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Electrochemical Detection of Cadmium and Lead in Rice on Manganese Dioxide Reinforced Carboxylated Graphene Oxide Nanofilm.

İlknur Üstündağ[1], Aslı Erkal[2], Zafer Üstündağ[3]* Ali Osman Solak[4]

[1] Dumlupınar University, Faculty of Arts and Science, Department of Chemistry, Kütahya, Turkey
[2] Alanya Alaaddin Keykubat University, Rafet Kayış Eng. Faculty, Alanya, Antalya, Turkey
[3] Dumlupınar University, Faculty of Arts and Science, Department of Chemistry, Kütahya, Turkey
zustundag@gmail.com
[4] Kyrgyz-Turkish Manas University, Faculty of Eng., Chem Eng Department, Bishkek, Kyrgyzstan

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Abstract: *Manganese dioxide decorated carboxylated graphene oxide (Mn-GO-COOH) attached onto the glassy carbon (GC) electrode to develop a new method for the simultaneous determination of* Cd^{2+} *and* Pb^{2+} *ions in rice samples. Graphene oxide (GO) was attached on 4-aminophenyl covalently modified glassy carbon surface via amide reaction. As-prepared modified material was characterized with XPS, SEM and electrochemical methods. A novel differential pulse anodic stripping voltammetric (DPASV) method was developed for the simultaneous determination of* Cd^{2+} *and* Pb^{2+} *on the GC/Mn-GO-COOH nanoplatform electrode. A linear response was found for the heavy metals in the range from 5 to 100 µg/L. The limit of detections (LODs) of* Cd^{2+} *and* Pb^{2+} *were 0.04 µg/L and 0.08 µg/L respectively. Manganese dioxide decorated carboxylated graphene oxide electrode was applied to the detection of* Cd^{2+} *and* Pb^{2+} *present in different rice samples by developed voltammetric method, and the accessed results were found to be in accordance with that of ICP-OES.*

Keywords: *Heavy metals, food analysis, differential pulse anodic stripping voltammetry, manganese decorated graphene oxide.*

1. INTRODUCTION

Rice, an Asian origin cereal grain, is a very important food with regard to human nutrition and one of the much consumed nutrient all over the world [1]. As in all foods, level of the toxic heavy metals contamination such as Pb and Cd is important in rice due to the environmental pollution. Since these metals have been extensively used in metal industry and in batteries besides many other areas, they can easily be adsorbed from contaminated soil by plants [2]. Both metals cause poisoning, and exhibit adverse effects on kidney, liver, heart, vascular and immune system of a person. In addition, exposure to these metals causes DNA aberration, cancer and birth disease [3]. Therefore, determination of these heavy metal concentrations is important especially in rice, because heavy metals exist in surface waters in colloidal, particulate, and dissolved phases in a substantial watery planting of rice.

Two-dimensional Graphene as a single layer is an allotrope of carbon in an hexagonal lattice [4]. Graphene oxide derivative modified electrodes for determination of Pb^{2+} and Cd^{2+} have begun to be used as electrode materials in literature over the last decade. Among the different electrochemical techniques for the determination of these ions in food samples on graphene oxide based electrode, the most preferred technique is the anodic stripping voltammetry using differential pulse or square wave voltammetry [5-8]. Graphene oxide (GO), which is a graphene derivative, contains a range of oxygen bearing functionalities such as hydroxyl, carbonyl, epoxide, and carboxyl groups [9]. When functionalized with some molecules such as –OH, -COOH, etc., graphene is likely to gain new materials having the different properties [10]. When activated with the chloroacetic acid, most of the epoxide, ester and hydroxyl groups on GO are converted to carboxylic acid groups [11, 12]. The carboxylated graphene oxide (GO-COOH) has begun to be widely used in recent years [11, 12].

There are several analytical methods used in the determination of metals in samples containing trace amounts. These are X-ray fluorescence spectroscopy [13-15], atomic absorption spectroscopy [16], inductively coupled plasma (ICP) spectroscopy [17, 18], and electrochemical methods such as amperometry [19], impedimetry [20] and voltammetry [21-23]. Recently, stripping voltammetry with differential pulse [24] and square wave [25] techniques are mostly preferred to determine trace elements in food.

Present investigation is focused on the preparation of manganese dioxide decorated carboxylated graphene oxide electrode (GC/Mn-GO-COOH) and its applicability for monitoring of Cd^{2+} and Pb^{2+} metals in various kinds of rice samples.

2. EXPERIMENTAL

2.1. Chemicals and Reagents

All chemicals and reagents were purchased from Merck, Fluka, Sigma-Aldrich and Riedel chemical company. GO and its derivatives were synthesized in our laboratory. The glassy carbon (GC) working electrode (MF-2012) was purchased from Bioanalytical Systems Company (USA). Bare GC electrodes were cleaned and polished in an aluminum oxide slurries with 0.1 and 0.05 micron sized particles (Baikowski, USA) on microfiber cloth pad (Buehler microfiber cloth, , USA). The polished electrodes were sonicated with an ultrasonic bath cleaner (Bandelin-Sonorex, Germany) for approximately 5 min in ultrapure water (UPW, Human Power 1$^+$, S. Korea) and mixture of 1:1 (v/v) isopropyl alcohol/acetonitrile (MeCN) solutions.

2.1. Preparation of Manganese Dioxide Reinforced Carboxylated Graphene Oxide Electrode

GO was synthesized from graphite by electrochemical exfoliation method, as described elsewhere [4]. Pristine graphite was used as anode, in a mixture of 2.5 g H_2SO_4 and 10 mL of 30% KOH in 100 mL ultrapure water (UPW, 18.3 MΩ cm). A platinum stick was used as cathode electrode. The electrochemical exfoliation was performed under the constant DC potential of +20 V by direct current (DC) power source (Yıldırım Electronics, Turkey). The exfoliated materials were precipitated with a Hermle (Z36HK, Germany) ultracentrifuge under 15.000 rpm for 10 min. The raw GO was washed with UPW for three times. The GO was dried at 70 °C under vacuum for 12 h.

The GO-COOH was prepared according to the "Hongjie Dai and coworkers" method [11]. 1.2 g of NaOH and 1.0 g of chloroacetic acid were added into a GO suspension (4 mg GO/10 mL UPW). The suspension was sonicated for 1 h. The –OH terminated groups on GO was converted to carboxylic acid (-COOH) moieties. The functionalized GO-COOH in suspension solution was precipitated with an ultracentrifuge under 12.000 rpm for 10 min and washed with UPW for three times. The GO-COOH was dried at 70 °C under vacuum oven for 12 h.

12 mg GO and 0.5 g $MnCl_2.4H_2O$ were sonicated in isopropyl alcohol (100 mL) with an ultrasonic bath for 1 h [22]. The solution was heated to 85ºC. 0.3 g $KMnO_4$ involved 10 mL UPW was poured in the solution. The suspension solution was held at 85˚C for 30 min on the magnetic stirring. Manganese oxide included carboxylated graphene oxide was centrifuged at 5000 rpm for 10 min and washed with UPW three times. The material was dried at 70°C under vacuum oven for 12 h. The nanomaterial was denoted as Mn-GO-COOH.

10 mg of Mn-GO-COOH was diluted with 10 mL UPW. The bare GC electrode was covered with 5 µL to 25 µL of Mn-GO-COOH suspension by microsyringe, and then dried under an infrared lamp (75 W) for 10 min for optimization study of Cd^{2+} and Pb^{2+} analysis by DPV. The electrode was denoted as GC/Mn-GO-COOH. Similarly, the GO-COOH and GO modified GC electrodes (GC/GO-COOH and GC/GO) were prepared for comparison.

2.2. Characterizations of Materials

All electrochemical measurements were performed under a highly purified Ar (99.999 %) atmosphere by Ivium CompactStat, (US) electroanalyzer at room temperature (25 ± 1°C) with triple electrode system. Ag/AgCl/KCl(sat) and platinum wire were used as reference electrode and counter electrodes, respectively. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used for electrochemical characterization of the modified electrodes. XPS measurement was carried out with an X-ray photoelectron spectrometer (PHI 5000, Versa Probe, ULVAC-PHI. Inc., Japan/USA). SEM images were recorded using a scanning electron microscopy (SEM, Zeiss-Evo, Germany). Infrared (IR) data was observed with a FT-IR spectrometer (Bruker, Tensor 27).

2.2. Sample Preparation and DPASV Procedure

Two commercial rice samples (Baldo and Jasmine) were purchased from a local supermarket and analyzed. The samples were digested as described elsewhere [26]. The rice samples were ground into fine powder in a planetary ball mill (Retsch, PM100, Germany). The samples were dried in oven at 105 °C for 12 h. 0.5 g of the rice flour was treated with 1.5 mL of concentrated $HClO_4$ and 1.5 mL of concentrated HNO_3. The suspension was heated to boiling on a hot plate until white fumes appeared. The evaporated mixture was diluted with 5 mL of 0.5 M HCl. The mixture was heated until a clear solution was obtained. The solution was filtered via a 400 nm syringe filter. The filtrate solution was diluted to 10 mL at 25 °C with 0.5 M HCl.

Differential pulse anodic stripping voltammetric method for the simultaneous determination of Cd^{2+} and Pb^{2+} was developed. Current-concentration linear response was found for the heavy metals in the range from 5 μg/L to 100 μg/L. Some optimization parameters, the limit of detections (LODs), precision and accuracy results of the developed method were investigated. The modified electrode was used for determination of Cd^{2+} and Pb^{2+} in two different rice samples. DPV results were recorded by positive scanning at a rate of 20 mV /s, a pulse amplitude of 25 mV, a pulse rate of 0.5 s, and a pulse width of 60 ms for a holding time of 2 s.

3. RESULTS AND DISCUSSIONS

3.1. Characterization of Materials

Electrochemical characterization of GC/Mn-GO-COOH electrodes were performed using 2 mM $K_4Fe(CN)_6/K_3Fe(CN)_6$ redox probe by CV and EIS. Cyclic voltammograms (CVs) of the redox probe on GC, GC/GO, GC/GO-COOH and GC/Mn-GO-COOH are given in Fig. 1.

Anodic peak current of the redox probe on GC, GC/GO, GC/GO-COOH GC/Mn-GO-COOH was calculated as 3.2 μA 108.9 μA 93.2 μA, and 180.8 μA. Anodic and cathodic peak current of the redox probe on GC/Mn-GO-COOH surface was significantly increased as is seen in Fig. 1. Electron transfer rate of the redox couple was probably accelerated with tunneling effect of the Mn-GO-COOH due to the high porosity and high surface area of the film on GC.

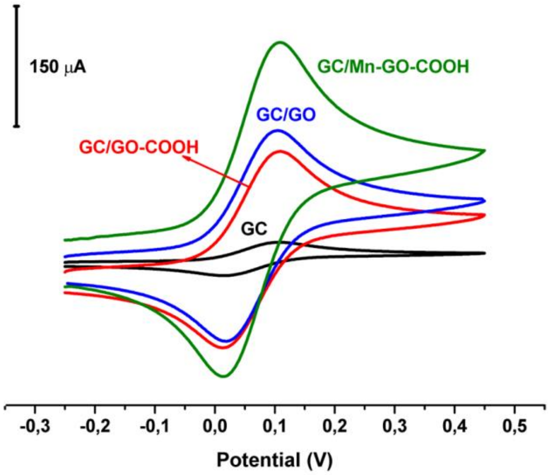

Figure 1. *CVs of 2 mM $K_4Fe(CN)_6$/ $K_3Fe(CN)_6$ redox probe on GC, GC/GO, GC/GO-COOH and GC/Mn-GO-COOH vs. Ag/AgCl (scan rate 200 mV/s).*

Nyquist plots of the redox probe on GC, GC/GO, GC/GO-COOH and GC/Mn-GO-COOH are given in Fig. 2. Charge transfer resistant (Rct) of the redox couple on the electrodes was determined with fit of Nyquist plots. All the plots were fitted as Warburg effected diffusion controlled CPE equivalent electrical circuit (inset in Fig. 2). Rct values of the redox couple on GC, GC/GO, GC/GO-COOH and GC/Mn-GO-COOH were determined as 0.87 kΩ, 0.53 kΩ, 0.77 kΩ, and 0.36 kΩ. Rct of the redox probe was dramatically decreased with GC/Mn-GO-COOH. This result is consistent with the currents measured in CV experiments. Electron transfer rate of the redox probe increased while charge transfer resistant decreased, as expected on GC/Mn-GO-COOH electrode.

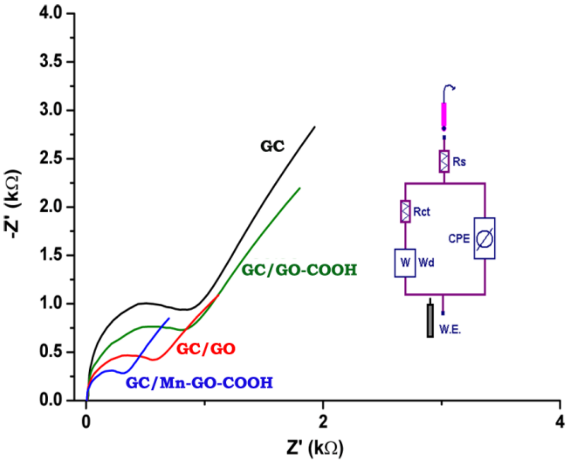

Figure 2. *Nyquist plots of 2 mM $K_4Fe(CN)_6$/$K_3Fe(CN)_6$ redox probe on GC, GC/GO, GC/GO-COOH and GC/Mn-GO-COOH vs. Ag/AgCl (0,1 Hz-100 kHz, DC potential is 0.13 V) and their equivalent electrical circuit (inset).*

GO and GO-COOH were characterized with XPS. C_{1s} spectra of GO and carboxylated graphene oxide (GO-COOH) are given in Fig. 3a. Mn2p XPS core spectrum of Mn-GO-COOH is given in Fig. 3b. In Fig. 3a, the weak C_{1s} core spectrum of GO is assigned to carboxyl group included carbon. The C_{1s} spectrum of carboxylated graphene oxide (GO-COOH) increased significantly [27]. In Fig. 3b, a Mn_{2p} core spectrum apparently indicates the presence of manganese in Mn-GO-COOH film at the surface [22].

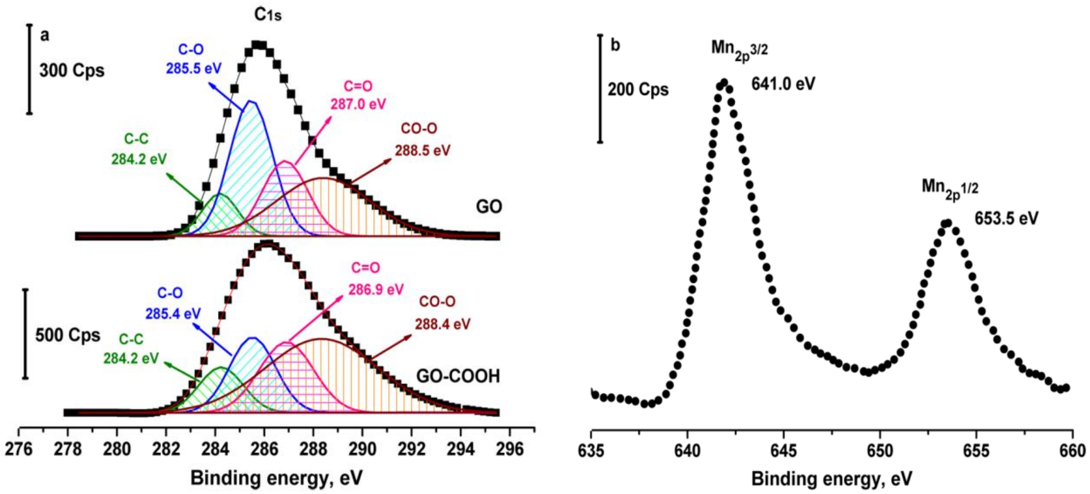

Figure 3. *C1s XPS core spectra of GO and GO-COOH, and Mn2p core spectrum of Mn-GO-COOH.*

SEM image of manganese dioxide reinforced carboxylated graphene oxide (Mn-GO-COOH) and its EDX spectrum are given in Fig. 4. In Fig. 4a, manganese dioxide clusters on the carboxylated graphene oxide can apparently be seen. Principal elements of C, O, Mn and residual amount of K (trace amount of K from $KMnO_4$) are seen in Fig. 4b [28].

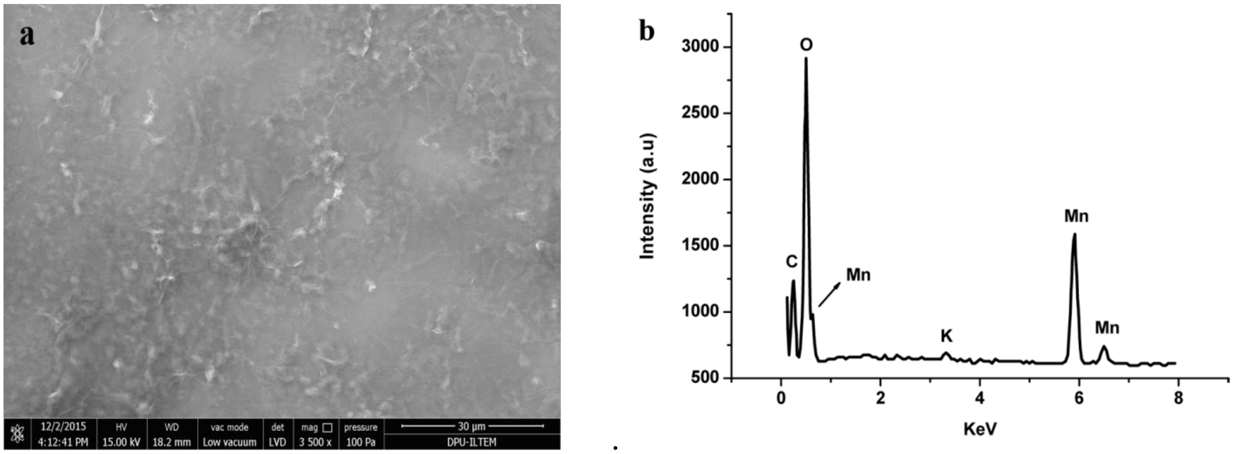

Figure 4. *SEM image (a) and EDX spectrum (b) of Mn-GO-COOH*

3.2. Simultaneous Determination of Cd^{2+} and Pb^{2+} Using DPASV

Analytical parameters of the method developed, such as pH of the aqueous media, deposition potential, deposition time, and volume of Mn-GO-COOH suspension were determined with 25 μg/L of Cd^{2+} and Pb^{2+} in 0.1 M sodium acetate/acetic acid buffer solution using DPASV technique to acquire the highest current response of both ions, i.e. of Cd^{2+} and Pb^{2+} simultaneously. The optimization results as anodic peak current vs. optimization parameter are given in Fig. 5. Different pHs of 0.1 M solution were tested in the range of 3.0 - 5.5. It was found that a pH of 4.5 proved the highest anodic peak currents (Fig. 5a). Thence, calibration studies, 0.1 M sodium acetate/acetic acid buffer solution at 4.5 of pH with 120 s for deposition time (Fig. 5b) with 15 µL of Mn-GO-COOH suspension (Fig. 5c) dropped GC were chosen as the optimum parameters. The deposition potential was studied in the potential range of -0.8 to -1.4 V vs. Ag/AgCl. Deposition potential was selected as -1.2 V (Fig. 5d). Lower current values observed at the more negative potentials beyond -1.2 V may be due to the hydrogen gas evolution on the electrode surface -1.2 V [1, 29, 30].

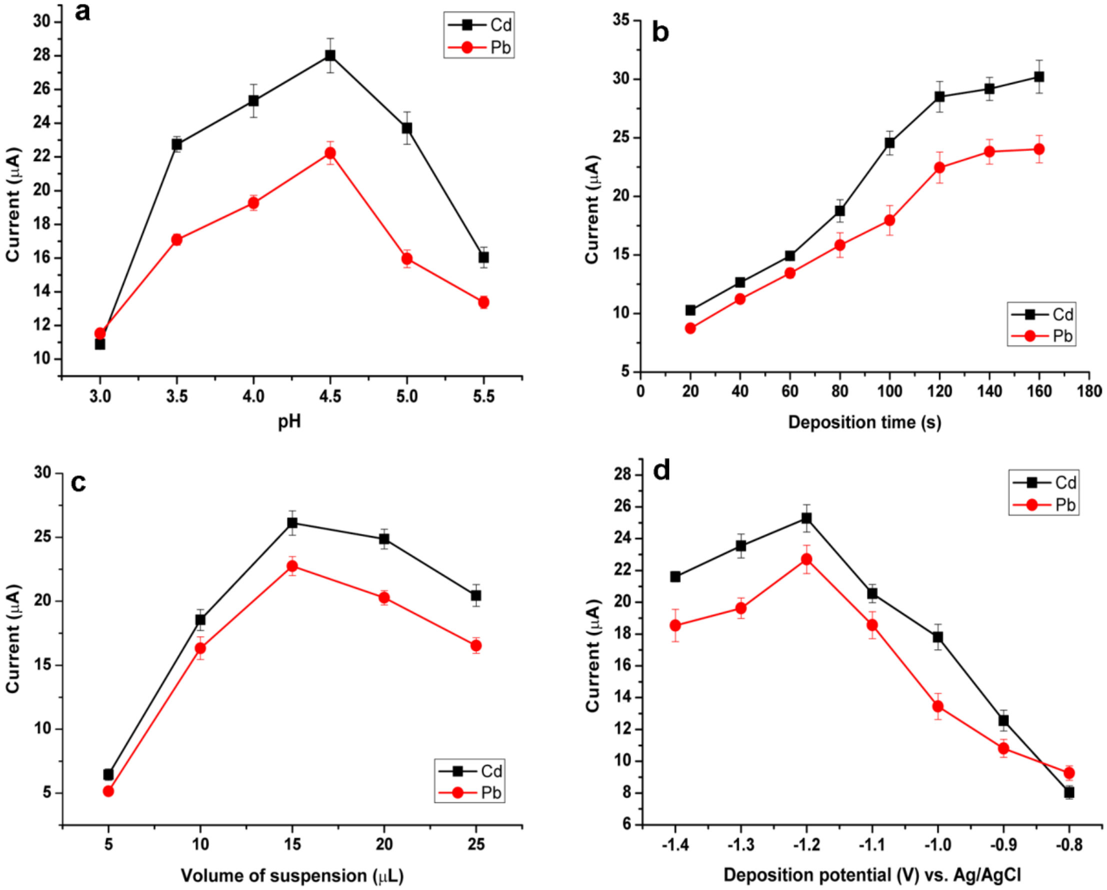

Figure 5. *Optimization study for 25 µg/L Cd^{2+} and Pb^{2+}. Effects of pH (a), deposition time (b), volume of Mn-GO-COOH suspension on GC (c), and deposition potential (d) on the anodic stripping peaks current.*

Differential pulse anodic stripping voltammograms for different concentrations of Cd^{2+} and Pb^{2+} between 5 µg/L - 100 µg/L under the optimized conditions were illustrated in Fig. 6. The linear calibration plots for the ions at different concentrations in the range of 5 to 100 µg/L are shown in Fig. 7. The linear equations for Cd^{2+} and Pb^{2+} were $Ip(Cd^{2+})=0.9494[Cd^{2+}]+5.0334$ (R^2: 0,9988) and $Ip(Pb^{2+})=0.7250[Pb^{2+}]+4.0398$ (R^2: 0,9968), respectively. LODs are 0.04 µg/L for Cd^{2+} and 0.08 µg/L for Pb^{2+} (S/N=3) with sensitivity of 0.9494 µA.L/µg and 0.725 µA.L/µg, respectively.

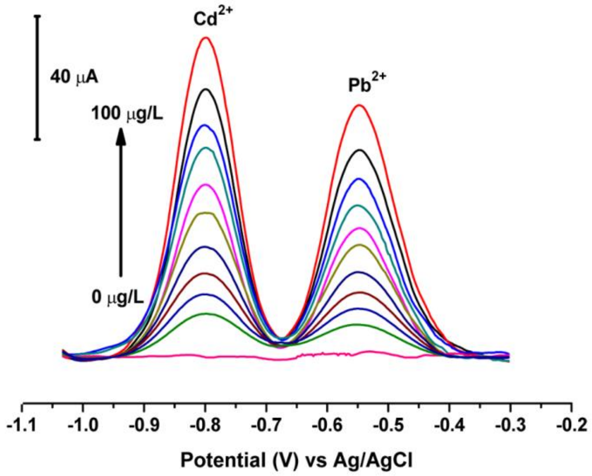

Figure 6. *Differential pulse anodic stripping voltammograms for different concentrations (0, 5, 10, 20, 30, 40, 50, 60, 70, 80, 100 µg/L) of* Cd^{2+} *and* Pb^{2+}.

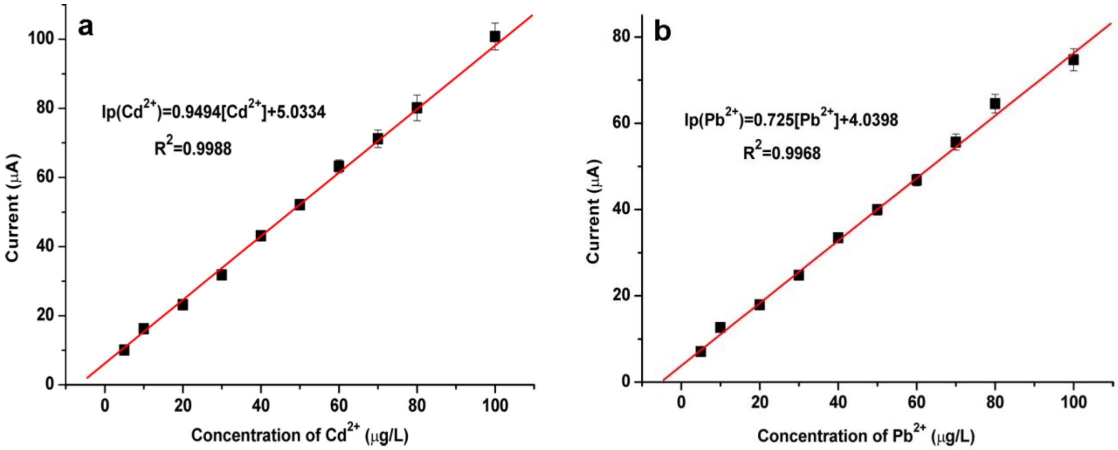

Figure 7. *Calibration curves for addition of 0, 5, 10, 20, 30, 40, 50, 60, 70, 80, 100 µg/L* Cd^{2+} *(a) and* Pb^{2+} *(b).*

Comparison of the sensor performance of DPASV and square wave anodic stripping voltammetry (SWASV) for the determination of Cd^{2+} and Pb^{2+} between different works in literature is given in Table 1.

The possible influence caused by interfering some ion species such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{2+}, Zn^{2+}, Cu^{2+}, Cr^{3+}, Mn^{2+} on the stripping current of 10 µg/L Cd^{2+} and Pb^{2+} under the optimized conditions are given in Table 2. The changes of peak current results of Cd^{2+} and Pb^{2+} in the presence of Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Cr^{3+}, Mn^{2+} (max: 100-fold) are within tolerable limits, i.e. lower than 5%. The tolerable limit for Fe^{2+} and Zn^{2}+ was 50-fold and 30-fold, respectively. The interference effect of copper was found to be very high. The tolerable limits of Cu^{2+} with 3-fold was determined as -4.77% for Cd^{2+} and -4.33 for Pb^{2+}. When 4-fold of copper ions was added, current responses of Cd^{2+} and Pb^{2+} were dramatically decreased by about 18.2% and 11.7%, respectively.

Table 1. *Sensor performance of DPVASV and square wave anodic stripping voltammetry (SWASV) for the determination of* Cd^{2+} *and* Pb^{2+}.

Electrode	**Technique**	**Calibration range**		**LOD**		**Ref.**
		Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	
Bi-D24C8/Nafion SPCE	SWASV	0.5 ppb – 60 ppb	0.5 ppb - 60 ppb	0.27 ppb	0.11 ppb	[1]
Pt/MWCNT/P1,5-DAN	SWASV	4 ppb – 150 ppb	4 ppb – 150 ppb	3.2 ppb	2.1 ppb	[31]
GO/ κ-Car/L-cys/GC	SWASV	5 nM – 50 nM	5 nM – 50 nM	0.58 nM	1.08 nM	[29]
Bi/GR/IL-SPE	SWASV	1 ppb – 80 ppb	1 ppb – 80 ppb	0.08 ppb	0.10 ppb	[30]
PolyL-GCE	DPASV	40 nM – 1000 nM	1 nM – 100 nM	10 nM	0.7 nM	[32]
MWCNT-RGO	DPASV	0.5 ppb – 30 ppb	0.5 ppb - 30 ppb	0.1 ppb	0.2 ppb	[33]
GO-MnO2	DPASV	0.01 nM – 100 nM	0.01 nM – 100 nM	0.14 nM	1.24 nM	[22]
Bi/MGF-Nafion/GCE	DPASV	2 ppb – 70 ppb	0.5 ppb – 110 ppb	0.437 ppb	0.210 ppb	[34]
GC/Mn-GO-COOH	DPASV	5 ppb – 100 ppb	5 ppb – 100 ppb	0.04 ppb	0.08 ppb	this study

Table 2. *Interferences of different ions on the simultaneous detection of 10 μg/L for both* Cd^{2+} *and* Pb^{2+} *as peak current signal percentage change.*

Interfering ions	**Concentration,** μg/L	**Signal change (%)**	
		Cd^{2+}	Pb^{2+}
Na^+	1000	+0.22	+0.17
K^+	1000	-0.71	-0.83
Ca^{2+}	1000	+1.29	+2.35
Mg^{2+}	1000	+1.78	+0.33
Al^{3+}	1000	-1.33	+2.27
Fe^{2+}	400	-4.86	+3.71
Zn^{2+}	300	+3.89	-4.98
Cu^{2+}	30	-4.77	-4.33
Cr^{3+}	1000	-2.48	-1.79
Mn^{2+}	1000	-2.2	-1.25

Reproducibility of GC/Mn-GO-COOH electrode was investigated under the optimum conditions for 25 μg/L each of Cd^{2+} and Pb^{2+} solution, on the as-prepared five different electrodes.

Precision and accuracy of the developed methods, for intra-day and inter-day, were studied with standard samples. Three different concentrations of 2.0 μg/L, 5.0 μg/L and 10 μg/L for both Cd^{2+} and Pb^{2+} in the linear range were determined in five independent series on the same day for intra-day precision and seven consecutive days for inter-day precision. The results for intra-day and inter-day experiments are given in Table 3.

3.3. Real Sample Analysis

The developed method was applied to determine of Cd^{2+} and Pb^{2+} on GC/Mn-GO-COOH electrode in rice samples by DPASV. The results from the method in the rice analysis were validated using ICP-OES method. Analytical recovery values of Cd^{2+} and Pb^{2+} in market rice samples are given in Table 4. The recovery rates for spiked ranged from 96.5 to 102.6% for Cd^{2+} and 97.5 to 103.1% for Pb^{2+}.

Table 3. *Five independent series on the same day for intra-day precision and seven consecutive days for inter-day precision of the method.*

Added, µg/L	**Intra-day**						**Inter-day**					
	Found Value, µg/L		**Precision * %**		**Accuracy %**		Found Value, µg/L		**Precision * %**		**Accuracy %**	
	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}
2	2.02±0.04	1.97±0.03	1.98	1.52	1.0	-1.5	1.98±0.05	2.03±0.02	2.53	0.99	-1.0	1.5
5	5.15±0.15	4.91±0.14	2.91	2.85	3.0	-1.8	10.25±0.25	10.20±0.17	2.44	1.67	2.5	2.0
10	9.88±0.33	10.17±0.26	3.34	2.56	-1.2	1.7	50.27±1.33	49.75±1.55	2.65	3.12	0.5	-0.5

*RSD

Table 4. *Concentration of Pb^{2+} and Cd^{2+} in rice samples found by DPASV and ICP-OES (n=3, Degree of confidence 95%).*

Samples	**Added, µg/L**	**DPASV, µg/L**		**ICP-OES, µg/L**		**Recovery %**	
		Cd^{2+}	**Pb^{2+}**	**Cd^{2+}**	**Pb^{2+}**	**Cd^{2+}**	**Pb^{2+}**
Jasmine-1	0	ND*	3.63±0.06	ND*	3.57±0.06	-	-
	2	1.98±0.04	5.80±0.11			99.0	103.0
	4	3.88±0.27	7.87±0.46			97.0	103.1
Jasmine-2	0	1.28±0.05	4.68±0.12	1.21±0.08	4.79±0.13	-	-
	5	6.33±0.13	9.50±0.48			100.8	98.1
	10	10.88±0.36	14.81±0.09			96.5	100.9
Baldo-1	0	2.17±0.05	5.33±0.17	2.20±0.11	5.43±0.17	-	-
	2	4.10±0.08	7.15±0.49			98.3	97.5
	4	6.33±0.21	9.20±0.65			102.6	98.6
Baldo-2	0	ND*	2.74±0.10	ND*	2.83±0.42	-	-
	5	4.88±0.40	7.85±0.31			97.6	101.4
	10	9.83±0.65	12.57±0.76			98.3	98.7

*ND: Not detectable

4. CONCLUSION

A novel Mn-GO-COOH electrode was prepared for the simultaneous determination of trace amount of Cd^{2+} and Pb^{2+} in rice samples by DPASV. Carboxylic acids terminated GO became more functional when reinforced with MnO_2 for the simultaneous determination of Cd^{2+} and Pb^{2+}. Probable enhanced synergic effects of MnO_2 on GO-COOH were evaluated due to more porous structure, higher specific surface area and hence larger amounts of the adsorption of ions. The electrode material was characterized using electrochemical methods such as CV and EIS. Spectroscopic and microscopic characterization of the surface materials was carried out by XPS and SEM. A novel analytical method was developed with the modified electrode for simultaneous determination of Cd^{2+} and Pb^{2+} in aqueous media. Calibration curves were linear within the range of 5 to 100 μg/L for both metals under the optimized conditions. The limit of detections were 0.04 μg/L for Cd^{2+} and 0.08 μg/L for Pb^{2+} (S/N=3). The possible interference effects of different ions were investigated for the simultaneous determination of Cd^{2+} and Pb^{2+}. Especially, Fe^{2+}, Zn^{2} and Cu^{2+} were found to be effective even at low concentrations. Reproducibility of the electrode was investigated under the optimum conditions. Precision and accuracy of the method were determined as intra-day and inter-day. The precision % values varied from 1.52 to 3.34 for intra-day and from 0.99 to 3.12 for inter-day precision for Cd^{2+} and Pb^{2+}. Accuracy of the developed method was calculated between -1.8 to 3.0 for intra-day and inter-day. The percent recovery values for Cd^{2+} and Pb^{2+} in real samples were calculated between 96.5 and 103.1.

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