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Original scientific paper

# Synthesis of Fe-based metal organic framework/MWCNTs for modification of glassy carbon electrode: application in the efficient stripping voltammetric determination of Pb(II) ions

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***Abstract***

*In the present work, a composite of multi-walled carbon nanotubes (MWCNTs) and Fe-based metal-organic framework (Fe-MOFs) has been prepared and utilized to construct modified glassy carbon electrodes (MGCE) by the drop-casting method. The MWCNTs/Fe-MOF-MGCE was used as a simple and sensitive electrochemical sensing platform for detecting Pb(II) ions. It has been found that modifying the GCE surface with MWCNTs/Fe-MOF significantly increased the Pb(II) stripping peak current. The effect of different parameters and conditions, such as pH of the supporting electrolyte solution, accumulation time and accumulation potential on the designed sensor's response, were evaluated. Square-wave anodic stripping voltammetry is used for the sensitive determination of Pb(II). Under optimal conditions, a linear dependence was observed between the anodic peak current of Pb(II) and its concentration in the range of 0.4 to 240.0 ng $mL^{-1}$. The limit of detection of the MWCNTs/Fe-MOF/MGCE was determined to be 0.1 ng $mL^{-1}$ for Pb(II) determination. Finally, the designed method was successfully used to determine Pb(II) ions in water samples, with high recoveries and low relative standard deviations, showing its applicability.*

**Keywords**

Lead(II) ion detection; heavy metal analysis; electrochemical sensing platform; environmental monitoring

## Introduction

The fast pace of industrialization, propelled by increased levels of both industrial production and mining activities, has significantly elevated heavy metal releases to the natural environment, leading to various environmental and public health concerns [1,2]. As predominantly human-driven contaminants, heavy metals present a persistent problem that societies worldwide continue to confront. Because of their non-degradability, these metals persist in the environment, bioaccumulate along food chains, and ultimately enter the human body, posing significant toxicological risks [3].

Lead(II) is a toxic heavy metal ion (HMI) and exhibits severe toxicity even at trace levels [4]. Pb(II) ions accumulate in bones and other soft tissues over time, eventually interfering with normal physiological processes. Long-term accumulation of Pb(II) will interfere with neurological development, impair renal and liver function, damage the reproductive system, the central nervous system, and even cause death in severe cases [5,6]. Because of its devastating toxic effects on multiple organ systems and its potential for bioaccumulation, the World Health Organization (WHO) has issued a stringent guideline that limits Pb(II) levels in drinking water to 10 ppb [4,7]. This standard is intended to protect public health by reducing the risk of neurological, renal, and other developmental effects from both acute and chronic exposures. Thus, these profound toxic effects justify the importance of monitoring Pb(II) contamination in environmental and biological samples. Several methods have been reported to determine Pb(II) ions, including atomic absorption spectrometry (AAS) [8], inductively coupled plasma-mass spectrometry (ICP-MS) [9], high-performance liquid chromatography (HPLC)-ICP-MS [10], fluorescence spectroscopy [11], colorimetric analysis [12], and capillary electrophoresis [13]. However, for some, it is typically restricted to the advanced laboratory. Such methods are limited by their reliance on expensive, complex instrumentation and/or extensive operator training and expertise required to provide accurate performance.

However, the electrochemical method has enjoyed a wide utilization for the determination of HMIs because of a number of advantages [14-17]. These techniques are not only low-cost, but they are also fairly easy to handle. They also enable fast analysis and with easy sample preparation, which is why they are very well fitted for on-site environmental screening tests as well as lines of routine surveillance.

Preconcentration was usually required to detect toxic HMIs at very low concentrations in complex real samples. Among electrochemical methods, adsorptive stripping voltammetry (ASV) is well-suited for the determination of HMIs due to its preconcentration capability for trace analytes [18-20]. Moreover, the utilization of nanostructured materials in the modification of working electrodes as sensitive platforms for heavy metal ions has attracted more attention [21]. The distinctive characteristics of nanostructure provide a significantly enlarged active surface area and remarkable catalytic activity. Such features not only improve the sensitivity of electrochemical sensors but also enable more reliable detection in complex environmental and biological matrices [22-24].

Metal-organic frameworks (MOFs), characterized by adjustable pore sizes, high porosity, and extensive surface areas, have attracted significant attention as promising porous materials [25,26]. These frameworks have been regarded as efficient electrode materials for the determination of various food and environmental pollutants [27]. However, they present several obstacles related to their low level of intrinsic electrical conductivity as well as issues related to achieving quick and effective electron transfer in electrochemical reactions; therefore, current approaches have primarily focused on combining MOFs with conductive materials to develop MOFs with a higher efficiency than currently available [28-30]. This strategy significantly enhances structural stability, electrical conductivity, and electron-transfer kinetics, all of which are needed for reliable electrochemical measurements. Several studies have used the combination of different materials with MOFs to improve their electrochemical properties for HMIs determinations, such as the utilization of $NH_2$-MIL-101(Cr)@ZIF-8/multi-walled carbon nanotubes (MWCNTs)-modified glassy carbon electrode for determination of Pb(II) and Cu(II) [31], MIL-101(Cr)-$(COOH)_2$@MWCNTs-modified GCE for simultaneous determination of Pb(II), Cu(II), and Hg(II) [32], Bi/UiO-66-$NH_2$@carbon nanohorns

(CNHs) composite-modified GCE for the determination of Pb(II) and Cu(II) [33], and triethanolamine-functionalized Au nanoparticles (NPs)-graphene oxide (GO)-UiO-66-$NH_2$ composite for simultaneous determination of Cd(II), Pb(II), and Cu(II) [34].

Recently, carbon nanostructures, especially MWCNTs, have been extensively employed in the design of electrochemical sensors for HMIs determination owing to their large surface area, high electrical conductivity, and ability to enhance electron transfer, such as the utilization of MWCNTs/ZnO NPs-modified GCE for Pb(II) determination [35], oxidized MWCNTs (o-MWCNTs)/graphitic carbon nitride (g-$C_3N_4$)-modified GCE for simultaneous detection of Cd(II), Pb(II), Hg(II), and Zn(II) [36], $Fe_3O_4$ NPs/fluorinated MWCNTs (f-MWCNTs)-modified GCE for simultaneous detection of Cd(II), Pb(II), Hg(II), Zn(II), and Cu(II) [37], $CeO_2$/MWCNTs-modified GCE for simultaneous detection of Hg(II), Pb(II), and Cu(II) [38], and Ag NPs/MWCNTs/nafion-modified GCE for detection of Pb(II) and Cd(II) [39]. In addition, CNTs have emerged as powerful substances to be used alongside MOFs, which offer a powerful conductive framework that has a significant effect on enhancing the functionality of MOF-based electrochemical sensors [40, 41].

On the basis of the good electronic characteristics of MWCNTs and the high adsorption capacity of the Fe-MOF towards the detection of Pb(II) ions, we have concentrated on constructing an effective electrochemical sensor using MWCNTs/Fe-MOF-modified GCE. The created electrochemical sensing system was very sensitive to square wave anodic stripping voltammetric (SWASV) Pb(II) determination. Then, the effectiveness of MWCNTs/Fe-MOF/MGCE as a sensitive platform to determine Pb(II) in water samples was investigated.

## Experimental

### *Chemicals and instruments*

The reagents here were; 2-aminoterephthalic acid (2-ATA) (99 %), iron(III) chloride hexahydrate ($FeCl_3 \times 6H_2O$) (97 %), N,N-dimethylformamide (DMF) (98 %), ethanol (96 %), MWCNTs (> 95 %), acetic acid glacial (≥ 99.5 %), sodium hydroxide (98 %), aluminum oxide powder (99 %). Sigma-Aldrich and Merck had all the above-mentioned chemicals.

The electrochemical experiments were conducted at ambient temperature in a standard three-electrode setup with unmodified and modified GCE working electrodes, an Ag/AgCl/KCl (3.0 M) reference electrode, and a Pt wire counter electrode, using an Autolab PGSTAT-302N potentiostat/ /galvanostat (Metrohm, Utrecht, the Netherlands).

### *Synthesis of MWCNTs/Fe-based MOF (Fe-MIL-101 ($NH_2$) and modification of GCE using the as-prepared nanostructure*

Fe-based MOF (Fe-MIL-101 ($NH_2$)) was prepared by adding 4.96 mmol of $FeCl_3 \cdot 6H_2O$ and 2.48 mmol of 2-ATA to 40 mL DMF. The mixture was stirred using magnetic stirrer until all components were dissolved. The resulting solution was transferred into an autoclave and heated under solvothermal conditions at 110 °C for 24 h. After completion of the solvothermal treatment, the autoclave was allowed to cool to ambient temperature. The precipitates formed during the process were separated by centrifugation and subsequently washed several times with ethanol and DMF to eliminate remaining impurities. It was dried under vacuum overnight, obtaining the Fe-MOF. Moreover, the MWCNTs/Fe-MOF was prepared through the dispersion of as-obtained Fe-MOF and MWCNTs (weight ratio 1:1) in ethanol, followed by ultrasonic processing for several minutes and then drying under vacuum at 65 °C overnight.

The GCE (geometrical area = 0.0314 cm$^2$) was further polished with an aluminum slurry, washed with distilled water and dried to obtain a clean surface of the electrode. Subsequently, the prepared MWCNTs/Fe-MOF were dispersed in distilled water and sonicated for 30 min to obtain a homogeneous aqueous suspension. To modify the GCE surface, 5.0 µL suspension was cast dropwise on a GCE for natural drying.

### *Analytical procedures for square wave anodic stripping voltammetry determination of Pb(II)*

Square wave anodic stripping voltammetry (SWASV) method was applied for quantitative determination of Pb(II) ions. For this purpose, the measurements were conducted as follows: the as-prepared MWCNTs/Fe-MOF/MGCE was initially placed into an electrochemical cell containing an acetate buffer solution (ABS, 0.1 M, pH 4.0) as the supporting electrolyte and a known concentration of Pb(II) ions. In the step of pre-concentration, a potential of -0.9 V versus Ag/AgCl/KCl (3.0 M) was applied for 400 s under controlled stirring of the stirrer (300 rpm), consequently facilitating the reduction of Pb(II) to Pb(0) and its accumulation on the MWCNTs/Fe-MOF/GCE surface. Following the pre-concentration step, the electrode was removed from the cell, washed with distilled water, and returned to a cell containing ABS (0.1 M, pH 4.0). In the stripping step, the SWASV response was recorded in the positive direction from -0.69 to -0.36 V *vs*. Ag/AgCl/KCl (3.0 M). Prior to each measurement, the modified electrode was subjected to a pre-conditioning step at -1 V *vs*. Ag/AgCl/KCl (3.0 M) for 40 s to ensure the complete removal of any residual Pb deposits from its surface.

## Results and discussion

### *Characterization of MWCNTs/Fe-MOF*

Figure 1 presents the XRD pattern of the MWCNTs/Fe-MOF. The observed peaks are consistent with those of Fe-MIL-101(NH$_2$) MOF, as reported in previous studies [42-44]. In addition, the characteristic peaks of MWCNTs may overlap with those of MOF.

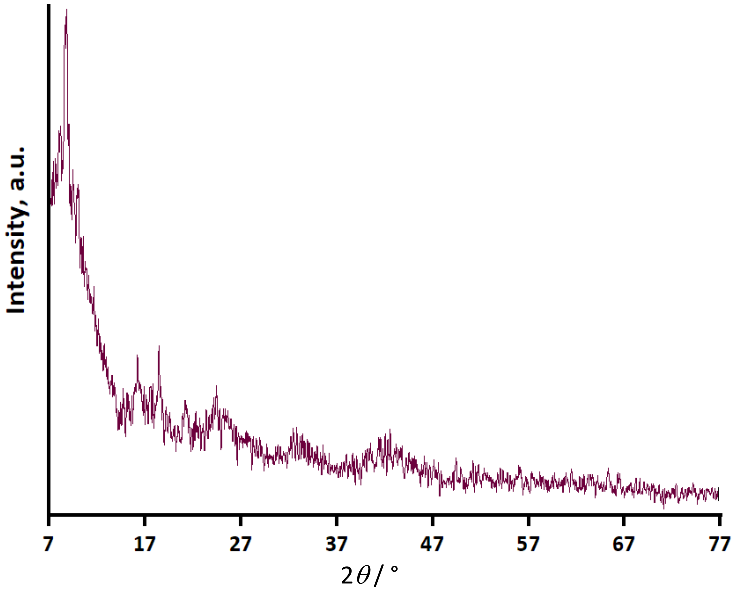

***Figure 1.*** *XRD pattern of the MWCNTs/Fe-MOF sample*

Brunauer-Emmett-Teller (BET) analysis was used to measure the specific surface area of the as-prepared MWCNTs/Fe-MOF. From the N$_2$ adsorption-desorption isotherm (Figure 2), the MWCNTs/Fe-MOF had a BET surface area of 87.531 m$^2$ g$^{-1}$.

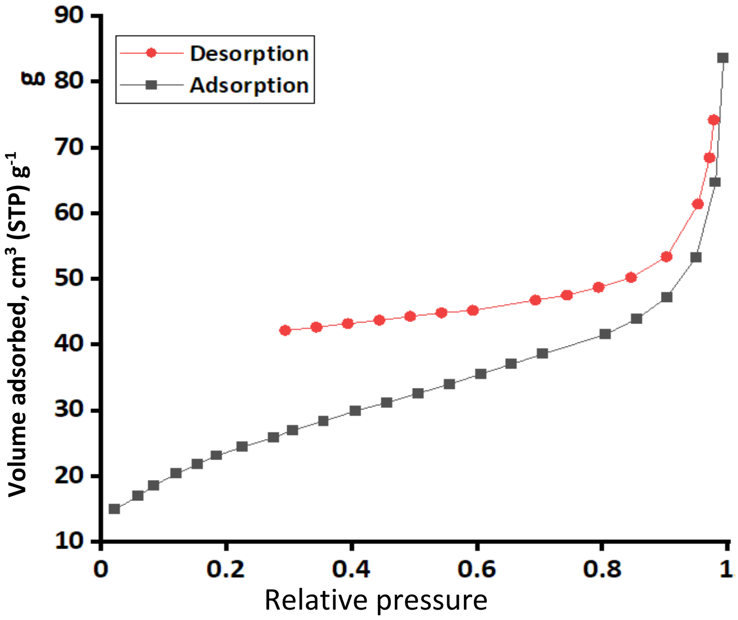

***Figure 2.*** *Nitrogen adsorption-desorption isotherm of the MWCNTs/Fe-MOF sample*

### *SWASV responses of bare GCE and modified GCEs toward Pb(II) determination*

SWASV was employed to evaluate the Pb(II) stripping signal across different electrode surfaces. As shown in Figure 3, the SWASV response of bare GCE, Fe-MOF/MGCE and MWCNTs/Fe-MOF/MGCE was measured after accumulation in ABS (0.1 M, pH 4.0) that contains Pb(II) at a concentration of 100.0 ng mL$^{-1}$. A weak Pb(II) stripping peak was also observed at the bare GCE, with an anodic stripping peak current ($I_{pa}$ = 10.4 µA), suggesting that the electrode did not promote interaction with Pb(II). After modification of the GCE with Fe-MOF (Fe-MIL-101 (NH2) MOF), the $I_{pa}$ increased by approximately 2.13 times ($I_{pa}$ = 22.2 µA).

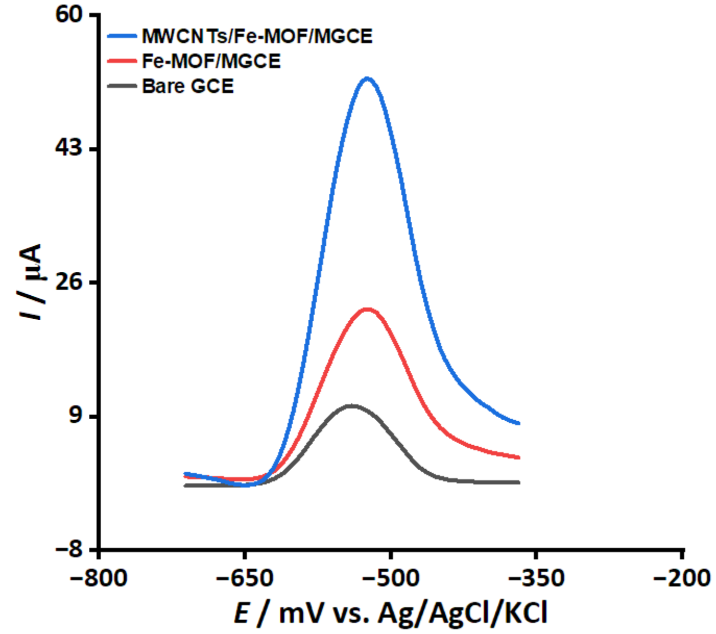

***Figure 3.*** *SWASV responses of bare GCE, Fe-MOF/MGCE, and MWCNTs/Fe-MOF/MGCE after pre-concentration in ABS (0.1 M, pH 4.0) containing 100.0 ng/mL Pb(II)*

The increase in the $I_{pa}$ at the Fe-MOF/MGCE can be attributed to the high chelating ability of the $NH_2$-functional groups in the Fe-MIL-101 ($NH_2$) MOF and its large surface area, which enhances Pb accumulation at the surface of GCE. Furthermore, at the surface of MWCNTs/Fe-MOF/MGCE, the $I_{pa}$

reached a maximum of 51.8 µA compared with the other electrodes, indicating that MWCNTs contributed significantly to the enhancement of the electrocatalytic ability of the modified GCE owing to its large surface area and high electrical conductivity.

### *Optimization of experimental conditions for SWASV determination of Pb(II)*

For obtaining the better detection ability of Pb(II) ions, the factors affecting the analytical performance of MWCNTs/Fe-MOF/MGCE were systematically investigated and optimized. As the stripping voltammetric response was significantly dependent on solution pH, accumulation potential and accumulation time, systematic investigations of these parameters were required. This section presents the optimization process and investigates the effect of each parameter on the SWASV signal intensity for Pb(II), thereby establishing the optimal operating conditions for the MWCNTs/Fe-MOF/MGCE sensing platform.

Initially, the effect of the pH of the pre-concentration solution (ABS, 0.1 M) on Pb accumulation was investigated using SWASV. SWASV measurements were performed at the MWCNTs/Fe-MOF/ /MGCE after the accumulation step in 0.1 M ABSs at pH values from 2.0 to 7.0, each containing 100.0 ng mL$^{-1}$ Pb(II). It was found that the $I_{\text{pa}}$ of Pb(II) increased with increasing pH until it reached 4.0 and then decreased as the pH increased further. Therefore, ABS 0.1 M, pH 4.0, was identified as the optimal condition in the pre-concentration step for subsequent measurements.

To assess the effect of accumulation potential on the determination of Pb(II), SWASVs were recorded at the MWCNTs/Fe-MOF/MGCE following the pre-concentration step in 0.1 M ABS, pH 4.0, containing 100.0 ng/mL Pb(II) over an accumulation potential range from -0.7 to -1.1 V at an accumulation time of 400.0 s. An increase in the $I_{\text{pa}}$ of Pb(II) was observed as the accumulation potential increased, reaching a maximum at -0.9 V (Figure 4). After this potential, the $I_{\text{pa}}$ increased very slightly. Thus, the accumulation potential of -0.9 V was selected for further measurements.

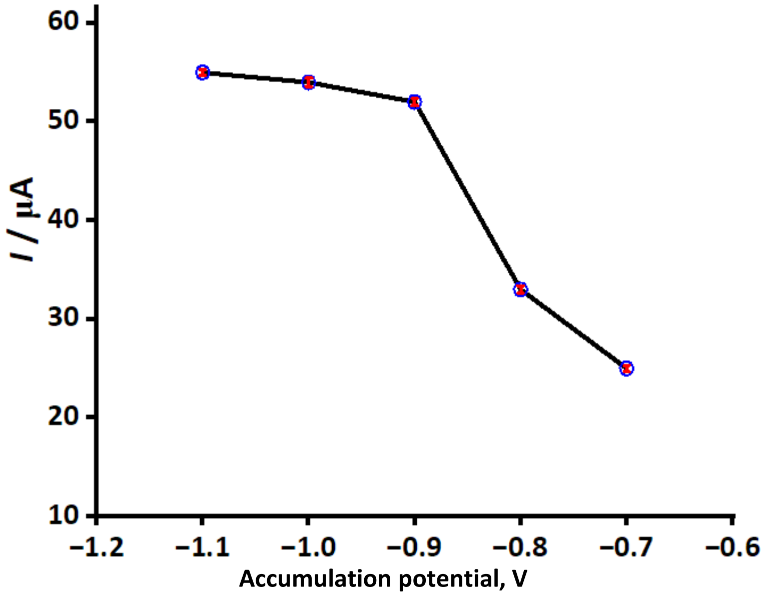

***Figure 4.*** *Effect of the accumulation potential (-0.7 V, -0.8 V, -0.9 V, -1 V, and -1.1 V) on $I_{pa}$ of 100.0 ng/mL Pb(II) at pre-concentration time of 400 s (supporting electrolyte solution: 0.1 M ABS, pH 4.0)*

Furthermore, to investigate the effect of accumulation time on the determination of Pb(II), SWASV measurements were performed at the MWCNTs/Fe-MOF/MGCE following the pre-concentration step in 0.1 M ABS, pH 4.0, containing 100.0 ng/mL Pb(II) at an accumulation potential of -0.9 V, while varying the accumulation time from 60 s to 600 s. As shown in Figure 5, an increase in the $I_{\text{pa}}$ of Pb(II) was observed with increasing accumulation time up to 400 s. However, the above enhancement did not occur when Pb(II) peak current only increased a little after reaching 400 s, which may possibly be attributed to the electrode surface area occupied by accumulation species approaching saturation and accordingly, just a limited increase in peak current was observed. Therefore, 400 s accumulation time was taken as the optimal condition for the determination of Pb(II).

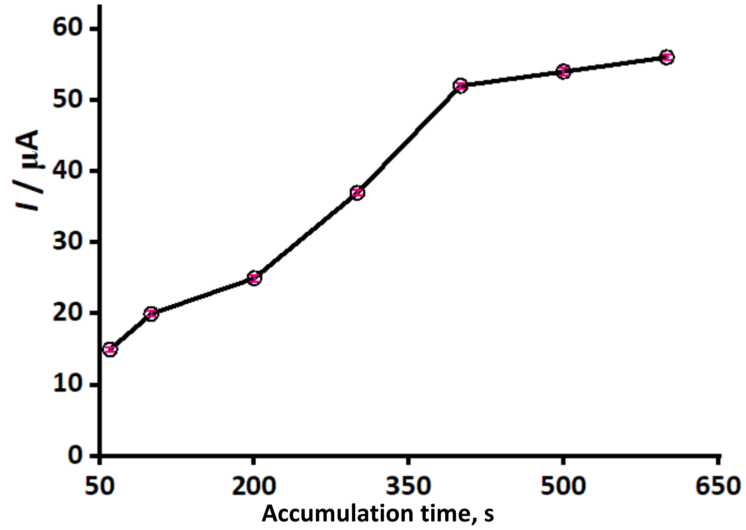

***Figure 5.*** *Effect of accumulation time on $I_{pa}$ of 100.0 ng $mL^{-1}$ Pb(II) at pre-concentration potential of -0.9 V (supporting electrolyte solution: 0.1 M ABS, pH 4.0)*

*SWASV responses of the MWCNTs/Fe-MOF/MGCE toward different concentrations of Pb(II)*

Under the optimal determination conditions, the $I_{pa}$ of Pb(II) at different concentrations was measured at the MWCNTs/Fe-MOF/MGCE using the SWASV method, and corresponding voltammograms obtained from these measurements are presented in Figure 6A.

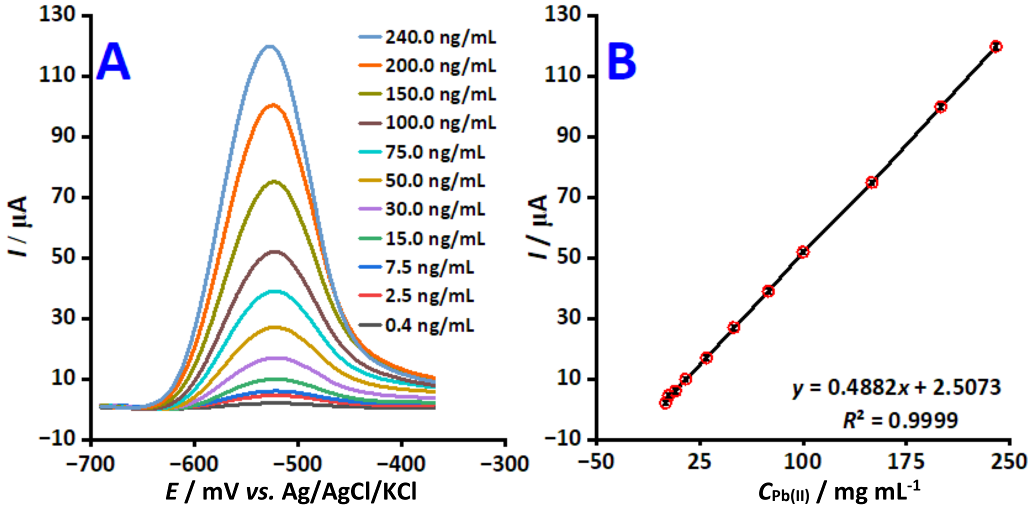

***Figure 6.*** *(A) SWASV responses of the MWCNTs/Fe-MOF/MGCE after pre-concentration in ABS (0.1 M, pH 4.0) containing Pb(II) at various concentrations (from 0.4 ng/mL to 240.0 ng/mL). Conditions: accumulation potential = -0.9 V and accumulation time = 400 s, (B) calibration plot for Pb(II) determination*

According to the resulting voltammograms, the $I_{pa}$ of Pb(II) gradually increased with increasing concentration. Furthermore, as shown in Figure 6B, a linear response of the MWCNTs/Fe-MOF/MGCE sensing platform to Pb(II) concentration was observed from 0.4 to 240.0 ng $mL^{-1}$. The linear regression equation was $I_{pa}$=0.4882 $C_{Pb(II)}$+2.5073 ($R^2$=0.9999). The LOD was found to be 0.1 ng $mL^{-1}$. Table 1 compares the MWCNTs/Fe-MOF/MGCE sensor with previously reported sensors for Pb(II) determination.

***Table 1.*** *Comparison of the sensing performance for Pb(II) determination of the MWCNTs/Fe-MOF/MGCE platform with those reported in recent studies*

| Electrode | Linear range | LOD | Reference |
|---|---|---|---|
| MWCNTs/Fe-MOF/MGCE | 0.4 to 240.0 ng mL | 0.1 ng mL$^{-1}$ | Present work |
| $ZnCo_2O_4$ porous nanosheets/screen-printed electrode | 0.001 to 0.025 ppb | 0.4 ppt | [4] |
| Bi/single-walled CNTs-nafion/ionic liquid/SPE | 1.0 to 100.0 µg/mL | 0.1 µg mL$^{-1}$ | [14] |
| $Bi_2O_3/MnO_2$/GO/GCE | 0.01 to 10 µM | 2.0 nM | [24] |
| Bi/UiO-66-$NH_2$@carbon nanohorns composite/GCE | 0.20 to 0.80 µM | 6.65 nM | [33] |
| ZIF-67/MWCNTs/nafion/GCE | 1.38 nM to 5 µM | 1 nM | [40] |
| Oxidized MWCNTs/Mn-MOF/GCE | 0.05 to 5 µM | 13 nM | [41] |
| β-cyclodextrin-reduced GO/GCE | 1.0 to 100.0 nM | 0.5 nM | [45] |

### *Reproducibility, repeatability, stability and selectivity studies*

To evaluate the performance of the MWCNTs/Fe-MOF/MGCE sensor for Pb(II) determination, we also examined its reproducibility for multiple electrodes, the repeatability of measurements under the same conditions, and the stability of its response over time. The reproducibility of the MWCNTs/ /Fe-MOF/MGCE was also evaluated for four individual electrodes by measuring 30.0 ng mL$^{-1}$ Pb(II), yielding a relative standard deviation (RSD) of 3.8%, indicating good reproducibility. The RSD was 4.8 % on three successive 30.0 ng mL$^{-1}$ Pb(II) determinations, which is indicative of sufficiently good repeatability. 7 days later, the $I_{pa}$ of 30.0 ng mL$^{-1}$ Pb(II) was 95.6% of the original value, indicating that storage was satisfactory.

More importantly, the effect of several non-target metal ions, which could be found in real water samples, such as Hg(II), As(III), Cd(II), and Zn(II), on the stripping peak currents of Pb(II) was investigated at a concentration ratio of 1 : 20 (Pb(II):interfering ion). The measurements demonstrated that the presence of these metal ions does not have a considerable effect on the peak current of Pb(II). A change of less than 5 % was observed in the recorded peak currents of Pb(II).

### *Application of the MWCNTs/Fe-MOF/MGCE for Pb(II) determination in the analysis of water samples*

The applicability of the as-developed sensing platform (MWCNTs/Fe-MOF/MGCE) for quantifying Pb(II) ions in tap and drinking water samples was assessed using a calibration-curve-based strategy. The analysis demonstrated that Pb(II) was not observed in these samples. Moreover, the reliability of the proposed method was assessed by recovery measurements. In this evaluation, known concentrations of Pb(II) were added to previously analyzed sample solutions, which were then analyzed. As shown in Table 2, the MWCNTs/Fe-MOF/MGCE sensing platform demonstrated satisfactory recoveries (98.0 to 104.3 %) for Pb(II) determination and low RSD values (2.2 to 3.6 %).

***Table 2.*** *Determination of Pb(II) in the water (tap water and drinking water) samples as determined by SWASV at the MWCNTs/Fe-MOF/MGCE*

| Sample | Amount of Pb(II), ng mL$^{-1}$ | | Recovery, % | RSD, % |
|---|---|---|---|---|
| | Added Pb(II) | Found | | |
| Tap water | 5.0 | 4.0 | 98.0 | 2.2 |
| | 7.0 | 7.3 | 104.3 | 2.9 |
| Drinking water | 5.5 | 5.7 | 103.6 | 3.6 |
| | 7.5 | 7.4 | 98.7 | 2.3 |

## Conclusion

In this study, a simple and efficient method has been developed for the SWASV determination of Pb(II) ions in real samples using a MWCNTs/Fe-MOF/MGCE sensing platform. The MWCNTs/

/Fe-MOF/MGCE, with good conductivity and numerous active sites, provides a favorable sensing platform toward Pb(II) ions. Under optimized operating parameters and conditions, the MWCNTs/Fe-MOF/MGCE linearly responded to Pb(II) concentration in the range from 0.4 to 240.0 ng mL$^{-1}$ with a low LOD of 0.1 ng mL$^{-1}$. Furthermore, the practical application of this sensing platform has been validated *via* its successful application in determining Pb(II) levels in the tap and drinking water samples.

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***Conflicts of Interest:*** *The authors have no conflict of interest.*

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