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Original scientific paper

Application of MWCNTs/Uio-66(Zr)-NH_2 MOF modified electrode for anodic stripping determination of Cu(II) in water samples

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Abstract

In this research, a procedure was developed for the detection of Cu(II) ions in water using a glassy carbon electrode modified with a nanocomposite of multi-walled carbon nanotubes and a zirconium-based metal-organic framework (MWCNTs/Uio-66(Zr)-NH_2 MOF/GCE). The analysis was performed by differential pulse anodic stripping voltammetry. The excellent sensitivity of the created sensor (MWCNTs/Uio-66(Zr)-NH_2 MOF/GCE) for Cu(II) determination is attributed to the synergy between the strong chelating ability of the terminal amino groups (-NH_2) on the Uio-66 (Zr)-NH_2 MOF for metal ions and the extensive surface area provided by the MWCNTs. The key parameters influencing the stripping current response of Cu(II), namely, pH, accumulation potential, and accumulation time, were systematically studied and optimized. Under optimal conditions, the stripping peak current of Cu(II) ions exhibited a linear relationship with concentration over the range of 0.001 to 10.0 µM. The limit of detection for Cu(II) ions was calculated to be 0.0005 µM. Finally, the MWCNTs/Uio-66 (Zr)-NH_2 MOF/GCE sensor was employed to determine Cu(II) ions in real water specimens, yielding acceptable recovery rates.

Keywords

Heavy metal ions determination; Cu(II) ions; environmental monitoring; chemically modified electrode; voltammetric sensor

Introduction

The main goal of environmental monitoring is to detect and quantify harmful substances—including chemical, microbial, biological, and radioactive agents - within water, soil, and atmospheric systems. The growing worldwide need for pure, fresh water is driving a greater necessity for accurate water quality assessment. The emergence of new contaminants poses a significant threat to water

quality [1]. Heavy metal ion (HMI) contamination constitutes a paramount environmental concern, directly endangering global sustainable development. The advancement of agricultural and industrial production processes has led to a growing crisis of environmental pollution by HMIs. Due to their non-biodegradability and high toxicity, HMIs can cause significant harm to living organisms [2,3].

For instance, metals such as mercury, arsenic, copper, lead and cadmium are widely employed on various fields of human activity, including technological applications in electronic devices, industrial processes, and agricultural practices [4]. Of these, copper ions are by far the most widely used medium in various sectors such as electronics, construction, medicine and consumer products. Although useful for industry, copper (Cu(II)) is also an important dietary component, acting as an essential enzymatic cofactor and as a trace element involved in red blood cell formation; however, only at low concentrations. On the other hand, high levels of Cu(II) ions can disrupt cellular homeostasis by competing with essential metal cations in living organisms, leading to cell death and severe poisoning. In addition, the Cu(II) ion is an important environmental contaminant, and its toxicity mainly originates from its catalytic production of oxygen radical species, which cause oxidative damage to organisms [5]. According to the permissible limit for Cu(II) ions in drinking water set by the US Environmental Protection Agency (USEPA), it is 1.30 ppm [6]. Consequently, the development of highly sensitive and selective analytical methods for the detection of Cu(II) ions is essential.

The detection of Cu(II) ions is usually carried out using analytical methods such as atomic absorption spectroscopy (AAS) [7,8], inductively coupled plasma-mass spectrometry (ICP-MS), ultraviolet-visible long wavelength (UV-Vis) spectrophotometry [9], fluorescence [10], and atomic emission spectrometry (AES) [11]. Nevertheless, those techniques often bring disadvantages as they depend on expensive instrumentation, complicated operational procedures and involve tedious, multi-step sample preparation.

The continual development in electrochemical sensing is paving the way to next-generation portable analytical devices. Such systems stand out for their simple operating principle, high sensitivity and fast response times [12,13]. As a result, this approach is becoming one of the most common methods for the quantitative analysis of HMIs. Well-documented and widely used electrochemical techniques such as differential pulse anodic stripping voltammetry (DPASV) greatly improve the detection sensitivity for trace-level heavy metal ions by enhancing the Faradaic signal while reducing the non-Faradaic background current [14,15].

The use of chemically modified electrodes for preconcentration of target analytes represents a significant advancement in HMI determination through anodic stripping voltammetry (ASV). Pre-concentration plays a key role in improving the sensitivity of HMI detection and decreasing its analytical limit of detection. The pre-concentration stage is fundamentally based on the adsorption of target ions from the bulk solution into the surface of the working electrode. This means that the careful engineering of new materials with a high density of adsorption sites is required to maximize many analytical characteristics [16,17].

Nanostructured materials are a very convenient platform for electrode modification because they combine the superior electronic, thermal, chemical and mechanical properties of nanomaterials with those exhibited in their bulk [18,19].

Recently, metal-organic frameworks (MOFs) have gained considerable research attention due to their potential applications in a wide range of areas, including energy storage and conversion [1], heterogeneous catalysis [2] and pollutant removal. High surface areas, large pore volumes and tuneable structures lead to the use of MOFs to modify electrode surfaces [20,21].

Several notable features allow the introduction of MOFs to HMI detection, including I) very high porosity and surface area that enhance metal-ion adsorption at the electrode surface, which more effectively amplify analytical signal for improving the sensitivity [21]; II) abundant active sites formed by versatile metal nodes and organic linkers incorporated in a porous structure enable specifically targeting HMIs recognition and ionization [22,23].

For surface modification of electrode materials, UiO-66 (Zr)-NH_2 is one particularly viable option among a great number of metal-organic frameworks. The surplus amino groups on UiO-6 (Zr)-NH_2 MOF provide active sites for the adsorption of HMIs [24].

This, however, posed a significant limitation due to the low electrical conductivity of most MOFs. A solution to surmount this hurdle is the compounding of MOFs with conductive materials [25]. In particular, carbon-based nanostructures have become excellent candidates to build MOF composites because of their large surface area, high electrical conductivity and chemical inertness. Multi-walled carbon nanotubes (MWCNTs) show potential for electrochemical sensing applications due to their high surface area, fast electron-transfer kinetics, and their functionalization. The individual components exhibit a synergistic effect that enhances electron transfer and catalytic activity, resulting in a significant improvement in detection sensitivity for the sensor [26,27].

In this work, the MWCNTs/Uio-66(Zr)-NH_2 organic–inorganic MOF-modified glassy carbon electrode (MWCNTs/Uio-66(Zr)-NH_2 MOF/GCE) nanocomposite was developed and investigated as a stripping voltammetry sensor for detecting Cu(II) ions. A composite material reaching a Zr-based metal-organic framework functionalized with amino groups was successfully synthesized and fulfilled the requirements for applications. Thanks to its rich -NH_2 groups, the composite has achieved excellent adsorption quality of Cu(II) and thus performs well in detection.

The Cu(II) ions were determined with high sensitivity (2.956 μA μM^{-1}) and a low limit of detection (LOD) 0.0005 μM using MWCNTs/Uio-66(Zr)-NH_2 MOF/GCE. Furthermore, the practical applicability of the MWCNTs/Uio-66(Zr)-NH_2 MOF/GCE was successfully demonstrated by detecting Cu(II) in real water specimens.

Experimental

Reagents and apparatus

All compounds were of analytical grade and required no purification before use. A 0.1 M acetate buffer solution (ABS) was prepared by mixing appropriate amounts of acetic acid and $NaCH_3COO$ in deionized water, and its pH was adjusted to 2.0-9.0 using an aqueous sodium hydroxide (NaOH) solution.

An Autolab PGSTAT302N system (Metrohm, Netherlands) managed by GPES software (v4.9) was employed for every electrochemical assay. All measurements were conducted at ambient temperature in a standard three-electrode system, utilizing a GCE (unmodified or modified) as the working electrode, an Ag/AgCl (3.0 M KCl) electrode as the reference, and a Pt wire as the counter electrode.

Synthesis of MWCNTs/UiO-66(Zr)-NH_2 MOF

MWCNTs/UiO-66(Zr)-NH_2 MOF was synthesized by dissolving 0.279 g of $ZrCl_4$ and 0.217 g of 2-aminoterephthalic acid into 75 mL of DMF under magnetic stirring for 15 min. Subsequently, 2.5 mL of acetic acid was added dropwise, and the mixture was ultrasonicated for 15 min. MWCNTs (0.0225 g) were then added to the above solution and dispersed by ultrasonication for 1 h to achieve a homogeneous suspension. The resulting suspension was transferred to an autoclave and subjected to solvothermal treatment at 120 °C for 24 h. The precipitate was collected by centrifugation, washed several times with methanol and DMF, and dried under vacuum at 70 °C overnight.

Pristine UiO-66(Zr)-NH_2 MOF was synthesized following a procedure similar to that described above, but without the addition of MWCNTs.

Modification of GCE surface using MWCNTs/UiO-66(Zr)-NH_2 MOF nanocomposite

Prior to modification, the GCE surface was polished with alumina slurry, meticulously rinsed with distilled water, and allowed to dry. Then, the MWCNTs/UiO-66(Zr)-NH_2 MOF nanocomposite (1 mg) was dispersed in 1 mL of deionized water. A stable, homogeneous suspension was then obtained by ultrasonic agitation for 30 minutes. A 2 µL aliquot of the dispersion was deposited on the GCE surface via drop-casting and left to dry under ambient conditions, yielding the MWCNTs/UiO-66(Zr)--NH_2 MOF/GCE.

Analytical procedures for Cu(II) detection by DPASV

We employed the DPASV strategy for the analysis of Cu(II). The DPASV measurements were achieved using the strategy below: i) preconcentration step: first, a specific concentration of Cu(II) solution was introduced into an electrochemical cell (25 mL) that contained a 0.1 M ABS (pH 4.0). The MWCNTs/UiO-66(Zr)-NH_2 MOF/GCE was then immersed in the cell, and Cu(II) was pre-concentrated onto its surface using an applied potential of -0.65 V relative to the Ag/AgCl/KCl electrode for a set duration (240 s) under constant stirring. Following the pre-concentration step, the MWCNTs/UiO-66(Zr)-NH_2 MOF/GCE was removed from the sample cell, rinsed with distilled water, and transferred to a clean electrochemical cell containing 0.1 M ABS (pH 4.0) for stripping measurements. ii) Stripping step: After Cu(II) preconcentration as detailed in step (i), the anodic stripping voltammogram was acquired over a potential window of -0.35 to -0.75 V (*vs.* Ag/AgCl/KCl).

Results and discussion

Characterization of MWCNTs/UiO-66(Zr)-NH_2 MOF

The X-ray diffraction (XRD) patterns of UiO-66(Zr)-NH_2 MOF and MWCNTs/UiO-66(Zr)-NH_2 MOF were analysed to characterize their crystalline structures (Figure 1). Fig. 1a displays the XRD pattern of UiO-66(Zr)-NH_2 MOF, which is consistent with previously published results [28,29], confirming the crystallinity of the synthesized MOF.

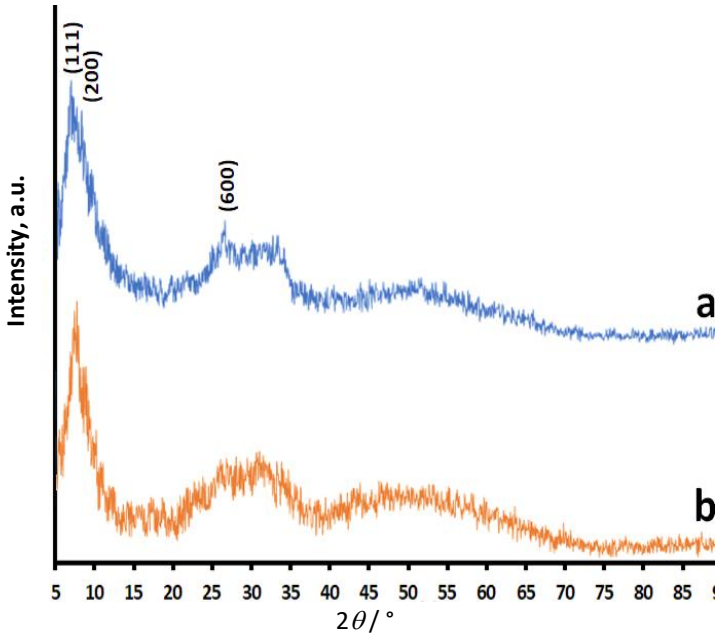

Figure 1. *XRD patterns of UiO-66(Zr)-NH_2 MOF (a) and MWCNTs/UiO-66(Zr)-NH_2 MOF (b)*

The distinct peaks observed at 2θ values of 6.9, 8.3 and 26.6° correspond to the (111), (200) and (600) crystal planes, respectively. For the MWCNTs/UiO-66(Zr)-NH_2 MOF, the XRD pattern (Figure 1b) closely resembles that of the UiO-66(Zr)-NH_2 MOF, confirming the successful incorporation of MOF among the MWCNTs *via* the solvothermal method used.

Stripping voltammetry responses of MWCNTs/UiO-66(Zr)-NH_2 MOF /GCE and bare GCE toward Cu(II) detection

The electrochemical behaviour of the fabricated sensors was assessed by comparing their stripping voltammetry signals for Cu(II) detection under optimal conditions. Figure 2 displays the DPASV responses of a bare GCE, a UiO-66(Zr)-NH_2 MOF/GCE, and an MWCNTs/UiO-66(Zr)-NH_2 MOF/GCE following pre-concentration in a 0.1 M ABS (pH 4.0) containing 4.0 µM Cu(II). Figure 2 reveals that the unmodified GCE yielded only a minimal stripping signal, with an anodic stripping peak current (I_{pa}) of 1.6 µA, indicating low sensitivity to Cu(II). The Uio-66(Zr)-NH_2 MOF/GCE exhibited a higher stripping peak current for Cu(II) compared to the bare GCE (I_{pa} = 6.84 µA). The signal enhancement at the UiO-66(Zr)-NH_2 MOF/GCE is due to the abundance of –NH_2 functional groups in the MOF, which act as effective coordination sites for Cu(II) adsorption, thus enhancing its accumulation on the electrode surface. A substantial enhancement in the anodic stripping peak current was observed with the MWCNTs/UiO-66(Zr)-NH_2 MOF-modified GCE, which reached 12.0 µA, representing a 2-fold increase compared to the UiO-66(Zr)-NH_2 MOF/GCE. The increase in the stripping signal indicates that MWCNTs contributed significantly to the enhanced electrocatalytic activity of the prepared sensor, which can be attributed to their high electrical conductivity and large specific surface area.

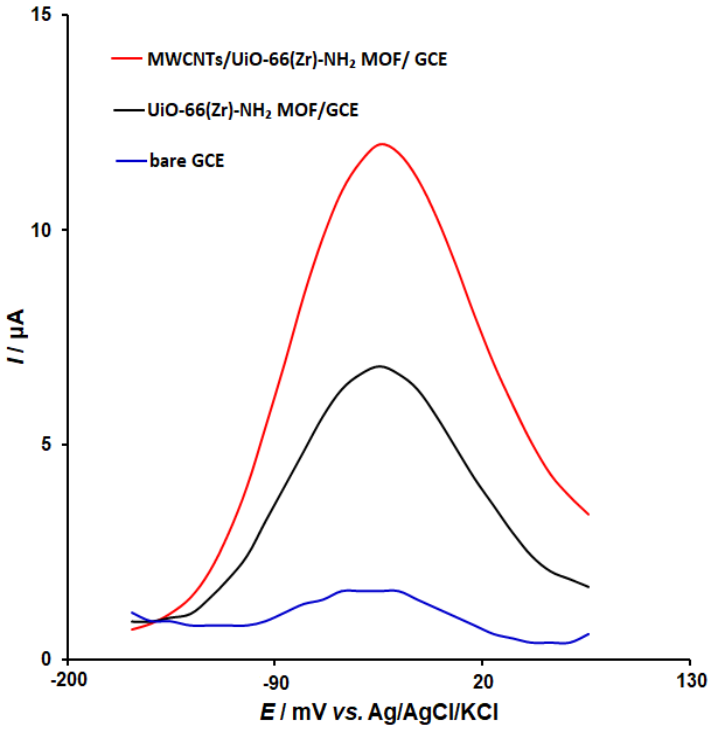

Figure 2. *DPASV curves of 4.0 µM Cu(II) for un-modified GCE, UiO-66(Zr)-NH_2 MOF/GCE, and MWCNTs/UiO-66(Zr)-NH_2 MOF/ GCE after pre-concentration in 0.1 M ABS (pH 4.0)*

Optimization of experimental conditions for DPASV determination of Cu(II) at MWCNTs/UiO-66(Zr)-NH_2 MOF /GCE

The influence of key parameters (solution pH, accumulation time, and accumulation potential) on the DPASV signal for Cu(II) detection was evaluated to improve the performance of the MWCNTs/UiO-66(Zr)-NH_2 MOF/GCE sensor.

The pH of the solution significantly influences the stripping voltammetry response of the working electrode. These findings demonstrate that pH significantly influences detection, necessitating pH optimization for accurate analysis. The DPASV response was assessed over the pH range 2.0 to 6.0. The experiments were performed in a 0.1 M ABS solution containing 12.0 µM Cu(II) ions at the MWCNTs/UiO-66(Zr)-NH_2 MOF/GCE surface. According to the results, the current increased across the pH range of 2.0 to 5.0 and declined at higher pH values. Maximum signal intensity was observed at pH 4.0. At lower pHs (pH < 4.0), the amino groups in UiO-66(Zr)-NH_2 MOF become protonated, which likely inhibits the adsorption of Cu(II) onto the MWCNTs/UiO-66(Zr)-NH_2 MOF/ GCE surface, which causes the DPASV currents to be low. At higher pH levels (pH > 4), the stripping peak current decreases due to metal ion hydrolysis, which reduces the quantity of metal preconcentrated on the MWCNTs/UiO-66(Zr)-NH_2 MOF/ GCE surface. Based on these findings, pH 4.0 was identified as optimal and used in all subsequent work.

The accumulation step is a crucial yet straightforward approach for enhancing sensitivity in voltammetric analysis, where selecting an optimal accumulation potential (E_{Acc}) is vital for achieving the best analytical signal. The effect of accumulation potential on the determination of Cu(II) was investigated by recording DPASVs at the MWCNTs/UiO-66(Zr)-NH_2 MOF/GCE following a pre-concentration step in a 0.1 M ABS (pH 4) containing 4.0 µM Cu(II), scanning a potential range from -0.75 to -3.35 V over an accumulation period of 240 s. The stripping peak current increases as the E_{Acc} varies from -0.75 to -3.35 V, with the highest value at -0.65 V. The current reached a maximum of 12.0 µA at -0.65 V; however, a further increase in the E_{Acc} to -0.75 V resulted in a slight increase in the stripping signal. Therefore, we selected an E_{Acc} of -0.65 V as the optimal value and used it in all subsequent investigations. The results of the accumulation potential optimization are presented in Figure 3.

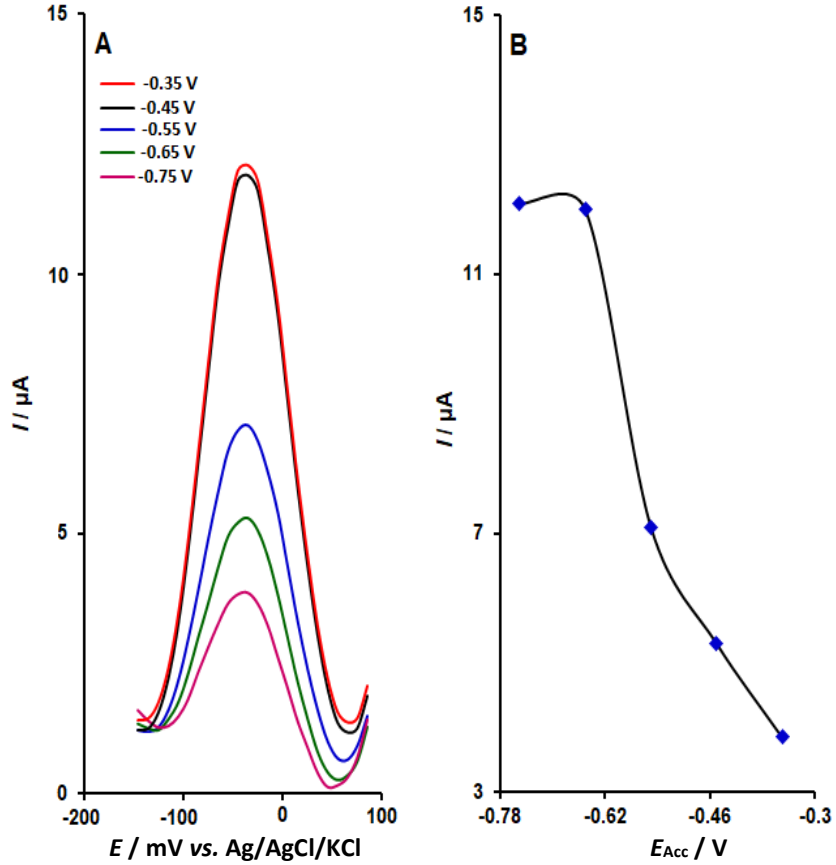

Figure 3. *A - Effects of the accumulation potential (E_{Accn} = -0.35, -0.45, -0.55, -0.65 and -0.75 V) on the DPASV signal of 4.0 µM Cu(II) at a pre-concentration time of 240 s in 0.1 M ABS (pH 4.0) at the MWCNTs/UiO-66(Zr)-NH_2 MOF/GCE surface; B - plot of I_{pa} versus $E_{Acc.}$*

Optimizing the accumulation time (t_{Acc}) is essential, as it directly controls the amount of preconcentrated analyte, thereby determining the method's ultimate sensitivity and LOD. We assessed the impact of accumulation time by recording DPASVs of a 4.0 µM Cu(II) solution in 0.1 M ABS (pH 4.0) at the MWCNTs/UiO-66(Zr)-NH_2 MOF/GCE. A constant accumulation potential of -0.65 V was applied, and the t_{Acc} was varied between 60 s and 300 s. The DPASV responses for different accumulation times are displayed in Figure 4. An increase in deposition time from 60 s to 240 s enhanced the Cu(II) peak currents due to the corresponding increase in adsorbed Cu(II) ions. After 240 s, the I_{pa} value of Cu(II) ions rose slowly, suggesting the electrode's adsorption sites were approaching saturation at this point (240 s). Based on these results, a deposition time of 240 s was identified as optimal and used for all subsequent experiments.

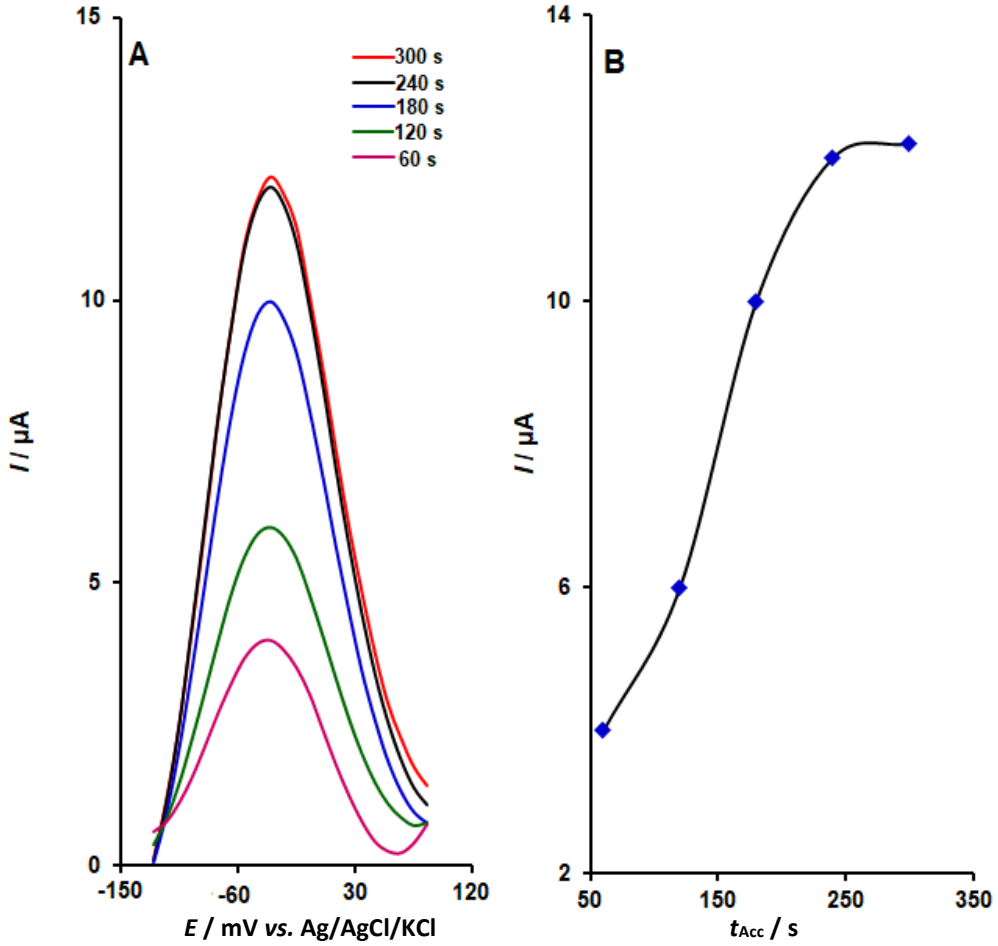

Figure 4. *A - effect of the accumulation time (t_{Acc} = 60, 120, 180, 240 and 300 s) on the DPASV signal of 4.0 µM Cu(II) at a pre-concentration potential of -0.65 V in 0.1 M ABS (pH 4.0) at the MWCNTs/UiO-66(Zr)-NH_2 MOF/GCE surface; B - plot of I_{pa} versus t_{Acc}*

Quantitative measurements of Cu(II) using DPASV method at MWCNTs/UiO-66(Zr)-NH_2 MOF/GCE

The analytical performance was evaluated under optimized deposition parameters (E_{Acc}: -0.65 V; t_{Acc}: 240 s) by measuring the DPASV response of the MWCNTs/UiO-66(Zr)-NH_2 MOF/GCE to varying Cu(II) concentrations in 0.1 M ABS (pH 4.0). Figure 5 presents DPASV signals for Cu(II) concentrations ranging from 0.001 to 10.0 µM at the MWCNTs/UiO-66(Zr)-NH_2 MOF/GCE in ABS (0.1 M, pH 4.0). As shown in Figure 5, the anodic peak current increased progressively with Cu(II) concentration, exhibiting a linear response over the range 0.001-10.0 µM. The sensor exhibited a linear response, described by the equation $I_{pa} = 2.956C_{Cu(II)} + 0.3152$ ($R^2 = 0.9997$) (Figure 5). From this calibration, a sensitivity of 2.956 µA μM^{-1} was determined, with a LOD of 0.0005 µM based on a signal-to-noise ratio of 3.

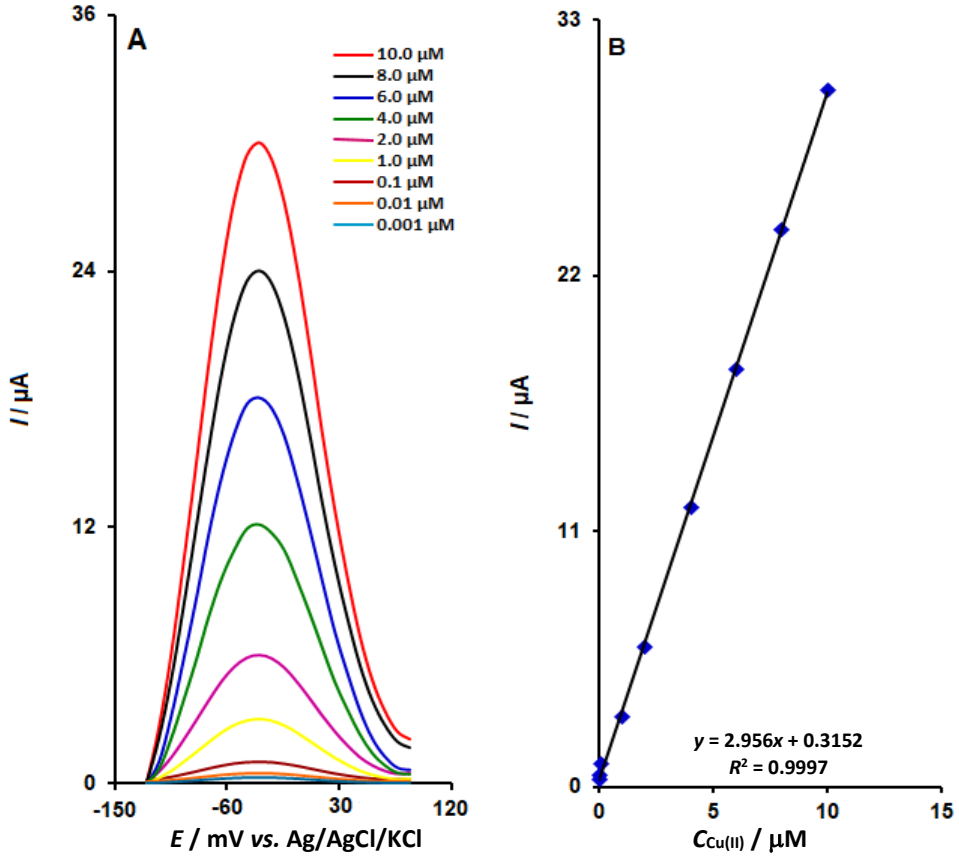

Figure 5. *A - DPASV signals of MWCNTs/UiO-66(Zr)-NH_2 MOF/GCE in 0.1 M ABS (pH 4.0) containing different Cu(II) concentrations (from C = 0.001 to 10.0 µM). Conditions: E_{Acc} = -0.65 V and t_{Acc} = 240 s; B - The linear calibration plot for different Cu(II) concentrations*

Application of the MWCNTs/UiO-66(Zr)-NH_2 MOF/GCE in the analysis of water specimens for Cu(II) detection

The practical applicability of the MWCNTs/UiO-66(Zr)-NH_2 MOF/GCE sensor was demonstrated through the successful determination of Cu(II) in real water specimens. Before analysis, the real water specimens were diluted with 0.1 M ABS. The DPASV analysis was conducted under the same experimental conditions detailed in the previous section. Analysis of the voltammograms revealed no discernible anodic stripping signals for Cu(II). To validate the method, a known concentration of Cu(II) was spiked into a real water sample and analysed by DPASV using the MWCNTs/UiO-66(Zr)--NH_2 MOF/GCE sensor. The corresponding results are summarized in Table 1. The average recoveries for Cu(II) across five replicate measurements ranged from 2.1 to 3.0 %, demonstrating the high accuracy of the proposed method.

Table 1. *Determination of Cu(II) in the water specimens (tap water and river water) at the MWCNTs/UiO-66(Zr)-NH_2 MOF/GCE by DPASV*

Sample	Amount of Cu(II), µM		Recovery, %	RSD, %
	Added	Found		
Tap water	1.0	0.99	99.0	3.0
	2.0	2.05	102.5	2.1
River water	1.5	1.55	103.3	1.9
	2.5	2.4	96.0	2.8

Conclusions

This work has successfully fabricated an MWCNTs/UiO-66(Zr)-NH_2 MOF-modified GCE and demonstrated its efficacy as a highly sensitive platform for the DPASV detection of Cu(II) in water samples. The MWCNTs/UiO-66(Zr)-NH_2 MOF/GCE sensor exhibits a synergistic combination of high electrical conductivity, a large electrochemically active surface area, and strong adsorption capacity, resulting in superior DPASV responses for Cu(II). The sensor demonstrated a highly selective response to Cu(II) ions across a linear range of 0.001 to 10.0 µM, achieving a LOD of 0.0005 µM. The practical utility of the MWCNTs/UiO-66(Zr)-NH_2 MOF/GCE was demonstrated through the reliable quantification of Cu(II) ions in water specimens.

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