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NEW GENERATION OF ELECTROCHEMICAL SENSOR FOR SUB-NANOMOLAR ZN (II) ION DETECTION BASED ON NANO- SIZED ION IMPRINTED POLYMER AND FUNCTIONALIZED MULTI-WALLED CARBON NANOTUBE COMPOSITE MODIFIED GLASSY CARBON ELECTRODE

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Abstract : A new selective and sensitive electrochemical sensor was prepared by film coating of Zinc (II) ion imprinted polymer (IIP) nanoparticle and functionalized multi-walled carbon nanotube (MWCN) composite on glassy carbon electrode (GCE). The prepared electrochemical sensor was applied for the sensitive determination of Zinc (II) ion by square wave anodic stripping voltammetry (SWASV) method. The GCE/IIP-MWCNT modified electrode showed improved electrochemical behavior as compared to bare GC electrode. An optimum procedure was used for the fixation of Zn(II)-8-hydroxyquinoline to styrene-ethylene dimethacrylate copolymer and the resultant IIP nanoparticles characterized by Fourier Transform Infrared (FTIR), thermal gravimetric analysis (TGA), and scanning electron microscopy (SEM). The effects of different experimental variables such as pH, deposition time, and deposition potential were optimized for electrochemical determinations. The resultant IIP showed a selective sorbent for Zinc (II) ion. Functionalized MWCNT was applied in construction of as prepared modified electrode, exhibits large surface area, enhanced electron transfer kinetics, and improved Zn (II) ion diffusion. Under the optimal conditions, the resulting calibration curve exhibited a linear response within a concentration range of 5×10^{-12} to 15×10^{-8} mol/L-1 with excellent detection limit 5×10^{-12} mol/L-1. Finally, the method was successfully applied for the determination of zinc (II) ion in the real water samples, and the obtained results were verified by inductively coupled plasma (ICP).

Keywords: Ion Imprinted Polymer; Multi-walled Carbon Nanotube, Square wave Anodic Stripping Voltammetry, Glassy carbon electrode.

摘要 : 通过在玻碳电极 (GCE) 上包覆锌 (II) 离子印迹聚合物 (IIP) 纳米颗粒和功能化多壁碳纳米管 (MWCN) 复合材料, 制备了一种新型选择性灵敏的电化学传感器。将制备的电化学传感器应用于方波阳极溶出伏安法 (SWASV) 法灵敏测定锌 (II) 离子。与裸 GC 电极相比

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· GCE/IIP-MWCNT 改性电极显示出改进的电化学行为。使用最佳程序将 Zn(II)-8-羟基喹啉固定到苯乙烯-乙烯二甲基丙烯酸酯共聚物上，并通过傅里叶变换红外 (FTIR)、热重分析 (TGA) 和扫描电子显微镜 (SEM) 表征所得 IIP 纳米粒子)。为电化学测定优化了不同实验变量 (如 pH 值、沉积时间和沉积电位) 的影响。所得 IIP 显示出对锌 (II) 离子的选择性吸附剂。功能化的多壁碳纳米管应用于制备的修饰电极的构建，具有大的表面积、增强的电子转移动力学和改善的 Zn (II) 离子扩散。在最佳条件下，所得校准曲线在 5×10^{-12} 至 15×10^{-8} mol/L-1 的浓度范围内表现出线性响应，检测限为 5×10^{-12} mol/L-1。最后，将该方法成功应用于实际水样中锌(II)离子的测定，所得结果经电感耦合等离子体(ICP)验证。

关键词：离子印迹聚合物；多壁碳纳米管，方波阳极溶出伏安法，玻碳电极。

1. Introduction

Analysis of Zinc (II) ion is very important not only from the biochemical point of view but also from the environmental one. Zinc (II) ion plays a central role in a variety of fundamental biological processes such as in cell reproducing and nucleic acid metabolism, and its low physiological concentration is connected with some pathological processes like retarded growth and immunity dysfunctions [1]. On the other hand, contamination of waters by Zinc (II), as a heavy metal ion, causes a worldwide environmental problem [2, 3]. Zinc (II) is often found in effluents discharged from industries [2-4]. The maximum acceptable Zinc (II) concentration in drinking water is 5 mg/L and toxicity for humans is 100-500 mg/d [5]. Therefore, determination and removing excess of Zinc (II) from wastewater is of great important.

Several techniques have been developed for the measurement of Zinc (II) such as spectrophotometric [6], chromatographic [7] and electrochemical [8]. Among these techniques, electrochemical techniques are an efficient one due to their fast response, excellent selectivity, high sensitivity, simplicity and low cost. Anodic

stripping voltammetry (ASV) is a commonly used electrochemical technique for electrochemical trace metal ion analysis. This technique comprises preconcentration and stripping steps, so in the first step, metal ions at a low concentration accumulated on the electrode surface which improves sensitivity and detection limit [9-11]. In trace analysis of metal ions, ASV is the most popular with square wave voltammetry (SWV) technique [12-14]. In these studies, many different electrodes are used, among them GCE offer many useful properties of low background current, low cost, wide potential windows and easy surface modification [15-16]. Whilst, bare GCE has useful properties, reports have shown shortcomings associated with use of bare GCE, such as its small surface area and sensitivity due to slow electron transfer kinetics on it [17-18].

However, the electrochemical performances of working electrodes have been improved by modification especially with multi-walled carbon nanotube (MWCNT) as a carbon-based nanomaterial owing to its remarkable active surface area, chemical inertness, high strength, and low charge-transfer resistance in both

aqueous and non-aqueous solutions [19-30]. Here we used functionalized MWCNT based ion imprinted polymer (IIP) as a modifier for GCE modification.

Today, IIP materials, as a class of smart polymers, containing a large number of metal ion recognition cavities were designed for the selective recognition and separation of target metal ions, due to its low cost, outstanding selectivity, and high electrochemical stability [30-32]. These polymers are prepared by using metal ions with a functional monomer used as a complexing agent in presence of cross-linking agent and initiator. Then, strong acid is used to leach out the metal ion from the imprinted polymer to form selective template cavities [33-37]. During the IIPs synthesis, the morphology of the prepared particles can be controlled by varying the experimental conditions such as solvent volume, temperature and stirring speed of polymerization solution, specially the cross-linker/monomer feed ratio as a decisive factor in selective adsorption of target metal ions [38, 39]. In this study, a novel electrochemical sensor for Zn (II) ion sensing was constructed by ion imprinting approach in the cross-linker/monomer feed ratio of 8. The synthesized IIP nanoparticles and its behavior after removing zinc (II) ions were described. The IIP and functionalized MWCNT nanocomposite was utilized for modification of GCE. Functionalized MWCNT was used to increase the surface area, enhance electron transfer kinetics, and facile Zinc (II) diffusion, resulting enhancement in modified electrode sensitivity. The electrochemical behaviors of Zinc (II) were studied in detail on modified electrode. After optimization of parameters, the calibration curve was prepared and its linear regression and limit of detection (LOD) were determined. The

prepared modified electrode was successfully applied to determine Zinc (II) ion concentration in the real sample.

2. Experimental

2.1. Instrumentation and Measurement Conditions

Electrochemical measurements were carried out using a Metrohm Autolab potentiostat/galvanostat (model 302N) under pure Argon atmosphere. A conventional three-electrode electrochemical cell was used in which modified GCE as a working electrode, saturated Ag/AgCl as a reference electrode, and platinum electrode served as counter electrode for electrochemical measurements. A BRUCKER vector 22 FT-IR spectrophotometer was applied to characterize imprinted and non-imprinted polymers using the KBr pressed disk method in the scan wave number range of 400-4000 cm^{-1} . The morphology of the IIP-MWCNT film was characterized by Scanning electron microscope (SEM, Philips model XL 30) Thermogravimetric analyzer (TGA, Rheometric scientific, Model STA1500) was used to evaluate a thermal stability of prepared IIPs.

2.2. Chemical and Solutions

Zinc Chloride tetrahydrate ($\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$), 8-Hydroxyquinoline (oxine), MWCNTs, 2,2'-azobisisobutyronitrile (AIBN), Ethylene glycol dimethacrylate (EGDMA), styrene, 2-methoxyethanol, Nafion solution (5wt%), and Hydrochloric acid were obtained from Fluka. All the above chemicals were of analytical grade and used as received without any further purification. Double distilled deionized water was used for preparation of solutions.

2.3. Preparation of Zn (II) ion imprinted and non-imprinted polymeric nanoparticles

A thermal polymerization technique was used to prepare the Zn (II) imprinted nanobeads. For this purpose, 1 mmol of Zn^{2+} , as imprint metal ion and 2 mmol of oxine, as ligand were added into 10 mL of 2-methoxyethanol, as porogen solvent and continuously stirred for 15 min to proceed complexation reaction. Then, 32 mmol EGDMA, as cross linker agent, 4 mmol styrene, as monomer, and 0.3 mmol AIBN as initiator, were added to the above mixture and to avoid polymerization retardation, nitrogen gas purged for 10 min to remove molecular oxygen from it, then sealed. The reaction vial was set-up in oil bath at 60°C for 24 h under magnetic stirring to complete the thermal polymerization. After polymerization, the resulting light yellow products were washed several times with deionized water, dried and then grinded. The obtained IIP nanoparticles, were used to leaching process under stirring condition with 6 mol L⁻¹ HCl for 12 h for removing Zn (II) ion and produce polymer cavities. Then, the precipitated particles were washed using high purity deionized water until a neutral pH value is set. Finally, the obtained white IIPs powders were dried at 60°C under vacuum condition. The non-imprinted polymer (NIP) was prepared in the similar manner to that of the IIP, but in the absence of Zn (II) ion. The prepared IIP and NIP were used to fabrication of modified GCE.

2.4. Preparation of IIP-MWCNT/GCE Modified Electrode

Prior to use, MWCNTs were functionalized by oxidative treatments with a mixture of nitric acid and sulfuric acid solution to enhance adsorption of Zinc (II) ions with imposed oxygen-containing

functional groups on MWCNTs at the preconcentration steps. Oxidation methods are an effective method to functionalize the surface of MWCNTs, but a bad control of the oxidation conditions causes serious structural damage in MWCNTs. To avoid MWCNT destruction, promote and increase in the -COOH groups onto MWCNTs surface, we followed the optimal condition to perform functionalization of MWCNTs as reported by L. Thi et al. [40]. Briefly, MWCNT was refluxed in a 1:3 mixture of 4.0 M HNO₃/10.0 M H₂SO₄ at the treatment time of 18 hours then washed with double distilled deionized water several times for acid neutralization, finally the functionalized MWCNTs were dried. To prepare IIP-MWCNT/GCE modified electrode, the bare GCE was polished with 0.05 μm Al₂O₃ slurry on a polishing micro-cloth and then washed by acetone and deionized water to remove the residues. Next, a homogenized IIP-MWCNT mixture was prepared by dispersing functionalized MWCNTs and IIP nanoparticles in deionized water and 0.5% Nafion, using a low power sonicator to form a stable dispersion for 15 min. A 10 μL aliquot of prepared dispersion was dropped on the GCE surface and left to dry in air before being used.

2.5. Electrochemical Measurements

All measurements were performed in a 50 mL solution containing HCl (pH 3.7) as a supporting electrolyte. The solution was transferred into a dry electrochemical cell and was purged by high purity argon gas for 10 min before performance of SWASV measurements. The preconcentration step was carried out at stirring speed of 650 rpm. The voltammogram was recorded between -0.4 and +0.4 V by applying

square-wave modulation with 0.0015 V step amplitude, 0.02 V pulse amplitude, and frequency of 8 Hz. All experiments were performed at room temperature.

3. Results and discussion

3.1. Characterization of Zn (II) Ion Imprinted Polymer Particles

The resulting IIP nanoparticles obtained from thermal copolymerization were characterized by FT-IR spectroscopy, scanning electron microscopy (SEM) and thermal gravimetric analysis (TGA).

Fig. 1 shows the registered FT-IR spectra of the un-leached (NIP) and leached IIP nanoparticles. A comparison of the two polymers spectra shows the similarity between two polymeric backbones (3557.06 cm^{-1} for OH, 2953.45 cm^{-1} for C-H stretching vibrations of the aromatic and aliphatic system, 1730.80 cm^{-1} for carbonyl group, 1635.34 cm^{-1} , 1459.85 cm^{-1} , and 1159.01 cm^{-1} for C-O aromatic ring bending vibrations). At the same time, there are evident differences between the leached and un-leached IIPs. The presence of the strong and broad bands around 3557.06 cm^{-1} are related to the free -OH groups in leached IIP, but in the un-leached polymer the strength of this band is weakened due to the interaction of Zn(II) ion with deprotonated OH group in oxine. Therefore, during leaching process only the Zinc (II) ion is removed from the polymeric network and the structure of oxine ligand dose not affected by leaching process.

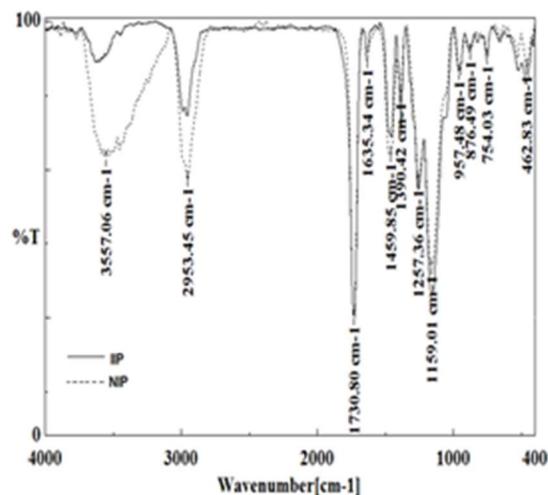


Fig. 1

In addition, the morphological structure of IIP-MWCNT film on modified GCE was evaluated by SEM. Fig. 2 shows the entangled network structure of functionalized MWCNTs entrapped into the globular IIPs nanoparticles and proves the more rigid composite formation accompany with accessible nanopores. It is clear that, the irregularity in nanopolymer size is observed but the most portions of the IIP particles are below 50 nm. However, it is well recognised that, in this type of polymerization, the morphology of the individual particles can be improved by varying the experimental conditions [38]. The prepared nanobead provides more available surface area for Zn (II) ions diffusion into the polymer.

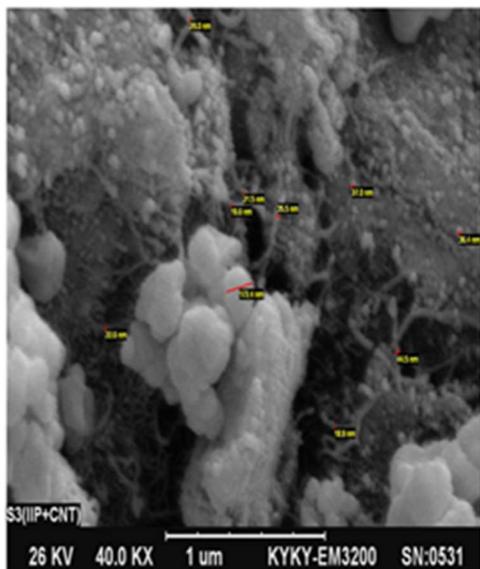


Fig. 2

For further investigation, the resulting IIP nanoparticles were characterized by thermogravimetric analysis (TGA). We have studied the thermal decomposition of this polymer in inert gas. The TGA curve shows the high thermal stability of this synthesized polymer (up to 300°C) (Fig. 3).

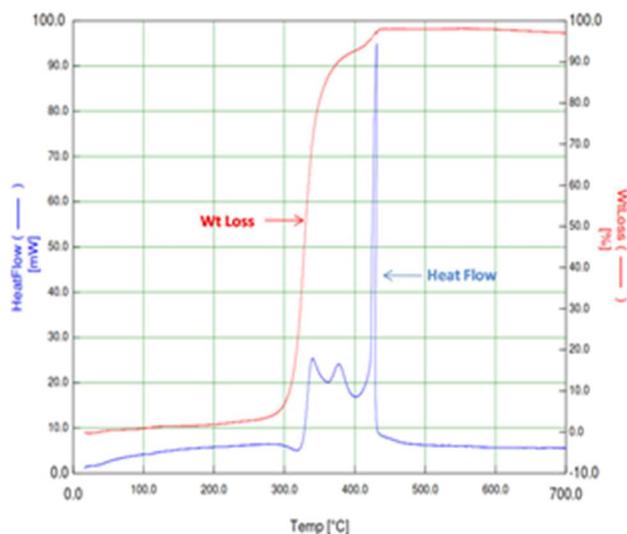


Fig. 3

3.2. Cyclic Voltammetry and Electrochemical Impedance Spectroscopy of IIP-MWCNT Film on Modified GCE

CV and EIS techniques were employed to characterize the modified electrode. Fig. 4A shows the CVs of 5 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ measured at bare GCE and modified IIP-MWCNTs/GCE electrodes in a 0.1 mM phosphate buffer solution (pH 7.0), recorded at scan rate of 50 mV/s.

As seen, the peak current at IIP-MWCNT/GCE is increased over that at the bare GC electrode. A pair of well-defined quasireversible redox peaks stands for the reduction and oxidation of $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple. The significant difference between the two CVs indicates the successful dispersion of MWCNTs into the IIP bulk. This results demonstrate that the successful dispersion of MWCNTs into the IIP opens an efficient path for ET between $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple and GCE by enhancing charge transfer kinetics [41].

EIS technique was applied in order to investigate the interfacial properties of the modified electrode. This technique is a powerful one for probing the conductivity properties of the coated films. Nyquist diagrams for 5.0 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ redox probe (1:1 molar ratio) in 0.1 M phosphate buffer solution (pH 7.0) for bare and modified electrode are showed in Fig. 4B. As it is seen, the resulting Nyquist plots shows a semicircle domain at higher frequencies reflects the electron transfer kinetics of the surface with a diameter equal to the charge transfer resistance (R_{ct}); while the linear part at lower frequencies corresponds to the diffusion process. The R_{ct} value, derived from the semicircle domain of the EIS plot, was found to be 2k Ω for GCE (Fig. 4B). However, the dramatically decrease of R_{ct} after modification of GCE with IIP-MWCNTs, indicated that electron transfer was much more efficient onto the modified electrode. The EIS result was consistent with the cyclic voltammetry

and both techniques showed successful modification of GCE.

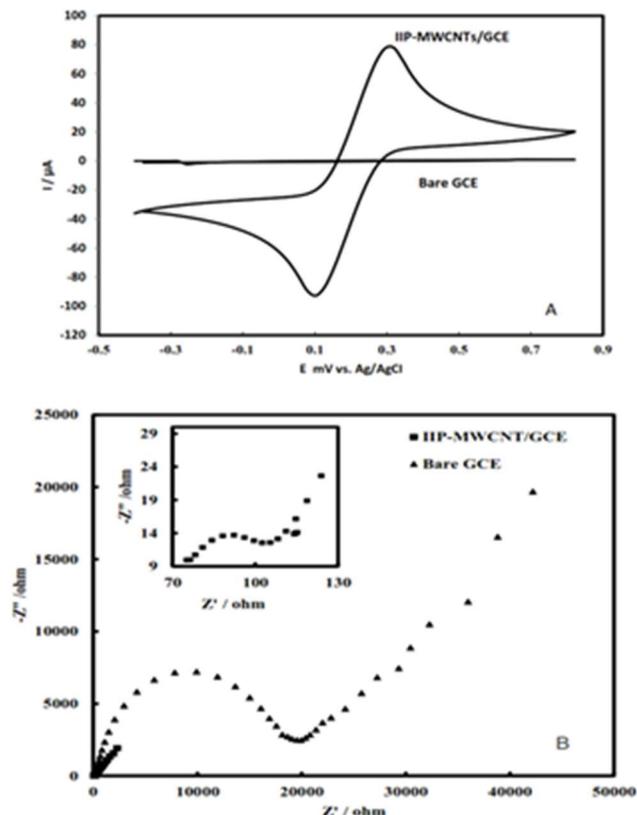


Fig. 4

3.3. Influence of the pH Value on Peak Current

As the sorption and desorption of metal ions into IIPs be considerably affected by solution pH, therefore, it is the first and most important parameter that should be optimized to find the most suitable condition for Zn (II) ion detection. Voltammograms were obtained using modified electrode for a zinc (II) solution of 1.0×10^{-6} mol L^{-1} in HCl according to the variation of the pH values in the range of 1.0 to 5.0. Several electrolytes were tested as a supporting electrolyte (Sodium Acetate, Sodium Nitrate, Sodium Citrate and HCl), but HCl gave the best response. The pH dependence of the anodic peak intensities is shown in Fig. 5. The results

revealed a gradually increased in the intensity of zinc (II) signal by increasing pH of solution with the best peak height at pH 3.7. The low analytical signal was observed at pH values lower than 3.7, probably due to competition between Zn (II) and H^+ ion to capture polymer binding sites. The solutions with higher pHs were not investigated because of Zinc (II) ion hydrolysis and its precipitation possibility, which decreases Zn (II) concentration in sample solution. Based on these results, HCl solution of pH 3.7 was chosen to be used in subsequent studies.

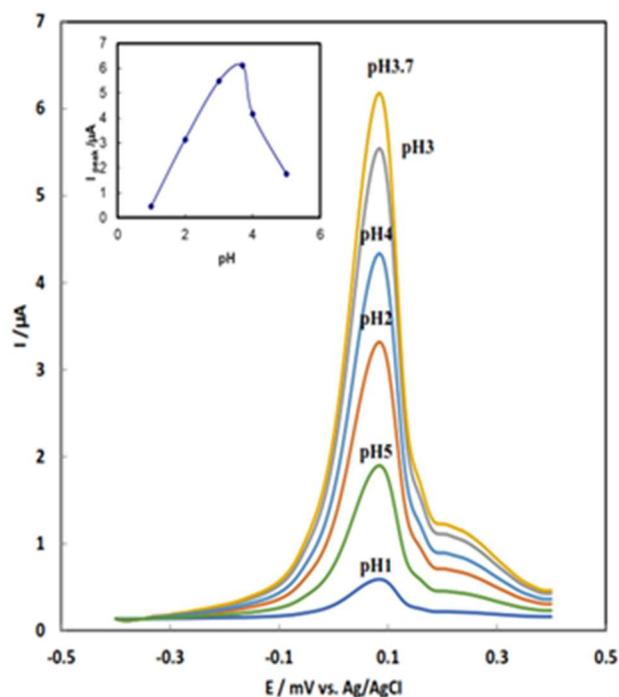


Fig. 5

3.4. Effect of Deposition Time and Potential

Preconcentration time is the main parameter in SWASV response of Zn (II) ions and resultant has an outstanding effect on sensitivity of the modified electrode. The preconcentration time was checked in the range of 100 to 1100 s to find the maximum electrochemical signal by applying the constant potential, -500 mV in HCl solution (pH 3.7). Fig. 6A shows an improvement in

response of Zinc (II) ion with increasing preconcentration time suggesting that a high amount of Zinc (II) ions were concentrated at the modified electrode surface. The maximum electrochemical signal occurs at 800 s of contact time therefore it was chosen to be employed in subsequent studies although a longer accumulation time is recommended for zinc determinations at concentrations close to detection limit.

In order to obtain the best value of applied potential for zinc (II) ion detection, the effect of preconcentration potential was investigated at -100 to -900 mV in Zinc(II) concentration of 1×10^{-6} M and deposition time of 800 s (pH 3.7). Fig. 6B shows the correlation of the anodic peak current intensity with the value of the applied potential. The results showed that the current intensity considerably increases first and reaches to the maximum at -400 mV, and then decreases. At more negative potential values the current decreases greatly, probably because of hydrogen evolution at the more negative potential. Thus, the optimum preconcentration potential should be -400 mV for sensitive subsequent experiments.

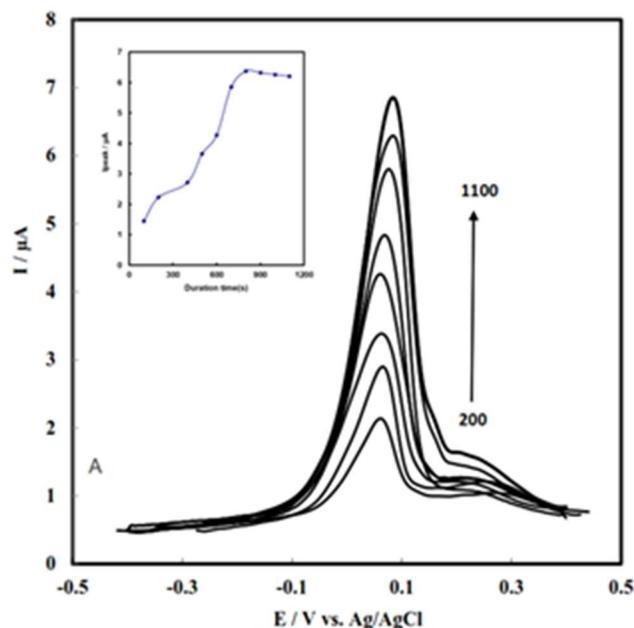


Fig. 6A

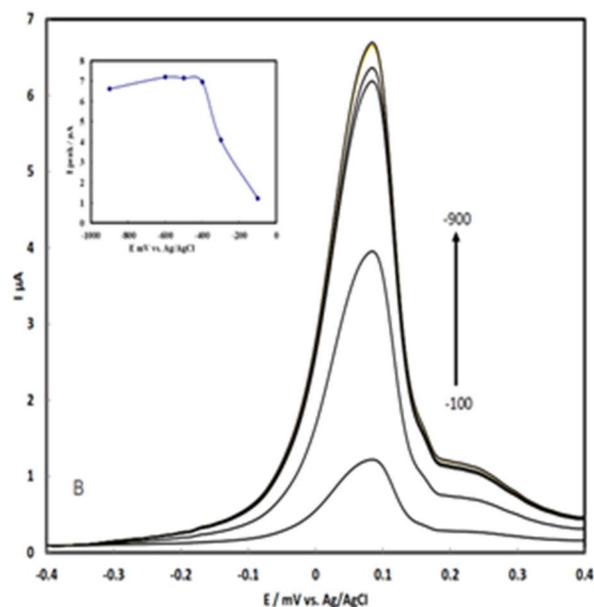


Fig. 6B

3.5. Calibration Curve

The analytical performances of the modified electrode for Zn (II) ion determination were evaluated under the best set of operational conditions. As shown in Fig. 7, the anodic response was linear with the concentration of Zinc (II) ranging from 0.001 to 1.5 nM, with a

correlation coefficient of 0.9987. The lowest detectable concentration (three times the blank signal/slope) of Zn (II) at accumulation time of 1000 s was evaluated to be 5×10^{-12} M, which indicates the sensitivity of the IIP-MWCNT/GCE. The relative standard deviation for ten replicate measurements of 2.0 nM of zinc (II) ion was found to be 3.3%. The reproducibility was evaluated by fabrication of three modified electrode under the same conditions. The RSD 4.1% resulted, suggesting that the IIP-MWCNT/GCE exhibits accurate reproducibility towards the determination of zinc (II) ion.

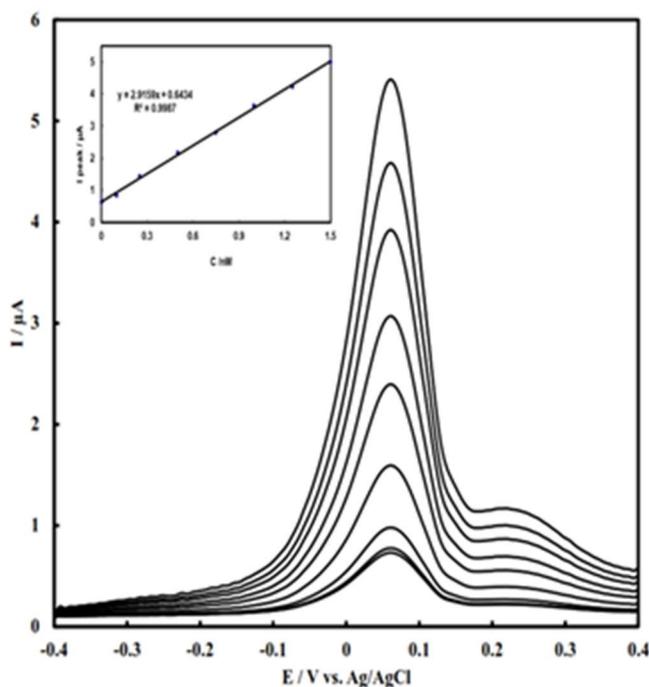


Fig. 7

In order to examine the reusability, the IIP-MWCNT/GCE was subjected to 16 times of detection/elution cycles under optimal conditions. After each use, 5.0 mL of 6 M HCl solution was used for elution of the adsorbed Zn (II) ions and regeneration of the IIP. The experiments showed that, the modified electrode lose its adsorption capacity by about 4.9% after

16 repeated uses. Thus, the IIP-MWCNT/GCE could repeatedly be used with high efficiency in selective detection of Zn (II) ions from aqueous solutions.

The electrochemical signal of Zinc (II) ion was investigated in the presence of some possible interference from common metal ion such as: Ni^{2+} , Co^{2+} , Cd^{2+} and Cu^{2+} . Voltammetric detection was performed in the presence of excess amount of these interferent ions. The change in Zinc (II) response was less than 4.5% in the presence of the above interferent ions. This means that there was no interference on the Zn (II) determination.

To evaluate the potential practical applications, the IIP-MWCNT/GCE was also used for determination of trace levels of Zn (II) ion in real samples under optimized conditions. The results for the analysis of tap water samples are summarized in Table. 1. Three replicates were analyzed by using the same electrode. The results obtained by the proposed method were in satisfactory agreement with those obtained by the ICP analysis as presented in Table 1. These findings clearly demonstrate that the constructed sensor could be applied for precise and accurate determination of trace-level of Zn (II) ion in real samples. A comparison between the proposed sensor and our previously reported ones [42] clearly shows that the high efficiency of the prepared sensor are related to the synergic effects of functionalized MWCNT and nanoparticle sized IIPs that produced in controlled ratio of cross linker/monomer equal to 8.

Table. 1

Sample	Concentration of zinc (μM)	
	Proposed method	ICP
Tape water1	5.29 \pm 0.01	6.1 \pm 0.02
Tape water2	5.76 \pm 0.01	6.38 \pm 0.02

Conclusion

A novel electrochemical sensor was developed for determination of Zn (II) ion by SWASV technique, through modification of GCE by IIP/MWCNT nanocomposite material. The nanocomposite material was successfully characterized by FT-IR, TGA, and SEM. The oxygen functionalized MWCNT was used to enhance the surface area, electron transfer kinetics, and enhance Zinc (II) diffusion during an electrochemical process. Under optimal conditions, the IIP/MWCNT exhibited an excellent electrochemical performance toward Zn (II) ions together with a wide linear range, high sensitivity, a low limit of detection (5×10^{-12} mol/L-1), and good repeatability. The fabricated sensor was also applicable in monitoring the Zinc (II) in real samples from tap water.

Acknowledgements

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Figure Captions

Fig.1 The FT-IR spectra of un-leached (NIP) and leached zinc imprinted polymers (IIP)

Fig.2 The SEM image of the three-dimensionally microporous structure of IIP-MWCNT films on the GCE surface

Fig.3 TGA curve of synthesized IIP

Fig.4 (A) Cyclic voltammograms of bare GCE and IIP-MWCNT/GCE modified electrode in presence of 5 mM K₄Fe(CN)₆, 0.1 M phosphate buffer solution (pH7.0) at a scan rate of 50 mVs⁻¹. (B) Nyquist plots for bare GCE (▲) and IIP-MWCNT/GCE (■) in 5 mM Fe(CN)₆³⁻/Fe(CN)₆⁴⁻, 0.1 M PBS solution (pH7.0), and at potential 250 mV. The frequency was swept from 100 to 0.01 kHz; modulation potential 10 mV

Fig.5 Effect of pH upon the stripping voltammetric response of 1.0×10⁻⁶ M Zn (II). The square wave voltammograms were recorded at scan rate of 50 mVs⁻¹; pulse amplitude, 50 mV

Fig.6 (A) Effect of accumulation time upon the response to 1.0×10⁻⁶ M Zn (II) after accumulation potential of -500 mV and pH 3.7 at scan rate of 0.05Vs⁻¹ and pulse amplitude of 0.05 V.(B) Effect of accumulation potential upon the response to 1.0×10⁻⁶ M Zn (II) after accumulation for 800s

Fig.7 Square wave Stripping voltammograms for concentration of Zn (II) from 0.001- 1.5 nM. The square wave voltammograms were recorded at scan rate of 0.05 V s⁻¹ and pulse amplitude of 0.05 V. Accumulation time and the accumulation potential were 800 s and -400 mV, respectively. (Inset) Calibration curve of Zn (II)