




Research Article

An electrochemical sensor and sorbent based on multiwalled carbon nanotube supported ion imprinting technique for Ni(II) ion from electroplating and steel industries

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Abstract

In this work for the rapid electrochemical sensing of Ni(II) ion, Multiwalled carbon nanotube based ion-imprinted polymer (MWCNT-IIP) fabricated on the platinum electrode was used. To prove the importance of MWCNT, ion imprinted (IIP) and non-imprinted polymer without MWCNT were also prepared. The synthesized polymers were characterized by FT-IR, XRD, TEM, EDAX, and TGA. The MWCNT-IIP modified electrochemical sensor could easily recognize Ni(II) ion in the presence of other metal ions. The limit of detection was found to be 0.028 μM using differential pulse voltammetric studies. The practical applicability of the modified electrode was studied using real samples collected from lake, steel and electroplating industry. The synthesized polymers were also used for the extraction of Ni(II) ion.

Keywords Nickel(II) · Ion imprinting polymer · MWCNT · MWCNT-IIP · Cyclic voltammetry · Differential pulse voltammetry

1 Introduction

In recent years the toxicity of hazardous metal ions on human health and environment has attracted significant attention. Among various metal ions, nickel is an essential element that exists in the environment at a very low level and in small doses, it is necessary to live organism [1]. According to the international guideline on water quality, the accepted nickel content in drinking water is 20.0 $\mu\text{g/l}$ [2]. The effect of nickel ion can be very risky when they go beyond the maximum tolerable limit [3]. Nickel enters into the environment through the electroplating, steel manufacturing, decomposition or degradation of soils and rocks, biological cycles, motor vehicles, and mainly from the waste disposal and industrial process. The toxicity of nickel may cause cancer, heart and liver damage, skin allergy, dermatological diseases etc. [4]. Therefore, it

is important to determine the nickel ion concentration in the environment and food samples.

Many analytical methods have been reported for the detection of Ni(II) ion in the environment such as atomic absorption spectrometry electro thermal atomization (AAS-ETA), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), inductively coupled plasma mass spectrometry (ICPMS) [5], flame photometry etc. [6]. Even though they are powerful techniques for the trace determination of Ni(II) ion in the environment, these methods require the pre-treatment of samples, high consumption of reagent and infrastructure backup as their disadvantage; therefore, these techniques were not convenient for the detection of Ni(II) ion in a large number of environmental samples. Thus, there is a significant need for the advance selective and inexpensive tool for the determination of Ni(II) ion.

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Recently ion-imprinted polymer (IIP) is an attractive method for the selective recognition of target ions by the polymer memory effect towards the metal ion interaction with a specific ligand, coordination geometry, metal ion coordination, charge, and size. This method has several disadvantages like slow mass transfer, low recognition sites per unit volume of the polymer and irregular material shape [7]. In recent years to overcome these drawbacks scientists has been developed nanofabrication technique on ion imprinting polymer [8–12], Multi-Walled Carbon Nanotube (MWCNT) is an active field for this due to their large surface area, thermal, electrical, chemical, structural and mechanical properties [13, 14]. It is already reported that the MWCNT improve the sensitivity of the electrochemical sensing, therefore, it has been used in this study.

Considering the advantages of the ion imprinting technique and electrochemical method, the main idea of this paper is to develop a sensor with excellent selectivity and high sensitivity for Ni(II) ion. In the present study nano-structured Ni(II) ion imprinted polymer has been created using vinyl group functionalized MWCNT, methacrylic acid (MAA), *N, N'*Methylene-bisacrylamide (NNMBA) and nickel chloride were used as the monomer, crosslinking agent, and template. The morphology, electrochemical studies, selectivity, extraction, sorption and desorption characteristic, kinetic studies, etc. have been studied in this work. The limit of detection was investigated using the differential pulse voltammetric technique. The developed sensor has been successfully used for the sensing of Ni(II) ion from the real samples. After the successful sensing of Ni(II) ion, MWCNT-IIP was also used for the extraction of Ni(II) ion from the same sample itself.

2 Experimental

2.1 Materials and methods

MWCNT of 10–15 nm was purchased from Reinsto Nano ventures Private Limited India. *N, N'*Methylene-bisacrylamide (NNMBA) and potassium peroxy disulphate ($K_2S_2O_8$) were obtained from Sigma Aldrich (Germany). Thionyl chloride ($SOCl_2$), dimethylformamide (DMF) and tetrahydrofuran (THF) were got from Merck (India). Methacrylic acid (MAA) and metal chlorides were acquired from SRL (India). Nafion (5wt %) was supplied by the Sigma Aldrich. Phosphate buffer solution was used as the supporting electrolyte for the electrochemical studies.

The FT-IR spectra were obtained from Perkin-Elmer 400 FT-IR spectrophotometer. X-ray diffract gram of the nano-materials was recorded using PAN analytic XPERT-PRO. Morphology was investigated by JEOL-2100 model tunneling electron microscope. Absorption spectra of Ni(II)

ion were determined by Perkin–Elmer Atomic Absorption Analyser 300. Thermogravimetric analysis was studied using the NETZCHSTA449C instrument. The electrochemical measurement was carried out at room temperature with an electrochemical workstation (Bio-Logic Science). Cyclic voltammetry and Differential pulse voltammetry technique were carried out with a three electrode system such as a platinum electrode modified by imprinted MWCNT-IIP were used as the working electrode, a platinum wire was used as the auxiliary electrode and saturated calomel electrode act as the reference electrode.

2.2 Preparation of vinyl functionalized MWCNT (MWCNT-CH=CH₂)

Firstly the MWCNT is purified according to the published method [15, 16]. The purified MWCNT (0.5 g) is suspended in 60 ml con. HNO_3 followed by sonication at 10 min. This mixture was refluxed for 24 h at 60 °C with stirring. The mixture was then diluted with distilled water and filtered through Whatman no.41 filter paper. This process was continued until the pH of the filtrate solution become neutral. Thus obtained the filtered solid was then dried under vacuum to obtain carboxyl group functionalized MWCNT (MWCNT-COOH). Carboxyl acid capacity of obtained MWCNT-COOH is found to be 1.8 mmol/g by acid-alkali titration [17]. MWCNT-COOH (0.4 g) is taken in a reaction flask and adds 10 ml thionyl chloride and 30 ml of chloroform, refluxed for 24 h at 60 °C with stirring. The mixture was then cooled and washed with anhydrous THF to remove excess thionyl chloride present in it. It was dried under vacuum for 24 h to obtain MWCNT-COCl. Vinyl functionalization of MWCNT is carried out by dispersing MWCNT-COCl (0.3 g) in 30 ml THF followed by the addition of 20 ml allylamine in 10 ml of DMF in round bottom flask fitted with a condenser and refluxed for 24 h at 60 °C with vigorous stirring. The mixture was then cooled and washed with anhydrous THF to remove unreacted reagent. The obtained MWCNT-CH=CH₂ solid was dried under vacuum and used for the further studies.

2.3 Preparation of Ni(II) ion imprinted and non-imprinted polymer on MWCNT-CH=CH₂

Ion-imprinted polymer (IIP) on the MWCNT-CH=CH₂ surface with Ni(II) ion as template molecule is prepared by free radical polymerization. In brief, 0.6 g of MWCNT-CH=CH₂ was added to the water (porogen) in a 250 ml round bottom flask and purged with N_2 under magnetic stirring. Nickel chloride (Ni(II), 0.6 g) and methacrylic acid (MAA, 0.025 mmol) was added to the flask and mixed for 20 min to form a template-monomer complex. Finally, *N, N'*Methylene-bisacrylamide (NNMBA, 8 g) and potassium

peroxo disulphate ($K_2S_2O_8$, 100 mg) were also added to it. The temperature was increased to 70 °C with constant stirring for 12 h. The resultant polymer was washed thoroughly with distilled water to extract Ni(II) ion until the absence of template ion in the eluent by AAS. The obtained polymer was dried under vacuum and used for the advanced studies. MWCNT-NIP is also prepared by the same procedure by not including template ion in the polymerization process. For the comparison purpose bulk, IIP and NIP were also prepared without using MWCNT.

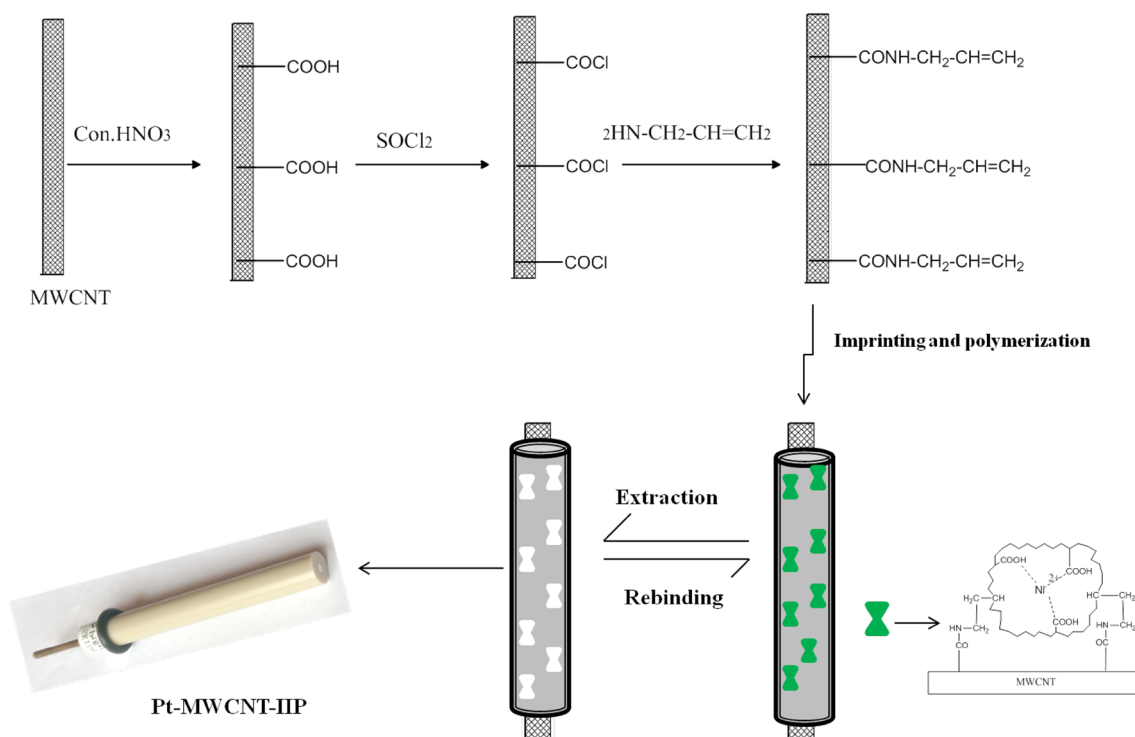
2.4 Preparation of modified platinum electrode and optimization of electrochemical studies

For fabrication of modified platinum electrode, the platinum electrode was sophisticated with 10 μm alumina slurry followed by flushing with de-ionized water for 15 min. 1.0 mg of Ni(II) ion imprinted MWCNT-IIP was added to 1 ml of 0.5% Nafion and mixed well to get MWCNT-IIP nafion complex. Nafion is a polymeric resin with properties like chemical and thermal stability and has high selectivity towards different cations. Nafion is used in this study for the fixation of imprinted polymer on to the platinum electrode surface [18–20]. The mixture was carefully coated on the platinum electrode

surface and dried at room temperature [21, 22]. Phosphate buffer solution (PBS) with pH 7 is used in this study to blend the reagents and supply conductivity to the paste. The modified platinum electrode was transferred into fresh phosphate buffer solution for further electrochemical studies. The modified platinum electrode was designated as Pt/MWCNT-IIP (Scheme 1). Cyclic voltammograms were performed by the potential between – 400 to 1000 mV for Ni(II) ion with a scan rate of 100 mVs^{-1} . Differential pulse voltammogram was recorded with a scan rate of 100 mVs^{-1} , a pulse amplitude 50 mV and a pulse width 500 ms to detect the current response of Ni(II) ions. Effect of scan rate, pH, and selectivity studies was also carried out with the modified platinum electrode.

2.5 Application of modified platinum electrode using real samples

Real samples were collected and evaluated by modified platinum electrode by the above-mentioned procedure. The water samples collected was filtered through 0.22 μm polar size filter paper to remove floating effluents. DPV studies were carried out with this samples as described above.



Scheme 1 Schematic representation of Pt-MWCNT-IIP

2.6 Extraction procedure

2.6.1 Optimization of adsorption condition

For extraction experiment, the varying solution of 10 ml Ni(II) ion with initial concentration ranging from 1 to 5 ppm was passed through the different sorbents (5 mg) such as MWCNT-IIP, MWCNT-NIP, IIP, and NIP. From the calibration curve of Ni(II) solution with different concentration, the concentration of Ni(II) ion range is found. The mixture was then centrifuged and the Ni(II) concentration in the eluent was measured by AAS. The Ni(II) uptake at equilibrium was calculated by the below Eq. (1).

$$Q = C_0 - C_e / M * V \quad (1)$$

where Q (μ mol/g) is the adsorption capacity, V (ml) is the volume of the metal ion solution, M (g) is the mass of the polymer, C_0 and C_e (mmol^{-1}) are the initial and final concentration of Ni(II) ion in the adsorption process [23].

The kinetic studies were calculated at different time interval varying from 0 to 100 min by maintaining Ni(II) ion concentration constant. The effect of pH on the Ni(II) process was investigated over a pH range of 2.0–5.0 without varying Ni(II) ion concentration. The aqueous solution of Ni(II) ion was adjusted to the required pH levels by adding 0.1 M HCl or 0.1 M NaOH.

Selective sorption of Cu(II), Fe(II) and Zn(II) ions in the presence of Ni(II) was examined for all the imprinted and non-imprinted polymers. Separation and selectivity factor was calculated by the below equation [24] (2)–(4).

$$\alpha = D_{\text{Ni(II)}} / D_{\text{M(II)}} \quad (2)$$

$$D = Q / C_e \quad (3)$$

$$\alpha_r = \alpha_i / \alpha_n \quad (4)$$

$D_{\text{Ni(II)}}$ and $D_{\text{M(II)}}$ represent the distribution coefficient of Ni(II) ion and other metal ions Q represents the adsorption capacity and C_e represents the final concentration of metal ions. α_i and α_n are the selectivity factor of imprinted MWCNT-IIP and MWCNT-NIP. α_r is the relative selective coefficient. Factors which affect the sorption studies such as the effect of mass and effect of solvent was also determined. Reusability studies were examined by adsorption-desorption experiment. Swelling studies were also carried out and EWC% (Equilibrium water content) was calculated by the below Eq. (5).

$$\begin{aligned} \text{EWC\%} &= \text{weight of wet polymer} \\ &\quad - \text{weight of dry polymer} / \text{weight} \\ &\quad \text{of the wet polymer} * 100 \end{aligned} \quad (5)$$

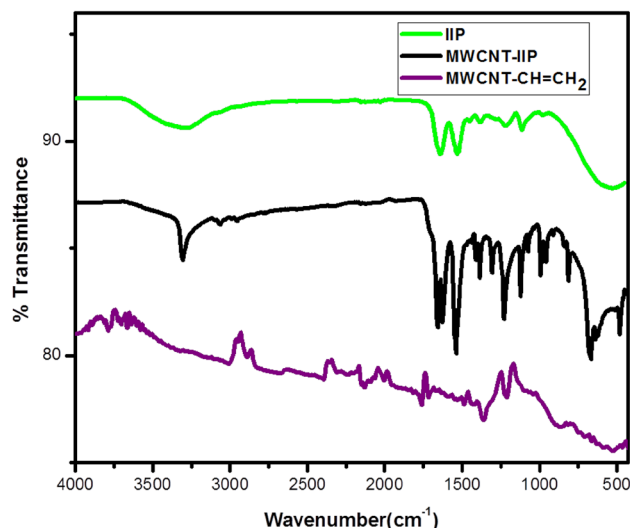


Fig. 1 FT-IR spectra of MWCNT-CH=CH₂, MWCNT-IIP, and IIP

2.7 Application of the extraction method

The waste water samples collected from lake, steel and electroplating industry were filtered using Whatman filter paper. The Ni(II) ion extraction by various ion imprinted and non imprinted polymers were carried out as detailed in the extraction procedure.

3 Results and discussion

FT-IR spectra were used to validate the molecular changes of all intermediate and product of synthesized MWCNT-IIP (Fig. 1). A peak at 1750 cm^{-1} and 1630 cm^{-1} were corresponded to the C=O and C=C stretching vibrations in MWCNT-CH=CH₂. This illustrates that the vinyl group is successfully set up on the MWCNTs surface. MWCNT-IIP and IIP show a characteristic peak at 3342 cm^{-1} and 1720 cm^{-1} corresponding to the group present in methacrylic acid which is used for the preparation of the polymers. This confirms the formation of IIP on the MWCNT surface. The main peaks of IIP and MWCNT-CH=CH₂ were present in the spectrum of MWCNT-IIP proved the formation of IIP layer on MWCNT-IIP.

The crystalline nature of MWCNT, MWCNT-IIP, and IIP was determined by X-ray diffraction technique (Fig. 2). From the XRD pattern of pristine MWCNT, two crystalline peaks at 28.1 and 47.2 were observed which was corresponding to the $d(002)$ and $d(100)$ of MWCNT [25]. MWCNT-IIP shows a sharp peak which is the characteristic peak of MWCNT in addition to the broad peaks of

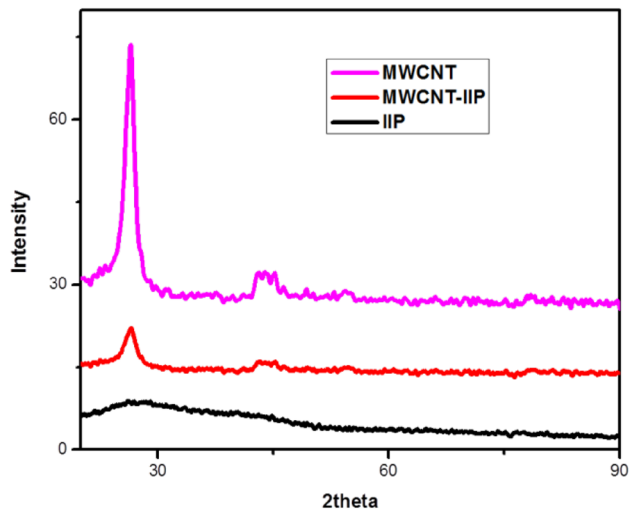


Fig. 2 Powder X-ray diffraction patterns of **a** MWCNT, **b** MWCNT-IIP and **c** IIP

amorphous polymer. Thus comparing XRD pattern of MWCNT-IIP and IIP, IIP shows only halo peaks due to the amorphous nature of the polymers and do not produce any strong reflection in the 2θ region ranging from 20° to 90° .

We carried out TGA experiment in this work to investigate the thermal stability of MWCNT, MWCNT-IIP and traditional IIP (Fig. S1). The result revealed that the MWCNT was stable up to 800°C without any weight loss. Thermogram of MWCNT-IIP is similar to that IIP in view. However, when evaluating the thermogram of MWCNT-IIP and IIP the degradation temperature and mass loss were lower and greater respect for IIP than MWCNT-IIP. The greater thermal stability of MWCNT-IIP may be due to the assimilation of MWCNTs.

The surface morphology of MWCNT, MWCNT-IIP, and IIP was revealed by Transmission Electron Microscopy (TEM). MWCNT give a thread like a nanotube structure with a diameter ranging from 6 to 8 nm. MWCNT by further functionalization and polymerization, it is found that the thickness of the nanotube was begun to increase from 22–26 nm (Fig. 3). This results clearly indicate the successful grafting of an imprinted layer on the MWCNT surface. Due to the agglomeration on the polymer surface IIP exhibit a coagulated morphology.

The elemental composition in Ni(II) ion loaded MWCNT-IIP and eluted imprinted MWCNT-IIP is verified by EDAX. From the Fig. 4 it is clear that in imprinted MWCNT-IIP, the signal due to Ni(II) ion is present while in the Ni(II) ion eluted MWCNT-IIP the signal of Ni(II) ion is absent. These results clearly verified the number of cavities on imprinted MWCNT-IIP ease diffusion of the target Ni(II) ions. This established that imprinted MWCNT-IIP has high affinity towards Ni(II) ions.

3.1 Swelling studies

The swelling studies were carried out using different adsorbents such as MWCNT-IIP, IIP, MWCNT-NIP, and NIP and the results are tabulated in Table 1. The swelling studies were checked by incubating known amount of adsorbent in water for 24 h. From the table, it is clear that EWC% is greater for MWCNT-IIP due to the large surface area and availability of binding sites in the MWCNT attached imprinted polymer.

3.2 Dispersibility test

The dispersion of crude MWCNT, functionalized MWCNT and MWCNT-IIP is shown in Fig. S2. Crude MWCNT were insoluble in water and sedimented at the bottom of the

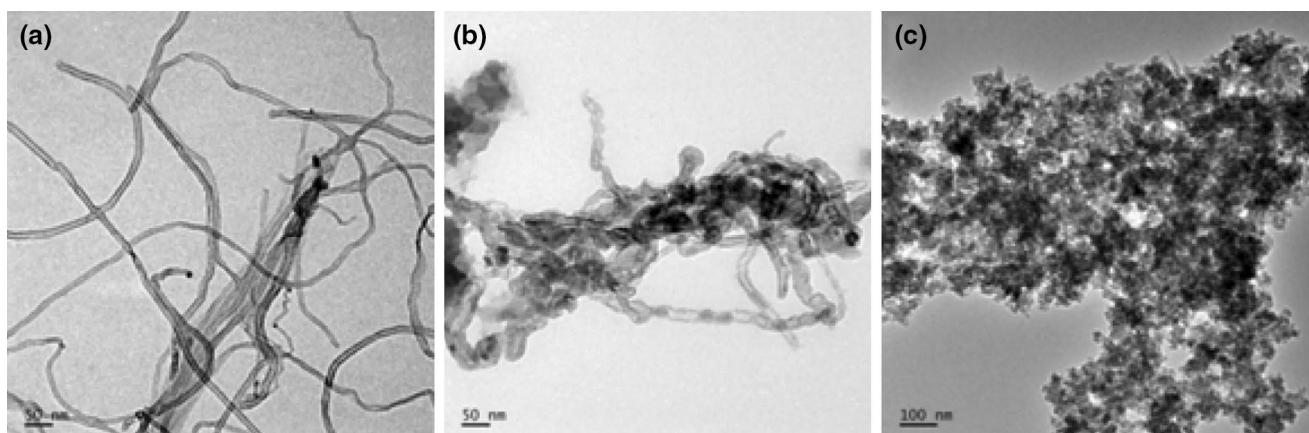


Fig. 3 TEM images of **a** MWCNT, **b** MWCNT-IIP, **c** IIP

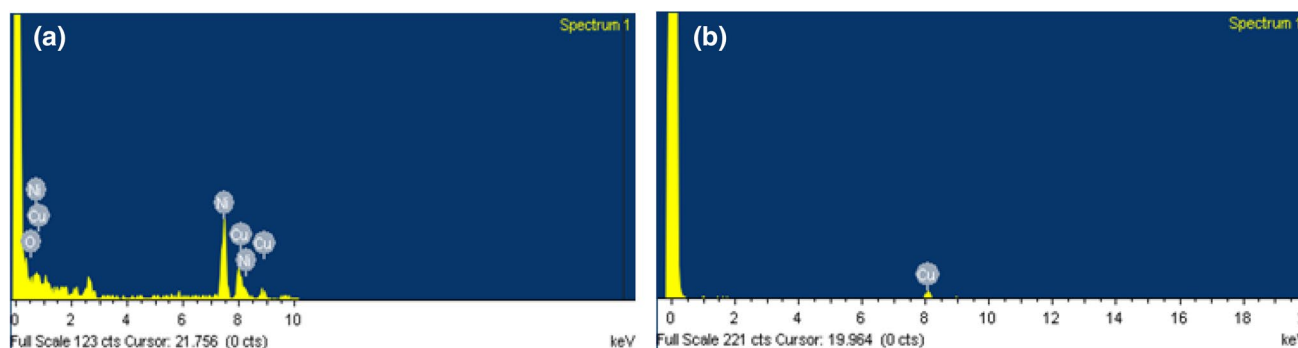


Fig. 4 EDAX images of **a** MWCNT-IIP, and **b** Ni(II) eluted MWCNT-IIP

Table 1 EWC% of Ni(II) ion binding on MWCNT-IIP, IIP, MWCNT-NIP, and NIP

Polymers	EWC (%)
MWCNT-IIP	95.22
IIP	87.64
MWCNT-NIP	64.85
NIP	41.81

container which indicates the absence of any considerable interaction between the MWCNT and water. Functionalised nanotube shows slightly increased dispersibility in water which indicates a weak interaction has taken place between the carboxyl groups with the solvent. On the other hand, MWCNT-IIP is highly dispersed in water and do not show any sedimentation at the bottom of the container which evidence indicates that the modification of IIP layer on functionalized MWCNT could improve its dispersibility and retains its dispersibility even after 6 months. The incorporation of the hydrophilic NNMBA crosslinked methacrylic acid on MWCNT imparts hydrophilicity to the support making it more polar and dispersed in water medium.

4 Electrochemical studies

The electrochemical determination of Ni(II) was analyzed with bare Pt electrode, Pt-MWCNT-IIP and Pt-MWCNT-NIP under similar conditions using cyclic voltammetry. From the Fig. 5 it is clear that Pt-MWCNT-IIP (-92.468 mV, -6.110 μ A) respond distinctly from other electrodes. The current responses of Pt-MWCNT-NIP (32.92 mV, -4.70 μ A) and bare Pt electrode (21.595 mV, 11.170 μ A) shows poor electrochemical behaviour due to the absence of template cavity. It is clear that all systems except Pt-MWCNT-IIP display no observable presence of both oxidation and reduction peaks upon addition of Ni(II) ions in their cyclic voltammograms. Oxidation and reduction peaks arise upon the addition of Ni(II) ions only in the case of Ni(II)

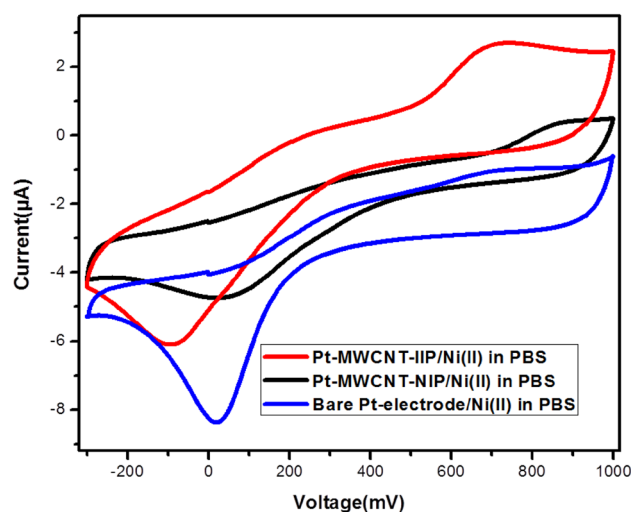


Fig. 5 Cyclic voltammograms of modified and bare Pt electrodes toward Ni(II) ions in phosphate buffer solution

ion imprinted MWCNT-IIP. The greater electrochemical response of Pt-MWCNT-IIPs due to presence of specific cavities located in MWCNT-IIP to bind Ni(II) ion while in other electrodes there are no such cavities and they show very poor response towards Ni(II) ion. Thus Pt-MWCNT-IIP is chosen for the further studies.

The influence of Ni(II) ion concentration on its detection by Pt-MWCNT-IIP was examined. The voltammetric experiments were limited to a maximum Ni(II) ion concentration of 5 ppm and the electrochemical measurement obtained are shown in the Fig. S3. The peak current increases linearly with the Ni(II) ion concentration up to 5 ppm. This is due to the increased availability of the electroactive species present in the solution. At higher concentrations, the peak current decreases due to the saturation of the imprinted cavities of MWCNT-IIP in Pt-electrode.

The influence of scan rate on the electrochemical behavior of Ni(II) ion at Pt/MWCNT-IIP was examined (Fig.

S4). The redox peak current was found to increase with scan rate from 10 to 100 mVs⁻¹. A linear plot of anodic and cathodic peak current versus scan rate was obtained with a correlation coefficient of $R^2 = 0.9952$, indicating that the reaction of Ni(II) ion on Pt-MWCNT-IIP is diffusion controlled electrochemical process [26, 27].

The peak shape, height, and stability of the voltammogram were greatly monitored by the pH of the medium. The influence of pH on the electrochemical response of Ni(II) ion at Pt-MWCNT-IIP was examined over a pH range of 1.5–6.5 by cyclic voltammetry. A small current response was attained at pH 1.5 and it gradually increased as the pH increases, till 5.5 and diminished beyond this limit of pH (Fig. S5). This evidently points out that the protons play an important role in the electrode process of Ni(II) ion.

The selectivity of the modified sensor was studied by adding same concentration of different metal ions such as Cu(II), Cd(II) and Zn(II) ions to the electrolyte solution where the Pt-MWCNT-IIP was dipped. From the Fig. 6 it is clear that the current response of Pt-MWCNT-IIP towards Ni(II) ion is much elevated than the other metal ions. The higher selectivity of Ni(II) ion on the modified electrode is due to the recognition of Ni(II) ions by the cavities with complementary in size, shape, and functionality to the Ni(II) ion existing on MWCNT-IIP layer.

Differential pulse voltammetric measurements are widely used for electrochemical sensing due to its high sensitivity. The DPV curve obtained for Ni(II) ion concentration ranging from 1 to 5 ppm at Pt-MWCNT-IIP in phosphate buffer solution is shown in Fig. 7. Preconcentration time is a vital factor while carrying out DPV experiments. The relationship between current and time would change from linearity when the time taken for the experiment was long. This may be due to the surface saturation of

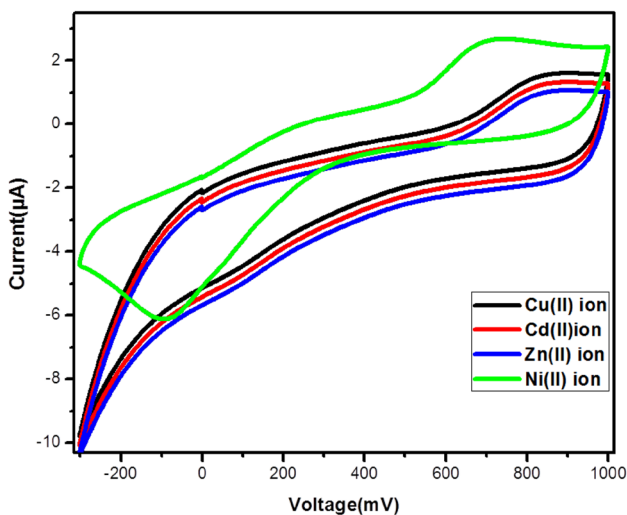


Fig. 6 Selectivity studies of Pt/MWCNT-IIP with various metal ions

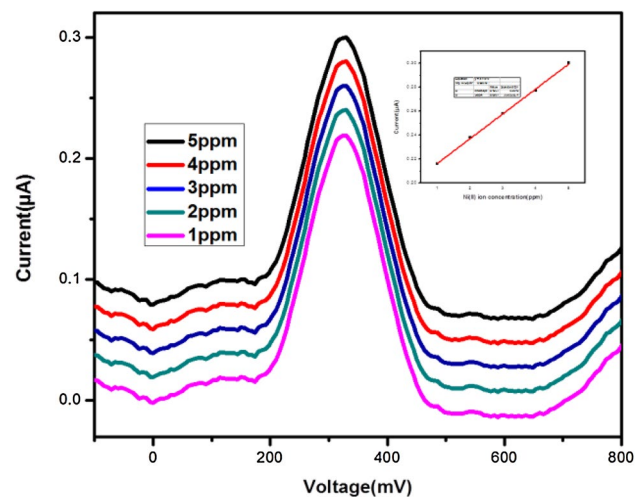


Fig. 7 Differential pulse voltammogram of different concentration of Ni(II) ion under optimum conditions. An inset shows the plot of peak height as a function of Ni(II) ion concentration

the cavities present in the MWCNT-IIP, thus the cavities are not free to accommodate Ni(II) ions. The straight line calibration curve obtained from the DPV analysis is shown in the inset plot of Fig. 7. A linear curve was obtained with correlation coefficient 0.9987 and slope 0.0207. From this, limit of detection was found to be 0.028 μM . When the Ni(II) ion concentration was greater than the detection limit, the potential of current responses diminished due to saturation of Pt-MWCNT-IIP.

4.1 Application of modified electrode

The practical applicability of the Pt-MWCNT-IIP and Pt-MWCNT-NIP was checked for the determination of Ni(II) in real samples. The real samples were collected from lake, steel and electroplating industries. DPV studies were carried out by Pt-MWCNT-IIP and Pt-MWCNT-NIP using these samples under the optimized conditions. The recovered percentage obtained is tabulated in Table 2. The attained recovery percentage confirms that the sensing of Ni(II) ion at Pt-MWCNT-IIP is a reliable method for the determination of Ni(II) ion in real samples.

5 Extraction studies

The effect of solvent on Ni(II) ion binding by MWCNT-IIP, IIP, MWCNT-NIP, and NIP were carried out using water, methanol, and acetonitrile as shown in the Fig. S6. From the Figure, it is understood that the binding is better in water which was used as the porogen during ion imprinting.

To assess the effect of concentration of Ni(II) ion on its binding, different concentration of Ni(II) ion ranging from

Table 2 Determination of Ni(II) ion in real samples by modified platinum electrode

Modified electrode	Samples	Ni(II) ion		Detected (%)
		Found (ppm)	Detected (ppm)	
Pt-MWCNT-IIP	Lake water	0.843	0.850 ± 0.0010	99.17 ± 0.0020
	Steel industry	4.89	4.912 ± 0.0016	99.55 ± 0.0012
	Electroplating industry	5.12	5.165 ± 0.0011	99.13 ± 0.0010
Pt-MWCNT-NIP	Lake water	0.843	0.528 ± 0.0010	62.63 ± 0.0001
	Steel industry	4.89	3.05 ± 0.0021	62.37 ± .0002
	Electroplating industry	5.12	3.15 ± 0.0009	61.52 ± .0012

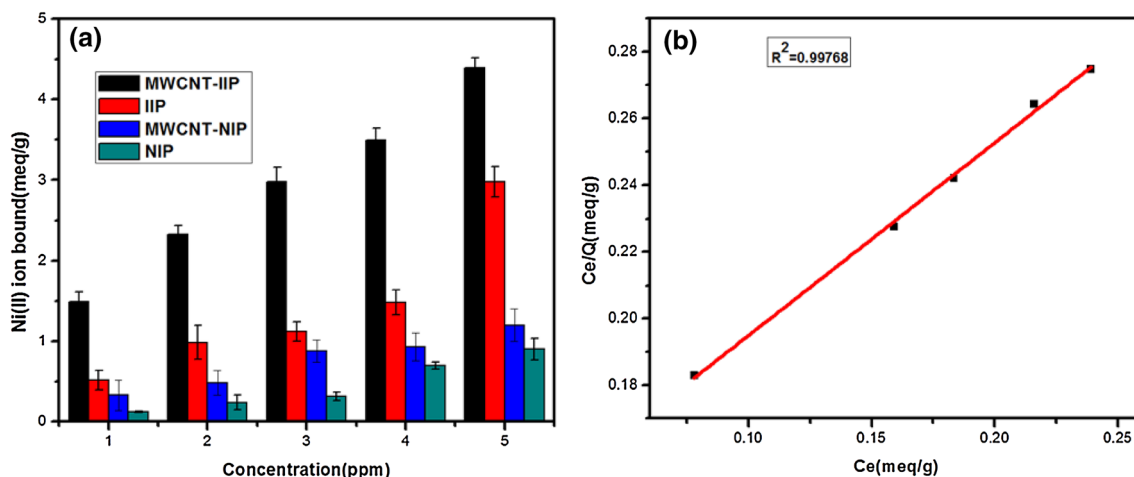


Fig. 8 a Effect of concentration of Ni(II) ion on its adsorption by MWCNT-IIP, IIP, MWCNT-NIP, and NIP b Langmuir adsorption isotherm of Ni(II) ion MWCNT-IIP

1 to 5 ppm were equilibrated with MWCNT-IIP, IIP, MWCNT-NIP, and NIP (Fig. 8a). It was found that the adsorption capacity increases from 1 to 5 ppm in each case. On comparing the binding capacity of different adsorbent, greater adsorption is found for MWCNT-IIP due to the incorporation of nanostructure into the polymer matrix which results in the high availability of binding sites and collision between binding sites in MWCNT-IIP and Ni(II) ion takes place. The weak adsorption of IIP, MWCNT-NIP, and NIP is due to the nonexistence of the imprinted layer in the polymer matrix. The Ni(II) ion adsorption data on MWCNT-IIP was fitted with Langmuir adsorption isotherm model with R² value 0.99768. Figure 8b implies that the adsorption process is mainly monolayer with a homogenous distribution of binding sites on the surface of MWCNT-IIP.

The adsorption of Ni(II) ion on different adsorbents such as MWCNT-IIP, IIP, MWCNT-NIP, and NIP are pH dependent. The Ni(II) ions show low affinity of binding at pH > 7.0 and maximum affinity at pH 7 (Fig. S7). At lower pH low adsorption of Ni(II) ion taken place due to the protonation of methacrylate ion diminishing the complexing ability of Ni(II) ion. As the pH values increase the binding sites get deprotonated, therefore, the negatively charged binding

sites increases favouring the adsorption of Ni(II) ion. At high pH due to the high concentration of hydroxide ion, precipitate is formed between Ni(II) ion and hydroxide ions thus adsorption is again decreased.

The adsorption of Ni(II) ion towards MWCNT-IIP, IIP, MWCNT-NIP, and NIP were studied as a function of time and shown in Fig. 9a. From the Figure, it is clear that the adsorption of Ni(II) ion increases with time and reaches equilibrium at 40 min. This may be due to the availability of binding sites in the initial stage and the template once bound in the cavity becomes unavailable for further Ni(II) ion binding. In the final stage the binding sites are saturated and the rate of binding decreases. The data obtained from the kinetic studies of Ni(II) ion binding to MWCNT-IIP is fitted with pseudo-second-order [28] with the R² value of 0.9987 and rate constant of 0.5612 (Fig. 9b).

The selectivity of MWCNT-IIP, IIP, MWCNT-NIP, and NIP toward Ni(II) ions were carried out with metal ions such as Cu(II), Fe(II), and Zn(II) ions. From the Fig. 10, it is clear that the binding capacity of MWCNT-IIP towards other metal ions are much lower than that of Ni(II) ion which confirms that MWCNT-IIP has a good selectivity towards the detection of Ni(II) ion. The selective binding for Ni(II)

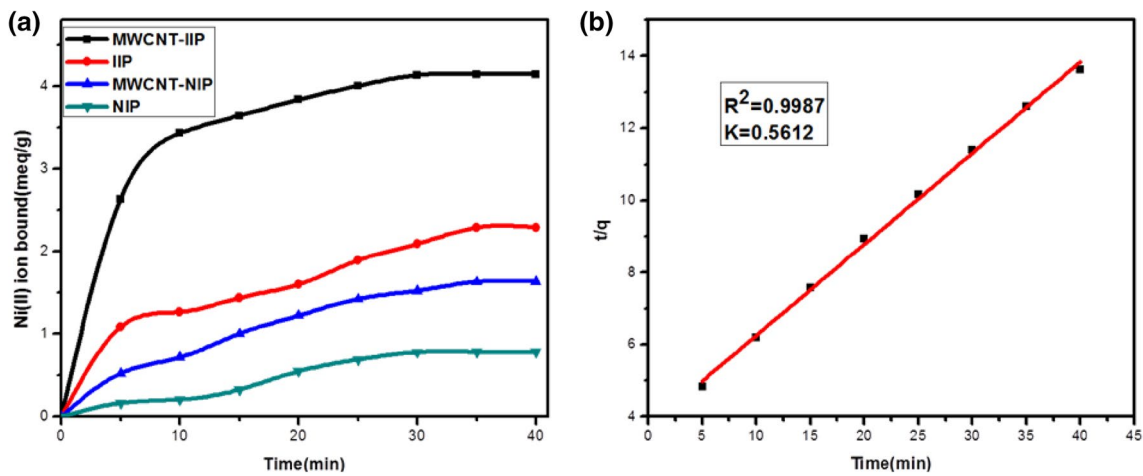


Fig. 9 **a** Effect of time on the adsorption of Ni(II) ion on MWCNT-IIP, IIP MWCNT-NIP, and **b** pseudo-second order kinetics for the adsorption of Ni(II) ion on MWCNT-IIP

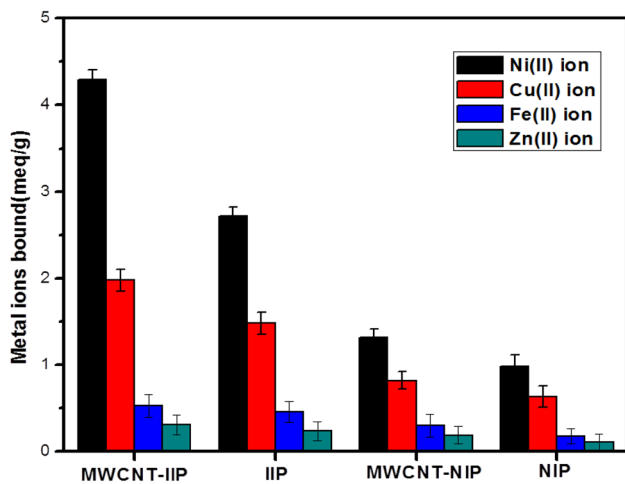


Fig. 10 Selectivity of Ni(II) ion with various metal ions on the different adsorbent

Table 3 Selectivity factors of adsorbent vs Ni(II)

Metal ions	$\alpha_{MWCNT-IIP} / \alpha_{MWCNT-NIP}$	$\alpha_{IIP} / \alpha_{NIP}$
Ni(II), Cu(II)	8.51	5.32
Ni(II), Fe(II)	2.31	1.55
Ni(II), Zn(II)	1.95	1.12

ion on MWCNT-IIP may be ascribed to the complementary cavities created in the MWCNT-IIP during the imprinting process. The selectivity factor was calculated and tabulated in Table 3. From the table it is clear that Ni(II) ion imprinted polymer showed high selectivity towards Ni(II), Cu(II) mixture and less selectivity for Ni(II), Zn(II) mixture and moderate selectivity towards Ni(II), Fe(II) mixture.

The influence of synthesized imprinted polymer on Ni(II) ion sorption was investigated by varying adsorbent dosage from 10 to 50 mg by keeping the concentration of Ni(II) ion constant. From the Fig. S8, it is seen that as the amount of adsorbent increases the extraction efficiency of Ni(II) ion also increases due to the increase in the number of binding sites in the adsorbent. On comparing the effectiveness of adsorption of different sorbent, MWCNT-IIP shows greater adsorption due to the increase in surface to volume ratio. MWCNT-NIP and NIP exhibit a reduced extent of adsorption due to the nonexistence of binding sites in the polymer matrix.

To check the reusability of MWCNT-IIP, IIP, MWCNT-NIP and NIP adsorption-desorption experiments were conducted. The saturated imprinted polymer can be easily restored by washing with porogen used for the polymerization process. The imprinting process becomes economical only when the adsorbent used for the imprinting process is regenerated. The experiment showed that even after five cycles of repeated desorption and sorption, the Ni(II) binding remains same for all adsorbents (Fig. S9).

5.1 Application of synthesized imprinted MWCNT-IIP and MWCNT-NIP for the extraction of Ni(II) ion from real samples

The application of the MWCNT-IIP and MWCNT-NIP was studied by using real samples collected from lake, steel and electroplating industries. The recoveries of Ni(II) ion were determined for these samples by imprinted MWCNT-IIP and MWCNT-NIP using AAS. The results show the appropriateness of MWCNT-IIP for the extraction of Ni(II) ion from the real samples (Table 4).

Table 4 Analysis of the real sample

Polymer adsorbent	Real samples	Ni(II) ion		Recovered (%)
		Found (ppm)	Recovered (ppm)	
MWCNT-IIP	Lake water	0.642	0.646 ± 0.001	99.40 ± 0.002
	Steel industry	3.891	3.915 ± 0.003	99.38 ± 0.001
	Electroplating industry	4.51	4.55 ± 0.001	99.12 ± 0.001
MWCNT-NIP	Lake water	0.642	0.399 ± 0.0020	62.15 ± 0.0010
	Steel industry	3.891	2.437 ± 0.0010	62.63 ± 0.0030
	Electroplating industry	4.51	2.880 ± 0.0030	63.8 ± 0.0021

Table 5 Comparative studies of a modified platinum electrode with other reported sensors

Different methods	Limit of detection (µM)	Reference
Electrochemical sensor	6.7	[29]
Fluorescent sensor	0.98	[30]
Colorimetric sensor	0.5	[31]
PVC plasticizer sensor	0.18	[32]
Pt/MWCNT-IIP sensor	0.028	This work

The limit of detection of this work was compared with the other reported Ni(II) ion sensors and summary of the results is given in Table 5. Accordingly, the other entire sensors except the present sensor had poor detection limit. Thus it can be considered that Pt/MWCNT-IIP sensor has a good position to detect the Ni(II) ion in environmental samples.

6 Conclusion

In summary, a novel electrochemical sensor for the determination of Ni(II) ion was developed by fabricating nanolayer of the Ni(II) ion imprinted polymer on platinum electrode. The good electrochemical property and large surface area of vinyl functionalized MWCNT and the template memory cavity of IIP made MWCNT-IIP as a good adsorbent of Ni(II) ions. MWCNT-IIP modified Pt electrode found to have linear calibration range from 1 to 5 ppm for Ni(II) ion sensing by cyclic voltammetry. The detection limit of Pt/MWCNT-IIP was found to be 0.028 µM using DPV. Pt/MWCNT-IIP provides a cost-efficient approach for the sensing of Ni(II) in real samples. The effect of concentration, time, pH, reusability etc was studied in details. The synthesized imprinted MWCNT-IIP has also been successfully applied for the extraction of Ni(II) ion. In the extraction studies, kinetic data are in agreement with pseudo-second-order kinetics. Selectivity studies showed that

MWCNT-IIP has a higher affinity towards Ni(II) ion in the presence of other metal ions. At last, we can conclude that MWCNT-IIP can be used as a keen sensor and for the extraction of Ni(II) ion from real samples.

Compliance with ethical standard

Conflict of interest The author(s) declare that they have no competing interest.

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