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An electrochemical sensor based on green tea extract for detection of Cd(II) ions by differential pulse anodic stripping voltammetry

Hilal Incebay[a,*], Leyla Aktepe[b], Zeliha Leblebici[a]

[a] Nevsehir Hacı Bektas Veli University, Faculty of Arts and Sciences, Department of Molecular Biology and Genetics, Nevsehir, Turkey
[b] Nevşehir Hacı Bektaş Veli University, Institute of Science Department of Biology Nevşehir, Turkey

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ABSTRACT

In this study, a simple, selective and inexpensive electrochemical sensor was developed to detect Cd(II) ions. To this end, the bioextract (BioExt) obtained by ethanol extraction of dry green tea leaves was decorated with functionalized carbon nanotubes (MWCNTs), and the obtained nanobiocomposite (BioExt/MWCNTs) was immobilized to the glassy carbon electrode (GCE) surface. X-ray diffraction (XRD), scanning electron microscopy (SEM) and cyclic voltammetry (CV) characterizations were applied. Differential pulse anodic stripping voltammetry (DPASV) was preferred for the quantification of Cd(II) ions on GCE modified with BioExt/MWCNTs nanobiocomposite (BioExt/MWCNTs/GCE). Under optimal conditions, the peak currents depending on the Cd (II) ions concentrations on the BioExt/MWCNTs/GCE surface showed linearity between the range of 0.05 ~ 6.0 μM and the correlation coefficient (R^2) was calculated as 0.9333, and the detection limit (LOD) as 1.01 nM. The proposed nanobiostructured-sensor (BioExt/MWCNTs/GCE) showed long-term stability, high selectivity, improved voltammetric behavior and good reproducibility. Cd(II) ions were successfully detected and quantified in both river and drinking water samples with this proposed nanobiostructured sensor using the standard addition method. It was observed that electrochemically obtained results were consistent with the results obtained with ICP-MS, which is a spectrometric comparison method.

1. Introduction

The gradual increase in technological developments also increases the needs of people and this situation has led to an increase in industry developments [1]. The increase in the development of the industry has caused environmental pollution to increase rapidly. However, soil, air and water were contaminated, human health and the habitats of all living things were adversely affected [2]. One of the biggest causes of environmental pollution is heavy metals emitted from industrial wastes to the environment. Heavy metal pollution in agricultural areas is one of the most important environmental problems encountered worldwide. Intensive use of agricultural areas along with untreated wastewater and atmospheric accumulation are the main sources of heavy metals in nature [3]. The uptake of heavy metals in the food chain through plants grown on farmland contaminated with heavy metals is adversely effective in human health, even at very low levels [4]. Cd(II), among heavy metals, has a toxic effect and is highly dangerous when taken into the body even at trace concentrations [5]. The daily Cd (II) intake in drinking water allowed by the World Health Organization is 3 μg L^{-1} [6]. On the other hand, the most common water sources contain much higher concentrations of Cd(II) ions [7]. The high biodegradation tendency of Cd(II) leads to permanent damage in the central nervous system and kidneys, and increases cancer cases as well [8–10]. Therefore, it is important to follow and monitor the amounts of Cd(II) ions in water samples to ensure a healthy human life.

In recent years, the use of precise, reliable and rapid detection methods (spectroscopic, voltammetric or chromatographic methods, etc.) for the detection of heavy metals has increased significantly [11]. Among these methods, electrochemical methods attract widespread attention due to the advantages of high precision, simple operation, high speed, good selectivity, good portability and low cost [12]. As a common electrochemical method, the differential pulse anodic stripping voltammetry (DPASV) is of great interest due to its high sensitivity for the analysis of analytes [13].

Electrochemical sensors; have many advantages such as being fast, low cost, portable and simple and offering fast sample preparation compared to traditional analytical techniques [14,15]. The materials used in electrochemical sensors are essentially expected to have electron transfer efficiency and selectivity to target analytes. Carbon nanotubes as a nanomaterial undertake an important role among excellent

* Corresponding author.
E-mail address: hilalincebay@gmail.com (H. Incebay).

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electrode materials thanks to their collective properties such as wide electrical potential, fast electron transfer, and large surface area [16,17]. Besides, carbon nanotubes tend to form modifications with covalent and non-covalent bonds [18]. In addition, they also have high surface areas thanks to their geometry, which allows them to have a good adsorption capacity [19,20]. Such properties sustain hopes about the development of electrochemical sensors through carbon nanotubes [21]. The designs of sensor technology with some biological materials are also of great importance, since they are both economic and environmentally friendly. The use of bioextracts and biocomposites instead of inorganic structures in these sensor designs has attracted great research interest and contributed to the development of electrochemical sensors in different fields and to increase their application areas. Bioextracts obtained by extraction of biological materials are used as sensor materials and they can detect heavy metals [22]. In this regard, green tea, which has an antioxidant function, is a strong candidate as a biomaterial, since it contains polyphenols, proteins, chlorophyll, polysaccharides, minerals, volatile compounds, amino acids, flavanols, phenolic acids, theanine and fragrance compounds in its structure [23,24]. Especially the flavanols in the structure of green tea exhibit redox activity with metals, which makes flavanols important for human health [25].

In this study, green tea extract, which is used as a biomaterial, was obtained through ethanol extraction. Afterward, a nanobiocomposite was obtained by being decorated it with functional MWCNTs to increase the electroactivity. An electrochemical sensor was developed for the quantitative determination of Cd(II) ions with the obtained nanobiocomposite and the applicability of the sensor to real samples was successfully demonstrated. The electrochemical results were compared with the results obtained through the ICP-MS technique and the accuracy was tested.

2. Experimental

2.1. Chemical Reagents

MWCNTs were purchased from Sigma; NaOH and Na_2HPO_4 from Sigma-Aldrich (Missouri, USA); acetonitrile from VWR (Pensilvanya, USA); KH_2PO_4, ethanol from Merck (Darmstadt-Germany), $CdCI_2$ from Alfa Aesar (Massachusetts, USA) companies and they were all used without any purification. The solutions used for electrochemical experiments were prepared with 0.1 M phosphate buffer solution (PBS) with pH 4.5. Ultrapure water was used in the preparation of solutions. Before each electrochemical experiment, nitrogen gas with 99% purity rate was passed through the solutions in the voltammetric cell and dissolved oxygen was removed. The solutions were kept in the refrigerator at +4 °C when not in use.

2.2. Instrumentation

A computer-controlled potentiostat, Gamry Interface 1000B Potentiostat/Galvanostat/Zra was used for all electrochemical measurements. GCE (BASi Model MF – 2012) working electrode, platinum wire counter electrode, $Ag/AgCl/KCl_{(sat)}$ (BASi model MF – 2052) were used as reference electrodes for the three-electrode cell system. pH measurements were performed through Thermo orion 4 star pH meter. FTIR spectra were recorded using a Thermo Scientific brand spectrophotometer. Morphological images of MWCNTs/GCE, BioExt/GCE and BioExt/MWCNTs/GCE surfaces were taken with a SEM-ZEISS LS-10 microscope. In real samples, Agılent 8800 TRIPLE QUAD ICP spectrometry was used as a second method for the determination of Cd (II) ions.

2.3. Green tea extraction

20 g of dried green tea leaves were washed with ultrapure water. After drying, they were wrapped in filter paper and placed in the Soxhlet extractor. To obtain bioextract, 150 mL of ethanol was placed in the lower chamber of the Soxhlet extractor at 30°C for 2.5 hours. After the obtained extract was centrifuged at 5000 rpm for 5 minutes, the remaining ethanol was evaporated. In addition, the extract was washed with ethanol for 3 times and then dried to remove all soluble impurities.

2.4. Electrode Preparation

To remove any impurities on the surfaces, GCEs were cleaned with 0.05 μm and 0.3 μm alumina slurries poured on the velveted fabrics by applying circular movements. Afterward, they were sonicated in ultrapure water and acetonitrile solutions for 3 minutes, respectively. To activate the cleaned GCE surfaces, cyclic voltammetry was applied at pH 3.0 PBS at a potential scanning rate of 100 mV/s between the potential range of -1.0 and +1.0. MWCNTs were functionalized according to a previously reported process [26] in order to increase the electroactivity and sensitivity of the bioextract. In order to prepare a nanobiocomposite (BioExt/MWCNTs), 1 mg of functional MWCNTs was first sonicated for 5 minutes in 1 mL of ultra pure water, then 10 mg of bioextract was added and sonicated for another 60 minutes. 0.5 μL of this BioExt/MWCNTs suspension was taken by micropipette and dropped onto the GCE surface and dried at room temperature. The BioExt/MWCNTs/GCE modified surface obtained in this way was used as an electrochemical sensor for detecting surface Cd (II) ions.

2.5. DPASV measurements

DPASV was used on BioExt/MWCNTs/GCE surface for detection of Cd(II) ions. To this end, BioExt/MWCNTs/GCE, $Ag/AgCl/KCl_{(sat)}$ and Pt wire were immersed in the electrochemical cell containing Cd(II) ions in 0.1 M PBS. In order to reduce Cd(II) to Cd within this electrochemical cell, a potential of -1.5 V disposition was applied to the BioExt/MWCNTs/GCE surface for 120 s. Following the deposition, the system was kept static for 10 seconds. Electrodeposited Cd atoms were then stripped from the BioExt/MWCNTs/GCE space by anodically sweeping between the potential range −1.0 V and −0.2 V. The optimized DPASV parameters were detected as 50 mV, 0.5 s, 4 mV, 50 mV/s for pulse amplitude, pulse time, step potential and scan rate, respectively. Besides, at least three DPASV voltammograms were recorded for each experiment.

2.6. Preparation real sample

Drinking water and Kızılırmak river water (38°,71'78.1''N-34°,84'85.3"E) were used for the real sample application. The river water sample taken was first filtered to remove possible sediments and the pH was adjusted to the optimum by mixing with 0.1 M pH 4.5 PBS (1:2, V:V). Then, DPSV voltamograms were recorded by calculating standard additions of Cd(II) ions (intracellular concentrations: 0.0 μM; 0.2 μM; 0.4 μM; 1.0 μM, respectively) into this solution, and their recovery percentage was calculated. The drinking water samples were used directly without any pretreatment.

3. Result and Discussion

3.1. Characterization of modified electrodes

Fig. 1 shows the FTIR spectrum of BioExt/GCE, and BioExt/MWCNTs/GCE surfaces. The symmetrical and asymmetrical vibrations observed at frequencies in the range 2584.32 ~ 3317.19 can be attributed to polyphenols and proteins in the BioExt structure. The peak at wavenumber 3317.19 cm^{-1}, which represents the O-H phenolic group and the presence of C-O group peak at wavenumber 1627.73 cm^{-1} indicate presence of polyphenols in BioExt and BioExt structures [27]. However, the peaks observed in the range of 1697.16 cm^{-1} ~

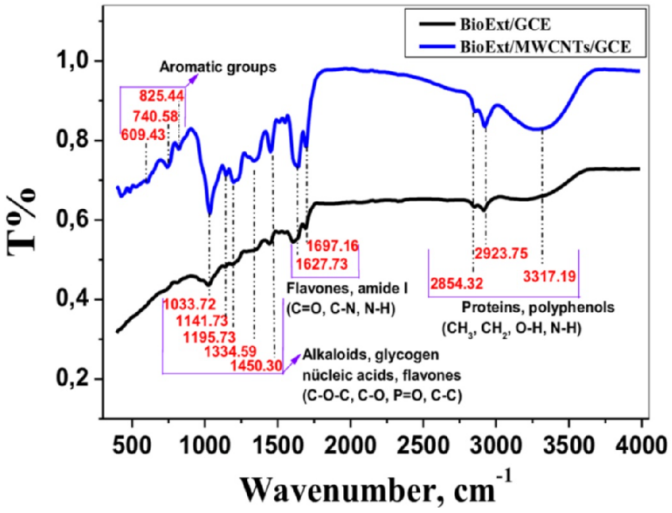

Fig. 1. FT-IR spectrum of BioExt/GCE and BioExt/MWCNTs/GCE.

1627.73 cm^{-1} and at 1033.72 cm^{-1} can be attributed to C=O and C-O, which is characteristic for flavones structures [28]. Meanwhile, the peaks corresponding to C-O-C, C-O, P=O, C-C in the range of 1033.73cm^{-1} ~ 1450.30 cm^{-1} also showed the presence of alkaloids, glycogen, nucleic acids and flavones in the structure of the green tea extract. By decorating the BioExt with MWCNTs, the transmittance values of the FTIR spectra of the BioExt/MWCNTs nanobiocomposite increased and aromatic groups in the range of 609.43 ~ 825.44 cm^{-1} were activated. It was also observed that this situation increased the electroactivity on the surface of BioExt/MWCNTs/GCE during electrochemical experiments.

BioExt/GCE, MWCNTs/GCE and BioExt/MWCNTs/GCE surfaces were characterized with SEM. Fig. 2a presents that BioExt is homogeneously distributed on GCE surface and does not have clear lines. This can be explained by the relatively high solubility of green tea extract in water. Fig. 2b presents that MWCNTs are homogenously distributed and there is no agglomeration. Fig. 2c presents the homogenous distribution of MWCNTs in the structure of BioExt. The microscope images show that the surface morphology of BioExt immobilized on GCE surface is significantly different from that obtained with BioExt/MWCNTs.

3.2. Electrochemical behavior of Cd(II)

Voltametric behaviors of bare GCE, BioExt/GCE, MWCNTs/GCE and BioExt/MWCNTs/GCE were investigated to determine the electrochemical performance of the BioExt/MWCNTs nanobiocomposite in detecting Cd(II) ions. Fig. 3 presents DPSV voltamograms of 10 μM Cd (II) ions at pH 4.5 0.1 M PBS on bare GCE, BioExt/GCE, MWCNTs/GCE and BioExt/MWCNTs/GCE surfaces. No peak was observed regarding Cd(II) ions on the bare GCE surface. Cd(II) ions on the MWCNTs/GCE surface showed a peak current of 8.18 μA at -0.7 V. Peak current signals of BioExt/GCE (15.59 μA at -0.73 V) and BioExt/MWCNTs/GCE (25.47 μA at -0.73 V) surfaces were respectively 1.9 and 3.11 times higher than MWCNTs/GCE surface. This is due to the fact that the protein, alkaloids, glycogen, nucleic acids, flavones and polyphenols contained in the green tea structure increase the electron transfer performance of Cd (II) ions [29,30]. Besides, higher peak current to Cd(II) ions on BioExt/MWCNTs/GCE surface results from a property of nanostructured MWCNTs which increase electroactivity [31,32]. Due to these properties, the combination of BioExt and MWCNTs increased the specific surface area of the electrode and supported the accumulation of Cd(II) ions involved in the electrode reaction.

3.3. Optimization of experimental conditions

Parameters such as pH value of supporting electrolyte, accumulation potential, accumulation time and nanocomposite dispersion significantly affect DPASV response of the analytes [33]. Therefore, various parameters related to DPASV voltamograms were optimized to show the best performance of the proposed sensor for the detection of Cd(II) ions. A fixed Cd(II) concentration of 10 μM was used in all parameter optimization experiments. First, 0.1 M BR, HAc-NaAc, KNO_3, NH_3-NH_4CI, PBS solutions containing 10 μM Cd(II) ions were prepared and DPASV voltamograms were recorded for the selection of support electrolyte. As presented in Fig. 4A, the best defined voltammetric peak current was observed in PBS, and therefore was used as a supporting electrolyte in all subsequent experiments. The effect of pH values on the density of stripping peak current BioExt/MWCNTs/GCE surface was investigated by DPASV between the range of 4.0 ~ 5.0. Fig. 4B clearly presents the stripping peak current values increase in the pH 3.0 ~ 4.5 range and decrease in higher pH values. With increasing pH, the hydration of cadmium ions in the solution increases and therefore the stripping peak current signals decrease [34,35]. In addition to this, it was observed that hydronium ions partially prevent the accumulation of Cd(II) ions on the BioExt/MWCNTs/GCE surface and reduce peak current signals at pH values less than 4.5. Therefore, the pH 4.5 at which the maximum peak current signal occurred was chosen as the optimum pH.

The effect of deposition potential on stripping peak currents was investigated in deposition potentials ranging from -1.7 V ~ -1.3 V. Fig. 4C clearly presents that the stripping peak currents increase due to the easier accumulation of Cd(II) ions on BioExt/MWCNTs/GCE surface at more negative deposition potentials. However, a decrease was observed at stripping peak currents in negative potentials shifting to more positive after the -1.5 V deposition potential. -1.5 V deposition potential, where maximum peak current was observed, was used in all the experiments below. The effect of deposition time, which is another optimum parameter, on stripping peak current was investigated in periods ranging from 30s to 200s. With increasing deposition time (ranging from 30s to 120s), an almost linear increase was observed at DPAVS voltamograms of Cd(II) ions (Fig. 4D). This is attributed to the increase in the Cd(II) ions amount on the BioExt/MWCNTs/GCE surface. However, it was observed that longer deposition periods do not have a significant impact on the increase in peak currents. Therefore, the optimum deposition time was determined as 120s. The effect of the amounts of BioExt/MWCNTs nanobiocomposite varying between 2.0 μL ~ 10.0 μL immobilized on the GCE surface as the last optimum condition parameter on stripping peak flows was investigated. As presented in Fig. 4E, the maximum peak current was observed on the surface obtained by 5 μL nanobiocomposite immobilization. This indicates that the modified nanobiocomposite reaches saturation against Cd(II) ions on the surface. However, as the amount of nanobiocomposite increased, a decrease in peak current occurred. This is due to the fact that the amount of nanobiocomposite on the GCE surface reduces mass transfer and conductivity on the surface. For this reason, the optimum amount of BioExt/MWCNTs composite was chosen as 5 μL.

Based on the optimization results, the proposed mechanism of deposition, reduction and anodic stripping of Cd(II) ions on BioExt/MWCNTs/GCE by DPASV technique is explained by the following reactions. In the first step, Cd^{2+} ions were accumulated on the BioExt/MWCNTs/GCE surface at a deposition time of 120 s (1). The next step shows the reduction of the accumulated Cd^{2+} ions to Cd^0 under -1.5 V desposition potential (2). In the last step, the stripping step is where reduced cadmium ions (Cd^0) is electrochemically stripped back into the solution. Stripping peaks results show that Cd(II) ions can be detected by the presented mechanism on the BioExt/MWCNTs)/GCE surface.

$$(Cd^{2+})_{solution} + (BioExt/MWCNTs)/GCE)_{surface} \rightarrow (Cd^{2+} - BioExt/MWCNTs)/GCE)_{surface} \quad (1)$$

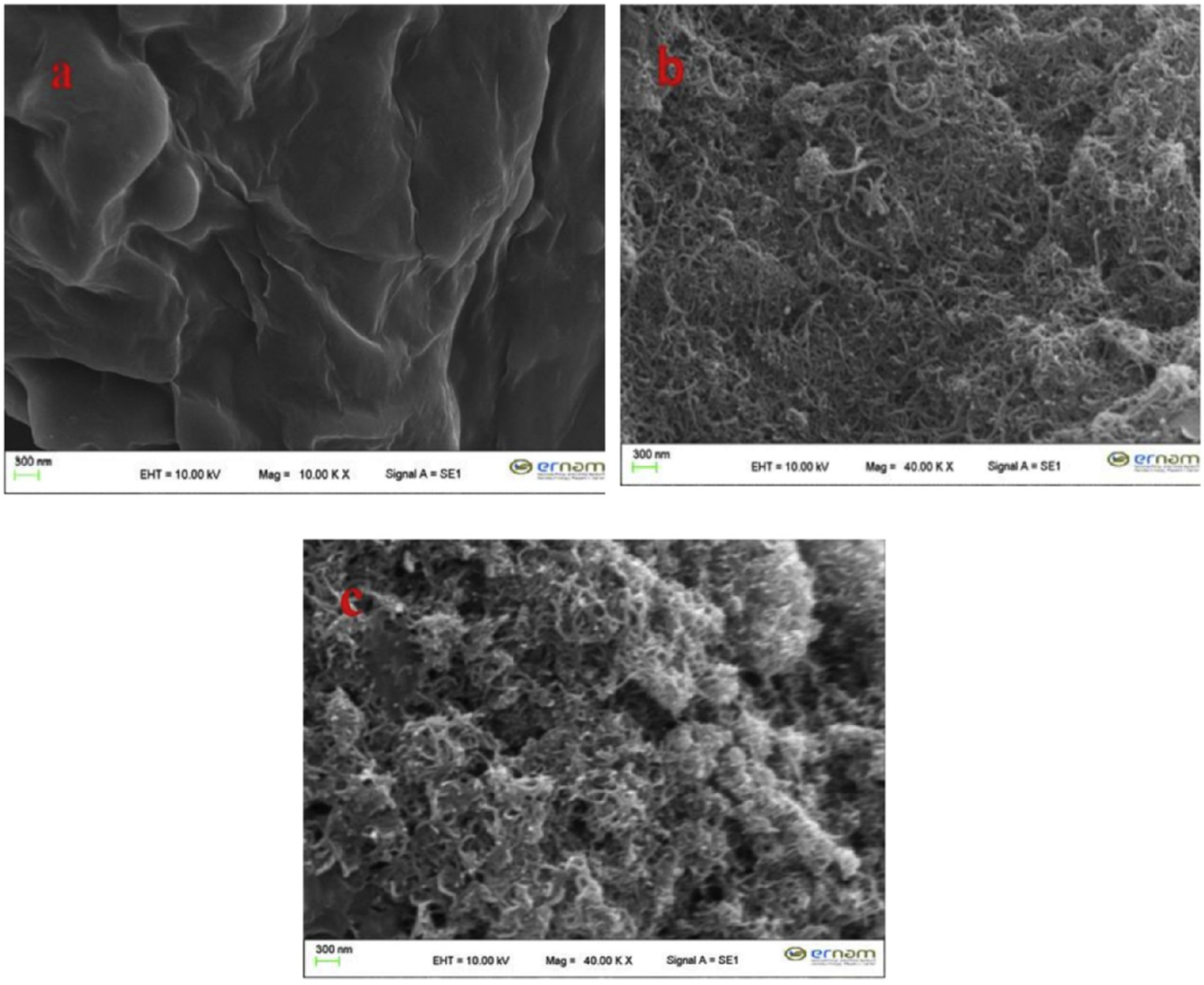

Fig. 2. SEM images of a) BioExt/GCE, b) MWCNTs/GCE c) BioExt/MWCNTs/GCE.

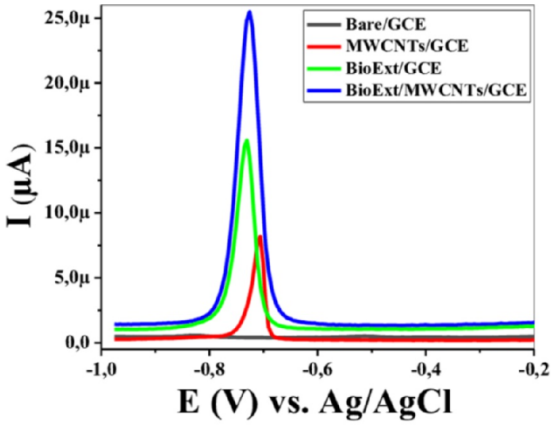

Fig. 3. CVs of 10.0 µM Cd(II) ions in 0.1 M PBS at pH 4.5 at Bare/GCE, BioExt/GCE, MWCNTs/GCE and BioExt/MWCNTs/GCE, deposition potential: −1.5 V; deposition time: 120 s, scan rate: 50 mV/s.

$$(Cd^{2+} - BioExt/MWCNTs)/GCE)_{surface} + 2e^{-} \rightarrow (Cd^{0} - BioExt/MWCNTs)/GCE)_{surface} \quad (2)$$

$$(Cd^{0} - BioExt/MWCNTs)/GCE)_{surface} \rightarrow Cd^{2+} + (BioExt/MWCNTs)/GCE)_{surface} + 2e^{-} \quad (3)$$

3.4. Linearity and detection limit

In order to determine Cd(II) ions on the BioExt/MWCNTs/GCE surface under the determined optimum conditions, the voltamograms taken with DPASV in PBS containing 0,0; 0.05; 0.5 0.9; 1.8; 2.8; 3.8; 4.6; 6,0 µM Cd(II) ions were recorded. Fig. 5A shows that well defined and peak current proportionally increased DPAVS voltamograms are obtained depending on the increasing concentrations of Cd(II) ions. The current values of these voltamograms were plotted against the increasing Cd(II) ion concentrations and the formed the calibration graph was presented in Fig. 5B. The regression equation was Ipa (µA) = 5.4807C (µM) + 8.9149 and the regression coefficient (R^2) was 0.9933. The calibration graph in Fig. 5B also showed excellent linearity between the concentrations of Cd(II) ions in the range of 0.05 ~ 6.0 µM and the peak currents obtained. Besides, the limit of detection (LOD) for Cd(II) ions on the proposed BioExt/MWCNTs/GCE platform was calculated to be 1.01 nM (0.11 µg/L) ($3S_b$/m). The safety value permitted by the World Health Organization for drinking water is 3 µg/L [6]. Compared with this value, the LOD of Cd(II) ions obtained in the proposed platform is lower. The analytical performance of BioExt/MWCNTs/GCE showed high sensitivity and low LOD compared to those of similar electrodes, reported for the determination of Cd(II) ions [7,35–39]. This can be attributed to the increase of active zones of a large number of functional groups in the bioextract, thanks to the catalytic and electrical synergistic activity of MWCNTs [40].

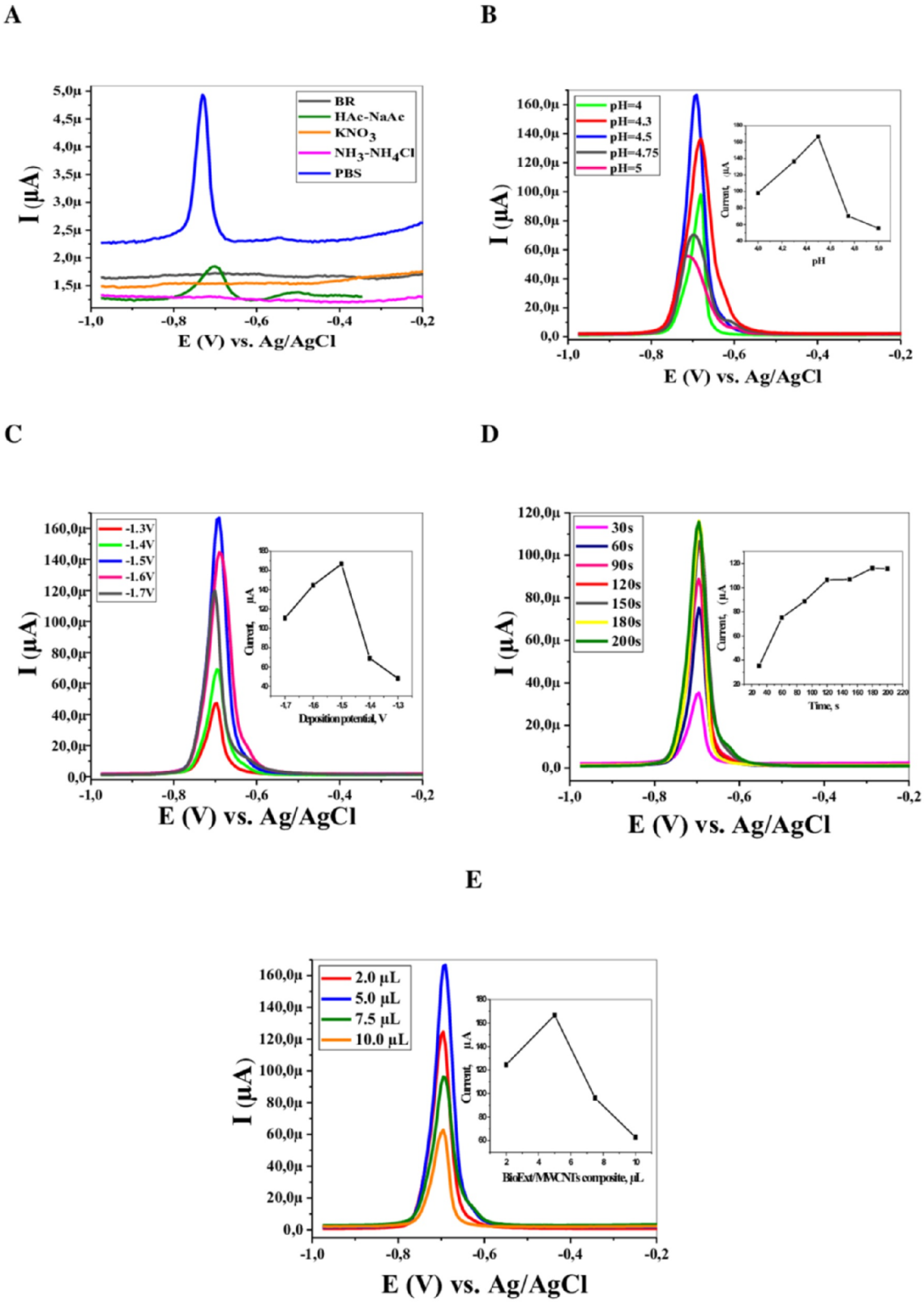

Fig 4. Influence of A) supporting electrolytes, B) pH values of PBS, C) deposition potentials, D) deposition times and E) amount of BioExt/MWCNTs composite on the stripping current. Datas were evaluated by DPASV of 10 µM Cd(II) ions.

3.5. Reproducibility, repeatability, stability and selectivity

DPVAS voltamograms of 5 µM Cd(II) ions were recorded individually under optimum conditions in 6 different electrodes prepared in the same way for reproducibility of BioExt/MWCNTs/GCE, and in electrodes prepared in the same way for 6 times for repeatability. (Fig. 6A). The relative standard deviations (RSD) derived from the peak currents of these voltamograms were calculated as 2.18% and 1.78%,

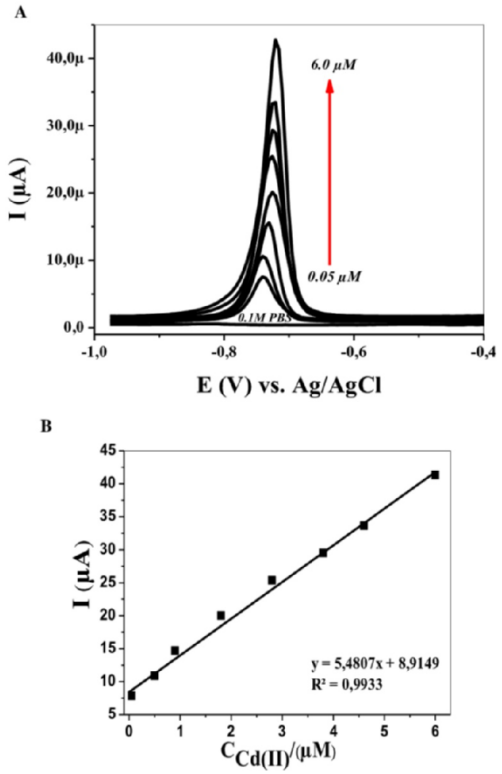

Fig. 5. A) DPASV voltammograms of 0.0 µM; 0.05 µM; 0.5 µM; 0.9 µM; 1.8 µM; 2.8 µM; 3.8 µM; 4.6 µM; 6.0 µM concentrations of Cd(II) ions in 0.1 M PBS (pH 4.5) at BioExt/MWCNTs/GCE. **B)** A plot of peak current versus the concentration of Cd(II) ions.

respectively. These very small RSD values showed that the BioExt/MWCNTs/GCE surface has good reproducibility and repeatability. For the stability of the suggested sensor, the once prepared BioExt/MWCNTs/GCE surface was incubated in pH 4.5 PBS and DPASV voltamograms of 5.0 µM Cd(II) ions were recorded at certain periods (Fig. 6B). The results showed that the intensity of the peak currents of DPASV voltamograms varied only by 3.37%. This indicates that the BioExt/MWCNTs/GCE surface has excellent stability for detecting 5 µM Cd(II) ions.

For the selectivity of BioExt/MWCNTs/GCE, a mixture containing Zn(II), Pb(II), Hg(II), Mn(II), Co(II), Ni(II), Cr(II), each with a concentration of 100 µM (in pH 4.5 PBS) was prepared and DPSV voltamograms were recorded by adding Cd(II) ions at different concentrations (0.25; 0.50; 1.00; 1.50; 2.00 µM) to this mixture (Fig. 6C). A linear increase was observed in peak currents of Cd(II) ions between the range of 0.0 ~ 2.0 µM. In addition, voltamograms of 1 µM Cd(II) solutions in the presence of interference species and solutions in the absence of interference species were recorded and compared at pH 4.5 PBS (Fig. 6D). It was clearly seen that the interference species did not have an effect on the voltammetric signal response (a decrease of 2.75%) of the Cd(II) ions. This can be attributed to the specific binding of Cd(II) ions to the anionic groups in the functional MWCNTs, which increase the activity of acids, alcohols, phenols, ethers, and hydroxyl groups in the structure of the BioExt/MWCNTs nanobiocomposite. Experimental results showed that interference types do not have a significant effect on the peak shape, peak potential and peak current of the Cd(II) ions, and the suggested sensor has excellent selectivity.

3.6. Analysis of real samples

The applicability of the nanobiostructured BioExt/MWCNTs/GCE sensor developed for the detection of Cd(II) ions was tested in two

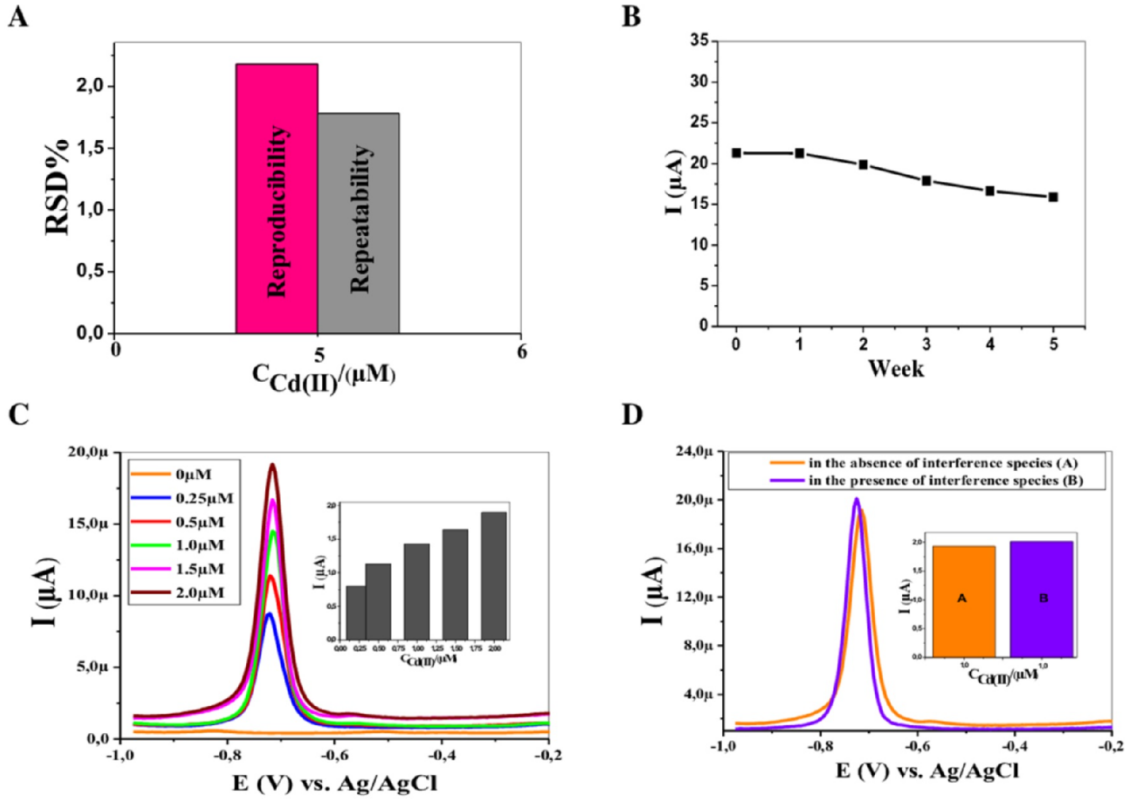

Fig. 6. A) % RSD of repeatability and repeatability **B)** stability **C)** DPASV voltammograms of increasing concentrations of Cd(II) ions in the presence of interference species **D)** DPASV voltammograms of Cd(II) ions in the presence of interference species and in the absence of interference species in pH 4.5 PBS of BioExt/MWCNTs/GCE for detection of Cd (II) ions.

Table 1
Concentration, recovery and RSD results calculated from the DPASV voltamograms of Cd(II) ions added to real samples.

Samples	Added (μM)	Found (μM)	Peak current (μA)	Recovery (%)	RSD (%)	Error (%)
River water	0	0.0205	4.77	0	0	0
	0.2	0.1911	5.35	95.58	1.52	-4.41
	0.4	0.4264	6.15	106.61	1.46	6.61
	1.0	1.0147	8.15	101.47	0.55	1.47
Drinking water	0	Not detected	0	0	0	0
	0.2	0.2017	3.60	100.86	1.52	0.86
	0.6	0.6138	5.03	102.30	1.70	2.30
	1.0	1.0028	6.38	100.288	2.76	0.28

n = 5
RSD (%) = (Standard deviation / The average of the data obtained by repeating 5 times.) x 100.
Error (%) = [(found value - added value)/added value)] x 100.

Table 2
Application of DPASV and ICP-MS methods in determining Cd (II) ions in river water and driking water samples.

Technique	Sample	N	Found Cd(II) ions (ppm)	RSD (%)
DPVS	River water	3	21.48 ± 1.96	7.6
ICP-MS		3	21.79 ± 0.82	3.2
DPVS	Drinking water	3	24.29 ± 1.92	6.6
ICP-MS		3	24.06 ± 0.45	1.6

n = 3
90% Confidence Interval

water samples. While the drinking water sample was used directly, the river water sample was filtered 3 times, and both samples were mixed with pH 4.5 PBS in a ratio of 1:2, V:V. Under optimal conditions, DPASV voltamograms were recorded before and after standard additions of Cd (II) ions. It was tested with 5 replicates for each concentration and summarized in Table 1. The suggested nanobiocomposite electrode offered good results with 95.58% and 106.61% good recoveries, minor errors between -4.41 and +6.61, and RSD values between 0.55% and 2.76%. These good results showed high sensitivity, good reliability and great potential in detecting Cd(II) ions in real samples by DPASV at BioExt/MWCNTs/GCE surface. In addition, the results obtained by DPASV were compared with ICPM-MS results under the same conditions and summarized in Table 2. The good compatibility of the results obtained by two different methods indicates that the BioExt/MWCNTs/GCE electrochemical sensor suggested for the determination of Cd(II) ions can be successfully applied to water samples.

4. Conclusion

This study demonstrates the nanobiocomposite prepared from carbon nanotubes and extracts obtained by a simple extraction of green tea leaves can be used as a modifying surface in the electrochemical quantification of Cd(II) ions. The proposed low-cost and easy-to-use BioExt/MWCNTs/GCE platform showed low-level determination limit, good linearity, high sensitivity and good repeatability. Furthermore, this platform was successfully applied in the determination and measurement of Cd(II) ions in the river and drinking water samples with good recovery results were obtained. Besides, the accuracy and reliability of the platform suggested in the analysis of real samples were confirmed by ICP-MS. BioExt/MWCNTs/GCE was simply produced at low cost and offered very compatible results in the determination of Cd (II) ions in both methods. The BioExt/MWCNTs/GCE platform suggested in this study can be used in maintenance zone detection systems to monitor the quality of drinking water thanks to its ease of use, high sensitivity and low cost.

CRediT authorship contribution statement

Hilal Incebay: Conceptualization, Methodology, Validation, Formal analysis, Resources, Visualization, Investigation, Supervision, Writing - review & editing. **Leyla Aktepe:** Formal analysis. **Zeliha Leblebici:** Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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