 4.8. CV runs of MWCNT-IIP/Zn/PE with different concentrations of Zn(II) ions

(C) Effect of pH

The effect of pH on the detection of Zn(II) ions using MWCNT-IIP/Zn/PE was examined and fine-tuned to enhance its electrochemical efficiency. The chosen pH levels for the study span from 3 to 6 within ABS. The strength of the redox peak amplifies with rising pH levels, reaching its peak at 6.0 (refer to Fig. 4.9).

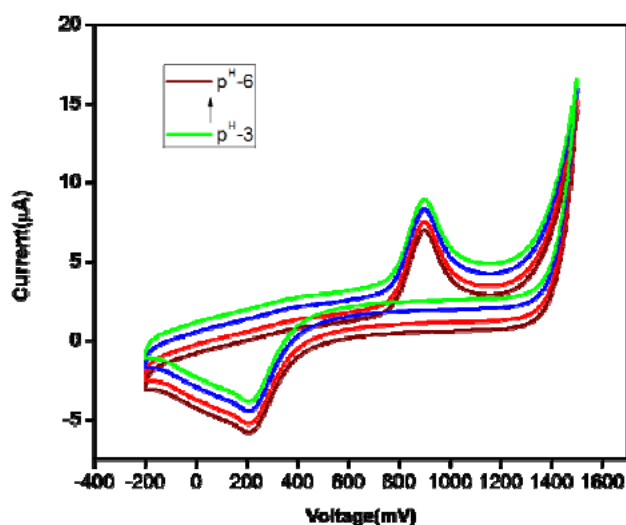


Fig. 4.9. Effect of pH on cyclic voltammogram of MWCNT-IIP/Zn/PE at different pH with a scan rate 100mV/s

(D) Effect of scan rate

The influence of scan rate on the electrochemical behaviour of the MWCNT-IIP/Zn/PE was examined using a Zn(II) ion solution at a concentration of 5 ppm and a pH of 6.0. The highest CV response was observed at a rate of 100mV/s. Consequently, the ideal scanning rate was determined to be 100mV/s (refer to Fig. 4.10). A steady rise in redox current is noted as the scan rate increases. The inset illustration depicts the correlation between the redox peak current and the square root of the scan rate.

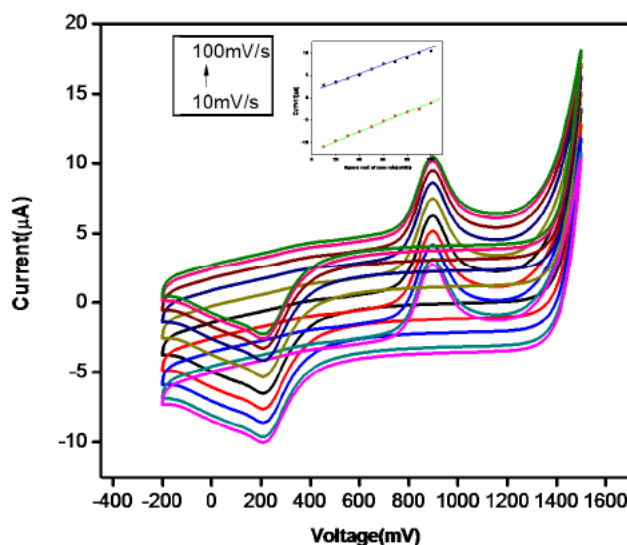


Fig. 4.10. Effect IIP/Zn/PE at pH 6.0 of scan rate on cyclic voltammogram of MWCNT-

(E) Selectivity study

In the investigation of the selectivity of MWCNT-IIP/Zn/PE for Zn(II) ions, various metals were chosen, and experiments were conducted under optimal conditions. Given that the binding locations of MWCNT-IIP on MWCNT-IIP/Zn/PE were specifically chosen for Zn(II) ions, a clearly defined redox peak was observed for zinc. Figure 4.11 demonstrates the specificity of MWCNT-IIP/Zn/PE in relation to the Zn(II) ion.

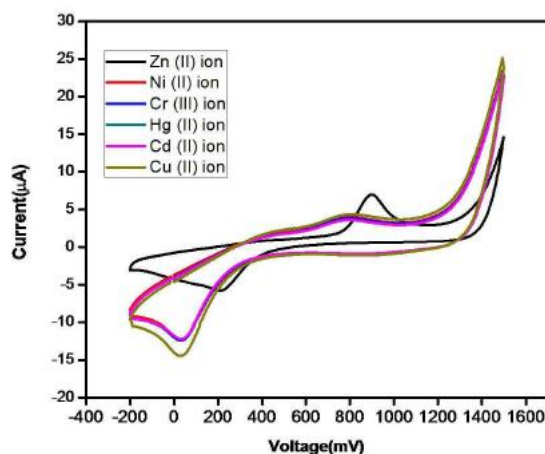


Fig. 4.11. Effect of selectivity of MWCNT-IIP/Zn/PE with different metal ions

(F) Differential pulse voltammetry

DPV was utilised to explore the detection threshold of the suggested modified electrode MWCNT-IIP/Zn/PE. The differential pulse voltammograms for MWCNT-IIP/Zn/PE at different concentrations of Zn(II) ions are depicted in Fig. 4.12. As the concentration of Zn(II) ions rises, there is a corresponding increase in the current response. Consequently, a linear graph was generated, from which the sensor's detection threshold was determined. A direct correlation between peak current and concentration reveals a detection threshold of $1.32 \times 10^{-4} \mu\text{M}$. The findings demonstrate the effectiveness of the sensor that has been developed.

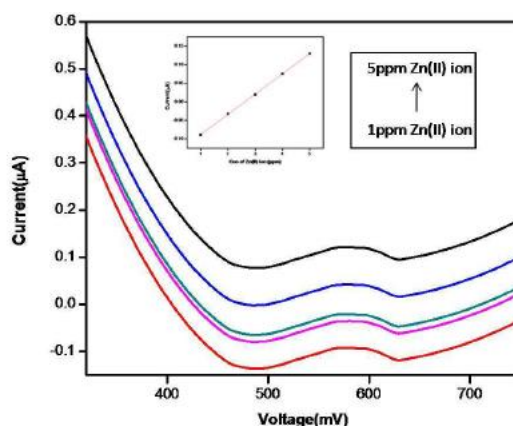


Fig.4.12. (A) DPV runs of different concentrations of Zn(II) metal ions, inset plot shows peak current as a function of Zn(II) ion concentration

4.6 Sensing of Zn(II) by MWCNT-IIP/Zn/PE in real samples

The performance of the electrochemical sensor designed for detecting Zn(II) ions was examined using wastewater sourced from the paint industry. The results acquired are presented in Table 4.2. The recovery rate achieved was an impressive 99.60% for MWCNT-IIP/Zn/PE, highlighting the effectiveness of the developed MWCNT-IIP/Zn/PE in relation to Zn(II) ions.

Table 4.2 Summary of sensing of Zn(II) ion in paint industry wastewater

Modified electrodes	Found (ppm)	Detected (ppm)	Detected (%)
MWCNT-IIP/Zn/PE	0.764	0.761± 0.002	99.60±0.001
MWCNT-NIP/Zn/PE	0.764	0.705±0.001	92.27±0.002

4.7 MWCNT-IIP as sorbent for Zn(II) ion extraction

4.7.1 Optimization of the conditions for adsorption study

(A) Effect of Zn(II) ion concentration

The adsorption capabilities of all synthesised sorbents (both imprinted and non-imprinted) were examined using different concentrations of Zn(II) ions ranging from 1 to 5 ppm, as illustrated in Fig. 4.13. The binding rate escalates with the concentration of the sorbent, peaking at 5ppm before subsequently declining. Similarly, MWCNT-IIP exhibits an enhanced affinity for Zn(II) ions, attributed to the presence of a Zn(II) ion imprinted polymer that is layered on the MWCNTs. This configuration provides a dual impact featuring engraved locations in conjunction with a nanostructured nucleus. The distinctive characteristics of nanostructures, such as their elevated surface-to-volume ratio, contribute to an enhanced binding rate. However, in the scenario of IIP developed through the bulk imprinting method, these nanostructures are not present, resulting in a diminished binding rate. For both MWCNT-NIP and bulk NIP, the imprinted sites are nonexistent, resulting in an extremely low binding rate. In terms of binding efficiency, the hierarchy of sorbents can be arranged as follows: MWCNT-IIP surpasses IIP, which in turn exceeds MWCNT-NIP, followed by NIP.

Due to the existence of unoccupied active binding sites within the imprinted polymer, the binding efficiency commenced at a notably elevated level, but abruptly the system attains a state of saturation. Figure 4.14 illustrates the Langmuir adsorption isotherm for MWCNT-IIP, while the inset displays the Freundlich adsorption isotherm. The analysis of the plot reveals that the adsorption process aligns closely with the Langmuir model, exhibiting a strong correlation coefficient.

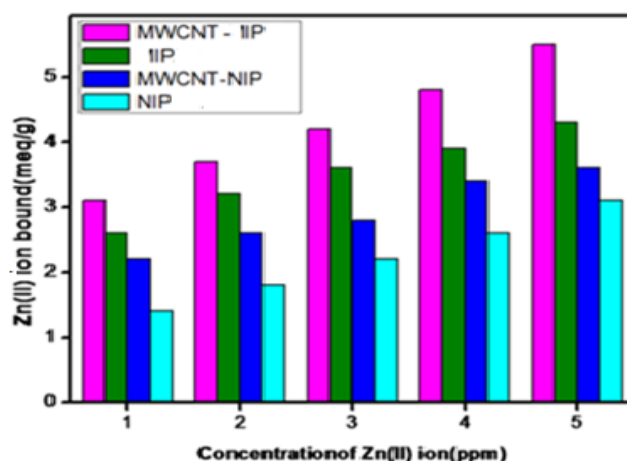


Fig. 4.13. Effect of concentration of Zn(II) ion binding by MWCNT-IIP, IIP, MWCNT-NIP and NIP

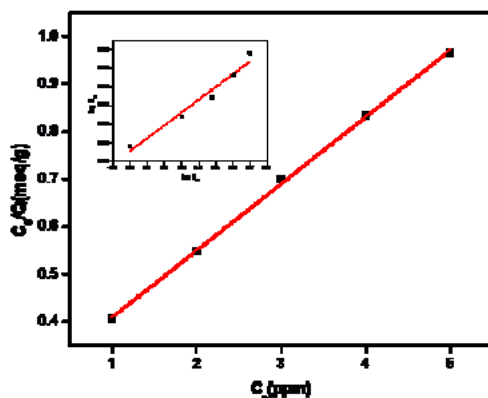


Fig.4.14. Langmuir isotherm of MWCNT-IIP; inset plot represents Freundlich isotherm of MWCNT-IIP

(B) Effect of time

The kinetic investigation monitored the binding rate over the course of time. The binding rate of Zn(II) ions across all sorbent systems, encompassing both imprinted and non-imprinted polymers, is depicted in Fig. 4.15. The binding rate demonstrates a direct correlation with time and reaches equilibrium after 90 minutes. The kinetic rate equations for MWCNT-IIP and IIP were examined and determined to follow pseudo-second order kinetics. The respective rate constants were found to be 0.7450 min^{-1} and 0.0312 min^{-1} , accompanied by correlation coefficients of 0.9988 and 0.9978.

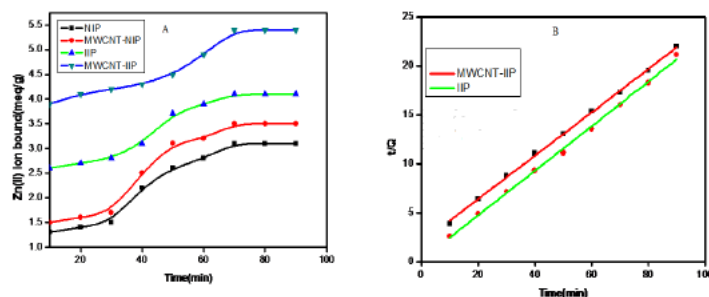


Fig. 4.15. (A) Effect of time on Zn(II) ion binding by MWCNT-IIP, IIP, MWCNT-NIP and NIP, (B)

Adsorption kinetics of MWCNT-IIP and IIP

(C) Effect of pH

The influence of pH levels ranging from 4 to 7 on the adsorption of Zn(II) ions by each of the sorbent systems was examined and depicted in Fig. 4.16. The binding rate of Zn(II) ions was observed to rise with increasing pH, reaching its peak at a value of 5.5 in ABS.

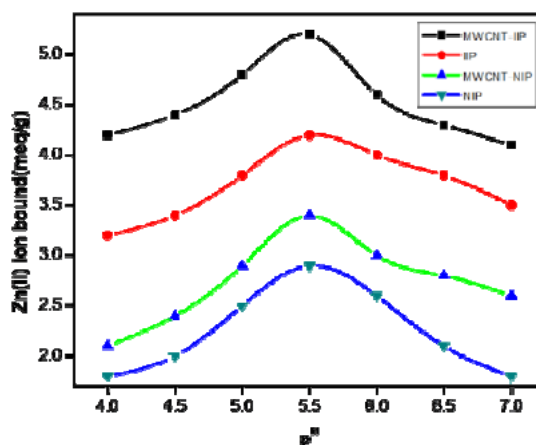


Fig. 4.16. Effect of pH on Zn(II) ion binding by MWCNT-IIP, IIP, MWCNT- NIP and NIP

(D) Adsorbent dosage

A range of sorbent quantities, spanning from 10 to 50 mg, was chosen, and the associated adsorption rates were recorded (Fig. 4.17). The rate of adsorption rises in a linear fashion as the dosage of the sorbent increases, attributed to the presence of imprinted sites. The highest level of adsorption was notably demonstrated by MWCNT-IIP, attributed to the incorporation of MWCNTs in conjunction with the imprinted polymer, which provides a nanostructured framework with an elevated surface-to-volume ratio.

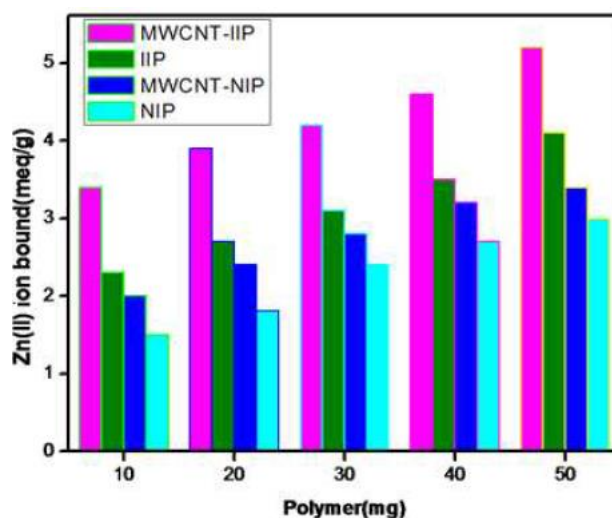


Fig. 4.17. Effect of adsorbent on Zn(II) ion adsorption

(E) Effect of binding medium

The binding medium serves as a crucial element influencing the interaction of metal ions. In the process of

polymerisation, it is essential to utilise an appropriate solvent to facilitate the formation of pores within the polymer matrix. Consequently, three distinct solvents were selected, namely water, DMSO, and THF. Based on the analysis conducted, the findings indicated that water serves as the ideal solvent for the adsorption of Zn(II) ions (Fig. 4.18). The alternative solvents exhibit reduced efficiency as they fail to produce an adequate porous framework, leading to diminished adsorption of Zn(II) ions.

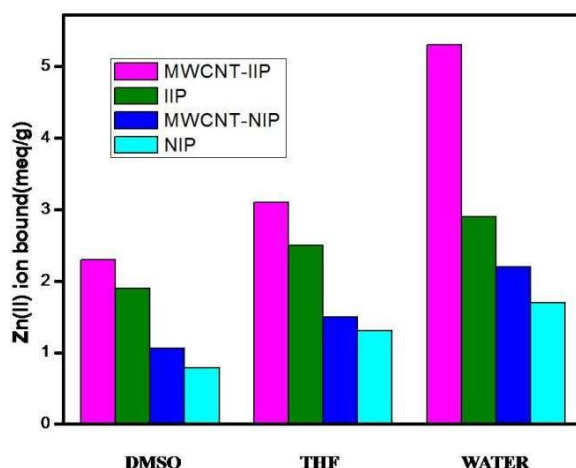


Fig. 4.18. Effect of binding medium towards Zn(II) ion adsorption

4.8 Selectivity study

The effectiveness of the synthesised sorbent system in relation to Zn(II) ions was examined alongside a range of metal ions. The metal ions chosen for the selectivity investigation comprised Cu(II), Cd(II), and Hg(II) ions. The findings indicate that the binding ability of Zn(II) ions with the imprinted polymers significantly surpasses that of the non-imprinted polymers (Fig. 4.19). This observation arises from the fact that the voids created by zinc ions within the imprinted polymers are precisely matched in both size and form to the template Zn(II) ion. In the scenario of MWCNT-NIP and bulk NIP, such distinctly defined pores are lacking. Based on these findings, it can be inferred that the created Zn(II) ion imprinted polymers exhibit a remarkable selectivity for the template Zn(II) ion amidst a blend of competing metal ions. The selectivity factor demonstrated that the Zn(II) ion imprinted polymer exhibits a significant preference for Zn(II) ions when compared to a blend of zinc and copper ions, as indicated by the high selectivity factor (Table 4.3).

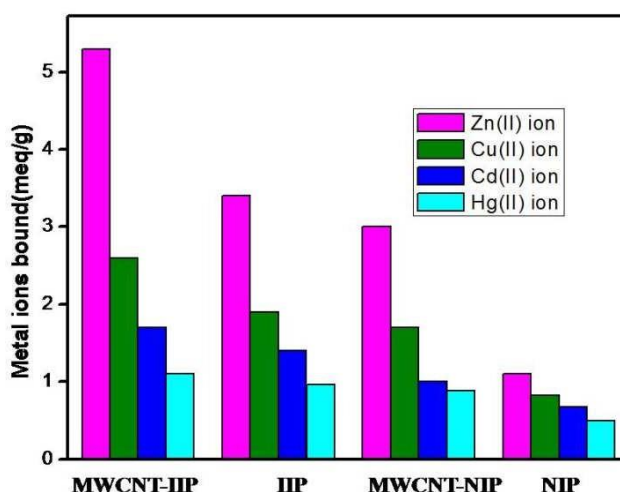


Fig. 4.19. Evaluation of the selectivity of various Zn(II) ion imprinted and non-imprinted systems

Table. 4.3 Selectivity factors of Zn(II) ion imprinted systems

Metal ions	MWCNT-IIP(ar)	IIP(ar)
Zn(II)-Cu(II)	9.06	6.53
Zn(II)-Cd(II)	3.45	1.30
Zn(II)-Hg(II)	2.05	1.06

4.9 Re-usability

The ability to reuse the developed system holds significant value as it highlights the potential and applicability of the sorbents. Therefore, under ideal circumstances, the adsorption procedure is conducted repeatedly using the same sorbent systems. The sorbents demonstrated the ability to be utilised repeatedly for six cycles while maintaining high efficiency, as illustrated in Fig. 4.20.

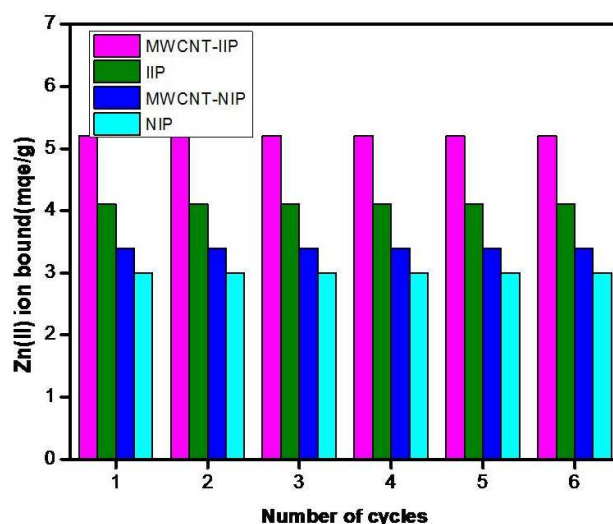


Fig. 4.20. Reusability of various Zn(II) ion imprinted and non-imprinted systems

4.10. Extraction of Zn(II) ions from real samples

The significance of the constructed system was evaluated using actual water samples obtained from the paint industry. The concentration of Zn(II) ions within the sample was examined using Atomic Absorption Spectroscopy (AAS). The results acquired are presented in Table 4.4.

Table. 4.4 Results of extraction of Zn(II) ions from real samples

Polymer Sorbent	Found (ppm)	Removed (ppm)	Recovered (%)
MWCNT-IIP	8.59	8.58±0.001	99.88±0.002
IIP	8.59	7.42±0.004	86.37±0.002
MWCNT-NIP	8.59	6.58±0.002	76.60±0.005
NIP	8.59	5.34±0.003	62.16±0.001



The engineered Zn(II) ion imprinted framework was successfully utilised for the detection and extraction of Zn(II) ions from actual samples. The system demonstrated significant sensitivity and specificity in relation to Zn(II) ions.

5. Discussion

Every escalating contamination of the water bodies with the heavy metals by the human being is indeed harmful to both the people and the nature. The extensive variety of metals of interest has pushed zinc (Zn^{2+}) to the number of the most prevalent pollutants as well as a direct contribution of industrial air pollution. This harmful nature of this substance even in small doses poses the need to use efficient and economical modes of purification. The study discusses the application of the multiwalled carbon nanotubes (MWCNTs) decorated with zinc ion-imprinted polymers (IIPs) as an alternative towards the SELECTive recovery of Zn^{2+} concentrations in polluted water bodies due to the high level of effectiveness and non-toxicity [1]. This aspect of combining MWCNTs as the foundation of ion-imprinted sorbent yields an immense gain on the features of literal adsorption facilitated by the ray in addition to provides the material fabric and integration strength of the element that converts it to an incredibly potent fabric to be used in application in a wide range of functions.

The acrylic acid and addition of the vinyl-functionalized MWCNTs with the Zn^{2+} used in the polymerisation formed MWCNT-IIPs. The suspending effect of N,N'-Methylenebisacrylamide (NNMBA) as the crosslinker and AIBN as the initiator enhanced the formation of a strong polymer base had been deliberate in considering adsorption of Zn^{2+} ions onto it [2]. Characterisation was incorporating a variety of the aspects that were Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive X-ray analysis (EDAX) to successfully polymerise the sample [3]. The FT-IR spectra revealed the presence of characteristic functional groups of C=O and C=C that were used in the case of the presence of the vinyl groups among others and O-H that was attached to acrylic acid among others, which were all critical species of the ion-imprinting process. The presence of the strong polymer matrix that surrounds the MWCNTs was confirmed by the use of SEM and TEM images that present the existence of the polymer layer surrounding the MWCNTs using the TEM images. The EDAX analysis reported some interesting results which provided considerable arguments to prove the successful binding of the Zn^{2+} ions to the MWCNT-IIP matrix that could enable to justify the viability of the ion-imprinting process [4]. MWCNT-IIPs efficiency in Zn^{2+} extraction was tested using a model of adsorption experiments, which examined the various parameters such as zinc ions concentration, timings, pH, grams of adsorbent, and the nature of binding media. The adsorption capacity of MWCNT-IIPs was important because it as indicated by the results that this capacity was much greater than that of non-imprinted polymers (NIPs). It is correlated to the characteristic etched spaces existing in the polymer matrix, the ones which are corrected in the sizes, structure and which are reasonable in fighting the role of the Zn^{2+} ions. Following a pseudo-second order equation, the mechanism of kinetics of adsorption was followed and demonstrated a chemisorption mechanism [5]. The active sites on the surface of MWCNT-IIP react with dictating the rate-limiting stage of the reaction to the Zn^{2+} ions. It was also observed that the adsorption capacity increased with the concentration of the Zn^{2+} ions in the solution that experienced a high-rate up to a specific concentration of 5ppm, and then saturation followed, according to Langmuir adsorption isotherm system. It means there are only some active sites provided to stand uptake of the Zn^{2+} ions and at that moment, when these active sites become saturated, the adsorption capacity becomes the optimal one [6].

Together with its capabilities of adsorption the MWCNT-IIP composite has been experimented in its roles as an electrochemical sensor via the techniques of cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The MWCNT-IIP-functionalized platinum electrode gave also a redox peak when Zn^{2+} was added which is believed to be synonymous to the electrode to determine the Zn^{2+} concentrations specifically at the low concentrations [7]. Its electrochemical performance was concentration-dependent whereby the size of the redox peak grew in the same way as the concentration of Zn^{2+} increased and at a concentration of 5 ppm, its biggest size was recorded. The limit of the pushed sensor was adjusted to 1.32×10^{-4} μM which happens to fall within the necessary range of signals to see a sample of the environment [8]. These qualities make MWCNT-IIP sensor phenomenally sensitive and specific hence qualifies to hold a high potential in real-time recording of the environmental condition and detection of heavy metals within the contaminated water streams. In addition, the sensor was selectively sensitive to Zn^{2+} compared with all the other competing ions, including Cu^{2+} , Cd^{2+} , and Hg^{2+} , which was also confirmed by selectivity determinations [9]. It was established that the selectivity of the MWCNT-IIP/ Zn /PE was very specific towards Zn^{2+} and therefore has a tremendous potential of application in the real life situation in resourceful tough waters. The key fact about MWCNT-IIPs compared to all conventional adsorbents is that they can be recycled. As discovered in the course of the reusability experiment, the MWCNT-IIPs retains their immense capacity to adsorb in spite of successful completion of six consecutive cycles, which are indicators of its suitability in long-term usage

in water purification project [10]. The capacity to regenerate such sorbent to the same magnitude of functioning is what is required to make sure that the running expenses of functioning are decreased and augur in the lifespan of the working purifying systems using water. In addition, in real industrial wastewater scenario, particularly, the painting industry, MWCNT-IIPs reached an impressive 99.60 color recovery in order to demonstrate that it can be used in the actual implementation. The efficacy was also high in the real samples that signify the great potential hold by MWCNT-IIPs with respect to the treatment of industrial and polluted water [11].

The MWCNT-IIPs are associated with numerous benefits as compared to the conventional processes, which include the use of precipitation, ion exchange, and filtration. The obsolete nature of the methods in use tends to cause problems with the low concentration of the heavy metal and a complex mixture which results in the fact that the unwanted material removed have been left insufficiently or a second waste produced [12]. MWCNT-IIPs on the contrary are extremely selective and efficient to reach Zn^{+} even in gold of a mixture of other competing metal ions. Further, the adsorption and electrochemical sensing properties incorporated in the MWCNT-IIPs gives it a distinct dual-characteristic advantage to the MWCNT-IIPs material, that performs even better in water purification besides environmental measurements [13]. MWCNT-IIPs is one of the promising technologies, which will offer an option to radical ways and will supply more effective functionality and diminished cost alongside an opportunity to achieve real-time observation. This paper has revealed significant information with regard to MWCNT-IIPs performance symbolize the efficaciousness of the chosen investigation upon the singleness approach of type II Zn^{+} in polluted water media. Nevertheless, additional studies will be required to enhance the production process and make MWCNT-IIPs significantly more effective [14]. The possibilities to dig deeper help us in discovering advantageous forces, which can be embodied in creating of MWCNT-IIPs which are concentrated on individual heavy metals, deliberate on the utilization of MWCNT-IIP with other nanomaterials in sinus with a view of enhancing the effect of a combination, and apply of the materials on a large scale with the view of making water clean. In addition, miniaturised, user friendly electrochemical sensors developed based on MWCNT-IIPs can transform the limits of environmental sensors owing to the possibility of detecting heavy metals present in the contaminated water catchment regions in real time [15].

6. Conclusion

This research illustrates well the possible application of MWCNT-IIPs as superior sorbents of the targeted extraction of the Zn^{2+} ions web in the contaminated water body. Long surface area coupled with great structural characteristics of the MWCNT-IIPs along with a moderate capacity associated with adsorbing ion-imprinted polymers (IIPs) yield increased activity as compared to the customary adsorbents. Not only does the polymerisation of these nanocomposites into strengthening the mechanical stability and strength of the sorbent that holds the recognition sites that attack different points to Zn^{2+} , it improves adsorption mechanism. Characterisation through the FT-IR, SEM, TEM and EDAX has proved that the MWCNT-IIPs have been synthesised and that there are hollows that are imprinted with Zn^{2+} . In the adsorption study, it has been found out that MWCNT-IIP has high affinity to Zn^{2+} ions and has a maximum adsorption capacity of 5 ppm concentration. Adsorption kinetics Center of mass corresponds to a pseudo second order model which is based on the hypothesis that adsorption of the Zn^{2+} ion onto the sorbent takes place via chemisorption. Moreover, the adsorptions are also analogous with using Langmuir model of isotherms of adsorption, which hypothesizes the adsorption of layer of a surface by adsorbs, whose active sites are solid and are found on a surface in finite numbers. With reference to efficiency on sensing on the electrochemical measurement theory, the MWCNT-IIP-modified and electrodes display a remarkable high quality ability in generalizing Zn^{2+} ions at low concentrations showing high sensitivity of recognition, as well as, selectivity. The outcomes of the electrochemical tests also proved that these materials could be used as the source of some immediate monitoring the surrounding environment and the gadget of permanent cleansing the waters. MWCNT-IIPs are quite reusable and the purification by adsorption can still be maintained after six dissimilar cycles thus making it an environmental friend variety to be ensured that purification of water will be done. It was also demonstrated that MWCNT-IIPs worked with an effect of 99.60 percent in extraction of Zn^{+} ions in the industrial wastewater in real life-time scenarios, which depicts their relevance in preventing the impacts of water contamination. In comparison to the conventional way, of doing things, MWCNT-IIPs are very selective, has a huge capacity and can be used again to achieve remarkable power in terms of cost- effectiveness to empower the element of curbing the initial pollution of water by the heavy metals. The future research efforts ought to involve enhancement of the production of MWCNT-IIPs to have a greater number of applications including the harvesting of other heavy metals, and into exploring its potential in large-scale implementation in the process of controlling Wastewater which arises in factories.

References

- [1]. Kalaras, M. D.; Richie, J. P.; Calcagnotto, A.; Beelman, R. B. Mushrooms: A rich source of the antioxidants ergothioneine and glutathione. *Food. Chem.*, 2017, 233, 429.
- [2]. Roupasa, P.; Keogh, J.; Noakes, M.; Margettsa, C.; Taylor, P. Mushrooms and agaritine: A mini-review. *J. Funct. Foods.*, 2010, 2, 91.
- [3]. Koyyalamudi, S. R.; Jeong, S. C.; Song, C. H.; Cho, K.Y.; Pang, G. Vitamin D2 formation and bioavailability from *Agaricus bisporus* button mushrooms treated with ultraviolet irradiation. *J. Agric. Food Chem.*, 2009, 57, 3351.
- [4]. Anandalakshmi, K.; Venugobal, J.; Ramasamy, V. Characterization of silver nanoparticles by green synthesis method using *Pedaliu murex* leaf extract and their antibacterial activity. *Appl. Nanosci.*, 2015, 16, 399.
- [5]. Vijayan, R.; Joseph, S.; Mathew, B. *Indigofera tinctoria* leaf extract mediated green synthesis of silver and gold nanoparticles and assessment of their anticancer, antimicrobial, antioxidant and catalytic properties. *Artif. Cells Nanomed. Biotechnol.*, 2017, 6, 1.
- [6]. Banerjee, A. N.; Anitha, V. C.; Joo, S. W.; Improved electrochemical properties of morphology-controlled titania/titanate nanostructures prepared by in-situ hydrothermal surface modification of self-source Ti substrate for high-performance supercapacitors. *Scient. Repor.* 2017, 16, 7.
- [7]. Sanghavi, B. J.; Srivastava, A. K. Adsorptive stripping differential pulse voltammetric determination of venlafaxine and desvenlafaxine employing Nafion–carbon nanotube composite glassy carbon electrode. *Electrochim. Acta*, 2011, 56, 4188.
- [8]. Doerr, B.; Wade, K. L.; Stephenson, K. K.; Reed, S. B.; Fahey, J. W. Cultivar effect on *Moringa oleifera* glucosinolate content and taste: A pilot study. *Ecol. Food Nutrit.*, 2009, 48, 199.
- [9]. Bennett, R. N.; Mellon, F. A.; Foidl, N.; Pratt, J. H.; Dupont, M. S.; Perkins, L. Profiling glucosinolates and phenolics in vegetative and reproductive tissues of the multi-purpose trees *Moringa oleifera* L. (Horseradish Tree) and *Moringa stenopetala* L. *J. Agric. Food Chem.*, 2003, 51, 3546.
- [10]. Francis, S.; Joseph, S.; Koshy, E. P.; Mathew, B. Microwave assisted green synthesis of silver nanoparticles using leaf extract of *elephantopus scaber* and its environmental and biological applications. *Artif. Cells Nanomed. Biotechnol.*, 2017, 6, 1.
- [11]. Joseph, S.; Mathew, B. Microwave-assisted facile green synthesis of silver nanoparticles and spectroscopic investigation of the catalytic activity. *Bull. Mater. Sci.* 2015, 38, 659.
- [12]. Girija, P.; Beena, M. Sorption of trace amounts of Pb(II) ions on an ion imprinted interpenetrating polymer network based on alginic acid and crosslinked polyacrylamide. *Separ. Sci. Technol.*, 2014, 49, 1053.
- [13]. George, B.; Mathew, B. Effect of the nature of the crosslinking agent on the metal ion complexation characteristics of 4 mol% DVB- and NNMBA-cross linked polyacrylamide-supported glycines. *J. Appl. Polym. Sci.*, 1999, 34, 3452.
- [14]. Fang, G. Z.; Tan, J. An ion-imprinted functionalized silica gel sorbent prepared by a surface imprinting technique combined with a sol-gel process for selective solid-phase extraction of cadmium (II). *Anal. Chem.*, 2005, 77, 1734.
- [15]. Sooraj, M. P.; Mathew, B. Highly selective nanocomposite sorbents for the specific recognition of S-ibuprofen from structurally related compounds. *Appl. Nanosci.* 2015, 6, 659.

