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Isophtalic acid terminated graphene oxide modified glassy carbon nanosensor electrode: Cd^{2+} and Bi^{3+} analysis in tap water and milk samples

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ABSTRACT

In this study, graphene oxide was derivative with 5-aminoisophtalic acid by amidization reaction. The nanomaterial in suspension was denoted as graphene oxide-isophtalic acid. The graphene oxide-isophtalic acid suspension was covered on the glassy carbon electrode surface under the infrared lamb. The graphene oxide was characterized with transmission electron microscopy and x-ray diffraction. Surface characterization of the glassy carbon/graphene oxide-isophtalic acid was performed with x-ray photoelectron spectroscopy, cyclic voltammetry, and electrochemical impedance spectroscopy. The ultrasensitive nanoplatform for the simultaneous electrochemical square-wave anodic stripping voltammetry assay of Bi^{3+} and Cd^{2+} in aqueous solution has been developed on the glassy carbon/graphene oxide-isophtalic acid. The linearity range of Bi^{3+} and Cd^{2+} were 1.0×10^{-8} – 1.0×10^{-12} M (S/N = 3). The responses of species were practically unaltered with the increase of various species concentration. The detection limits of Cd^{2+} and Bi^{3+} were determined as 8.1×10^{-13} M and 1.06×10^{-13} M, respectively. The electrode performance was checked with tap water and commercially milk samples.

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Introduction

Cadmium is an extremely toxic metal, it is an anti-corrosion metal and is used extensively in electroplating. Cadmium is also used in industrial paints and may present a hazard when sprayed.[1] The carcinogenic effect of cadmium has been proven by scientists.[2] According to researchers, cadmium and cadmium salts are very dangerous, that often stem from interference with some metabolic processes.[3] Despite the high toxicity of the element, cadmium is widely used in various industry such as electroplating, paint and polymer, glass, printing inks, alloys, Ni-Cd batteries, solar cells, automotive, and control rods in nuclear reactors. The source of the cadmium pollution are generally phosphate fertilizers, sewage sludge, and various industrial products such as Ni-Cd batteries, plating, pigments, and plastics.[4] Smoking cigarettes is the one of the largest sources of cadmium exposure. If the Cd^{2+} concentration is up to 15 µg/L in urine and 0.15 µg/L in human plasma, serious toxicity problems will be shown. Chronic disorders, gastrointestinal scintigraphy problems, and damage in liver are observed after long-time interaction with cadmium. A typical example that everybody knows that itai-itai disease is shown in Japan, where rice that was grown in cadmium contaminated irrigation water is consumed.[5–7]

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In the case of bismuth, is well known as a natural diamagnetic and has the lowest thermal conductivity properties. This metal is generally very useful in various alloys, electrode and catalyst materials, ceramics, cosmetic and pharmaceutical raw materials, magnets, the paint industry, electronics, and x-ray diagnostic media.[8,9] The one of the important bismuth toxicity sources is an increasing use of bismuth alloys in recent years. Researchers claimed that bismuth shows a low toxicity according to other heavy metals. Bismuth destroys or denatures these groups of enzymes. The low toxicity of bismuth is connecting to insolubility of bismuth salts in the water. Despite this, the low toxicity of bismuth, also known as an environmental element of bismuth, chronic poisoning can be dangerous when interacting with bismuth.[10]

Up until now, there been articles reporting for the electrochemical detection of Cd^{2+} and Bi^{3+}. Ouyang et al. prepared the carbon nanotube modified with Hg–Bi included electrode nanomaterial on glassy carbon (GC) electrode for simultaneous analysis of Zn^{2+}, Cd^{2+}, and Pb^{2+}.[11] They calculated that the limits of detection for Zn^{2+}, Cd^{2+} were lower than 2 ppb. Luo and co-workers studied an electrochemical method for the determination of Cd (II) using a bismuth derivative multi-walled carbon nanotubes doped carbon paste electrode with a detection limit of 0.3 ppb.[12] Wei et al. prepared highly sensitive nanosensor for Pb^{2+} and Cd^{2+} by using SWV on porous magnesium oxide/nafion-based nanostructure modified GC. Detection limits of the developed methods were calculated as 2.1 pM for Pb^{2+} and 81 pM for Cd^{2+} with the linear calibration curves range from 3.3 to 22 nm and 40 to 140 nM for Pb^{2+} and Cd^{2+}, respectively[13] Mandil and co-workers fabricated the screen-printed electrode by modifying the carbon ink surface with multi-walled carbon nanotube (MWCNT) and bismuth film. They reported the limit of detection as 1.5 nM for Cd^{2+} with a 120 s deposition time.[14] Afkhami et al. investigated a new highly sensitive simultaneous nanosensor for Pb^{2+} and Cd^{2+} by using square wave voltammetry (SWV) with MWCNT and a schiff base modified carbon paste electrode. They found the limit of detection as 0.74 ppb for Cd^{2+}.[15] Xu et al. prepared ultrasensitive nanosensor for Pb^{2+} and Cd^{2+} on MWCNT/Nafion/Bismuth composite GC electrode. They reported the limit of detection as 40 ng/L for Cd^{2+}.[16] Ashrafi and Vytřas developed to determine trace Bi^{3+} by using SWV on the Sb covered carbon paste electrode which was a detection limit of 1.55 ppb.[17] Khaloo et al. analyzed the Bi^{3+} and Cu^{2+} on hanging mercury drop electrode (HMDE) by using differential pulse voltammetry (DPV). The detection limits were determined as 0.05 ppb for Bi^{3+}.[18] Lexa and Stulík prepared a tri-n-octylphosphinic oxide in a poly(vinyl chloride) modified mercury film electrode for Bi^{3+} and Cu^{2+}. They determined from 0.002 to 0.5% of bismuth.[19]

Graphene has been known as a novel carbon allotrope since 2004.[20] Its structure is a flat monolayer of sp^2-carbon atoms attached and arranged in a honeycomb lattice.[21] Graphene oxide (GO) is a state of graphene-containing functional groups such as –OH, C=O, -COOH, etc. The single atomic layer carbon material has got high surface area, good thermal conductivity, outstanding electrical conductivity, and perfect optical properties.[22] The graphene-based nanomaterials have found their way into various technological applications such as fuel cells,[23] batteries/capacitors,[24,25] sensor studies,[26–34] nanocatalyzer,[35] electronic devices,[36] food,[37] and medicine studies.[38]

Recently, electrochemically[39–41] or self-ordered[42] modified electrodes[43–46] are very popular because of its remarkable properties such as high sensitivity,[47–51] simplicity,[52] low cost, and ease.[53] In this study, we developed a different method to determine both Cd (II) and Bi (III) at the same time. The GC electrode was modified with GO, and then isophtalic acid terminated on GO modified GC electrode (GC/GO) for determination Cd (II) and Bi (III) nanosensor. The effects of some parameters were investigated to determination of Cd (II) and Bi (III) as pH, deposition time, and suspension solution volume. The nanomaterials were characterized by using transmission electron microscopy (TEM), x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). The GC/GO-IPA electrode was utilized for the determination of Cd^{2+} and Bi^{3+} ions by square-wave anodic stripping voltammetry (SWASV). The electrode response performance was checked via tap water and commercial milk samples.

Materials and methods

All highest purity chemicals were gathered from Merck, Sigma-Aldrich, Fluka, or Riedel chemical companies. The water was used as ultrapure water (UPW) with a resistance of 18.3 MΩ (Human Power 1+ purification system, S. Korea) for solutions and electrode cleaning. In all electrochemical experiments were studied under the purified Argon gas (99.999%) atmosphere. Electrochemical experiments were performed at room temperature (25 ± 1°C) under a traditional three-electrode cell system for all electrochemical experiments. Ag/Ag^{+}(10 mM $AgNO_3$) in 0.1 M tetrabutylammonium tetrafluoroborate (NBu_4BF_4) in acetonitrile (CH_3CN) reference electrode was used in non-aqueous media. Ag/AgCl/KCl(sat) reference electrode was used in aqueous media. A platinum wire was employed as a counter electrode. GC electrode (Bioanalytical Systems, MF-2012, USA) were used in electrochemical characterization such as CV and EIS. Electrochemical application of nanomaterial was performed on the same GC electrode. The GC electrode was cleaned and polished with 100 and 50 nm Al_2O_3 suspension (Baikowski Int. Corp., USA) on polishing cloth (Buehler, Lake Bluff, IL, USA) for approximately 5 min and then washed with UPW. Polished GC electrodes were sonicated (Ultrasonic Cleaner, SK1200H, China) in UPW for approximately 5 min in the following sonication GC electrodes were dipped in to mixture of 1:1 (v/v) isopropyl alcohol/CH_3CN media.

Preparation of GO

GO nanoparticles were synthesized by using electrochemical exfoliation of graphite. As anode pristine graphite, as cathode a platinum foil and as the electrolyte solution a mixture of 2.4 g H_2SO_4 and 11 mL 30% KOH in 100 mL deionized water were used. The electrochemical oxidation was performed under the constant DC (Yıldırım Electronics, Turkey) potential of +20 V. The GO was sonicated with a Hermle (Z36HK, Germany) ultracentrifuge system under 10,000 rpm for 10 min and then washed with UPW. It was dried at 100°C for 10 min.

Nanoconstruction of GO-IPA and preparation of GC/GO-IPA

Two hundred milligrams of GO was added in 10 mM 1-ethyl-3-[3-dimethylaminopropyl] carbodiimide/N-hydroxysulfosuccinimide (EDC/NHS) solution in 25 mL phosphate buffer solution (PBS; pH = 7) and stirred via magnetic stirring for 8 h. The GO suspension was participated with the centrifuge and then washed with UPW. The activated GO was added in 1 mM 5-aminoisophthalic acid included PBS (pH = 7) solution and then stirred for 8 h. The GO-IPA suspension was sonicated and washed three times. It was dried at 80°C for 1 day under vacuum. GO-IPA was diluted with 10 mL CH_3CN as suspension solution. Bare GC electrodes were polished with Al_2O_3 slurry on a Buehler cloth. They were rinsed in an ultrasonic bath with isopropyl alcohol-CH_3CN mixture (1:1, v/v) and UPW for 5 min, respectively. The bare GC electrode was modified with 10 µL of sonicated GO-IPA solution by micro-syringe, and then dried under an infrared (IR) lamp for 10 min. The modified electrode was denoted as GC/GO-IPA.

Characterization of the nanomaterials

The GO was characterized by using a JEOL 2100 HRTEM instrument (JEOL Ltd., Tokyo, Japan) and v. a Rikagu Miniflex XRD, using mono-chromatic Cu Kα radiation and operating at a voltage of 30 kV and a current of 15 mA. The XPS data was acquired a PHI 5000 Versa Probe (Φ ULVAC-PHI. Inc., Japan/USA) model XPS with monochromatized Al Kα radiation source (1486.6 eV) as an x-ray anode operated with 50 W at 10^{-7} Pa. GC/GO-IPA nanofilm were characterized by using the XPS. Electrochemical measurements were performed using an Ivium compactstat potentiostat (Ivium Technologies, The Netherlands) equipped with C3 cell stand. The CV and EIS characterization of the modified electrode was carried out in the presence of 2.0 mM of $Fe(CN)_6^{3-/4-}$ in 100 mM KCl as redox probe couple.

Determination of Cd^{2+} and Bi^{3+}

Immersing of the GC/GO-IPA into the measuring solution containing Cd^{2+} and Bi^{3+} ions led to the accumulations of the ions on the modified electrode surface via complexation between the cations and the modified surface in a 0.1 M acetate buffer solution (pH 4.5). After accumulation of the ions, the modified electrode was taken off and washed with UPW. Before application the SWASV, metal ions on the modified electrode were reduced to metallic forms at –1.0 V under the constant potential for 10 s in a measuring 0.1 M acetate buffer blank solution (pH 4.5). The GC/GO-IPA electrode was used for the determination of Cd^{2+} and Bi^{3+} ions in tap water and milk samples. The samples were used as received the pH for all samples were adjusted using 0.1 M acetate buffer solution. Additionally milk samples were 1:1 (v/v) diluted with UPW. The measurements of the samples were repeated five times (n = 5).

Results and discussion

To determine the optimal condition for maximum signal (current) of Cd (II) and Bi (III), some analytical parameters including pH, deposition time, and suspension solution volume were examined.

Characterization of the GO and GC/GO-IPA

TEM imaging of GO is shown in Fig. 1a. The exfoliated nanosheets are shown in the figure. The graphite and graphene oxide (GO) were characterized by XRD, as shown in Fig. 1b. The (002) peak at 26.9° for pristine graphite is shown in Fig. 1b. The (002) peak of GO is shifted to 14.6° in the figure.[54] High-resolution XPS-core spectra of N_{1s} and C_{1s} of the GC/GO-IPA are shown in Fig. 2a and 2b, respectively. N_{1s} binding energies of amide's nitrogen (NH-C=O) included GC/GO-IPA was fitted at 406.3 eV.[39] The C1s binding spectra for the GC/GO-IPA were deconvoluted into four peaks, which were NH-C=O at 288.4 eV, C=O or C-N, 286.7 eV, C-C at 285.1 eV and C=C at 284.4 eV in Fig. 2b.[55]

Bare GC and GC/GO-IPA surface were characterized using 2 mM $Fe(CN)_6^{3-/4-}$ redox couple solution in 100 mM KCl aqueous media and the resulting voltammograms were shown in Fig. 3a. Cyclic voltammograms of the redox couple gave strong evidence that GO-IPA nanomaterial was formed on the GC surfaces, which decreased the electron transfer of the redox probe couple.

The Nyquist plots of the GC and GC/GO-IPA are shown in Fig. 3b. Nyquist plots were obtained at 300,000 Hz/0.1 Hz frequency range using a redox couple of 2 mM $Fe(CN)_6^{3-/4-}$ redox couple (1:1) in 100 mM KCl media by using EIS. DC potential was determined as 0.18 V by CV. In Fig. 3b, the Nyquist plots for 2.0 mM $Fe(CN)_6^{3-}$/2.0 mM $Fe(CN)_6^{4-}$ redox probe in 100 mM KCl at the bare GC

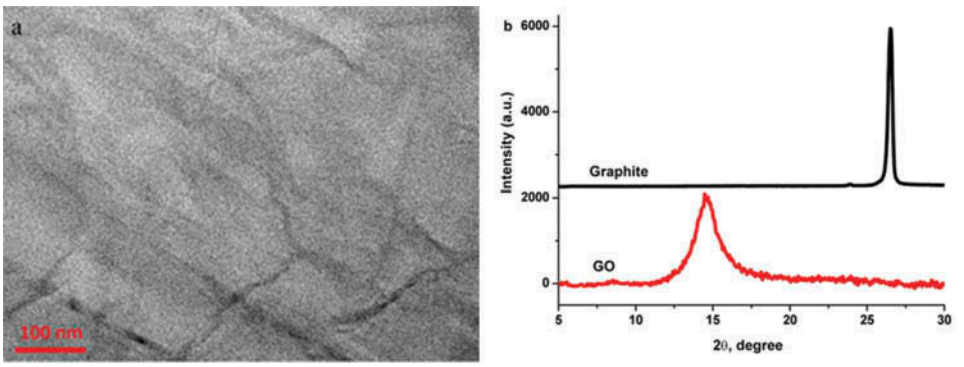


Figure 1. TEM imaging of A: GO and B: XRD pattern of graphite and GO.

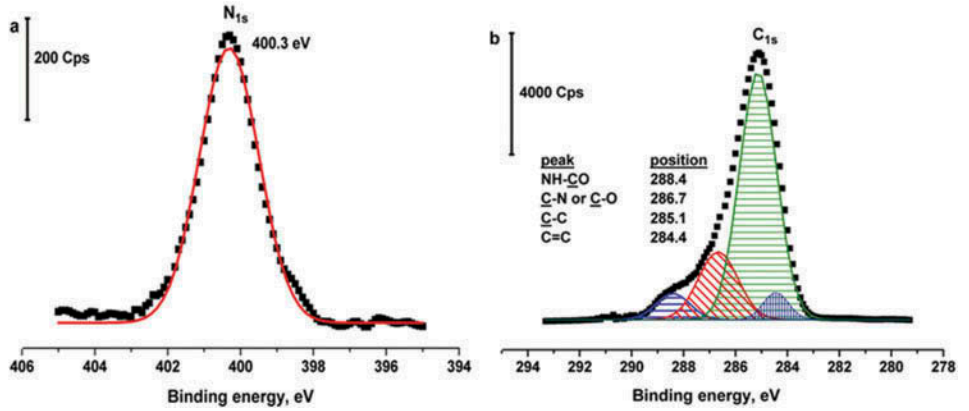


Figure 2. A: N1s and B: C1s core spectra of GC/GO-IPA.

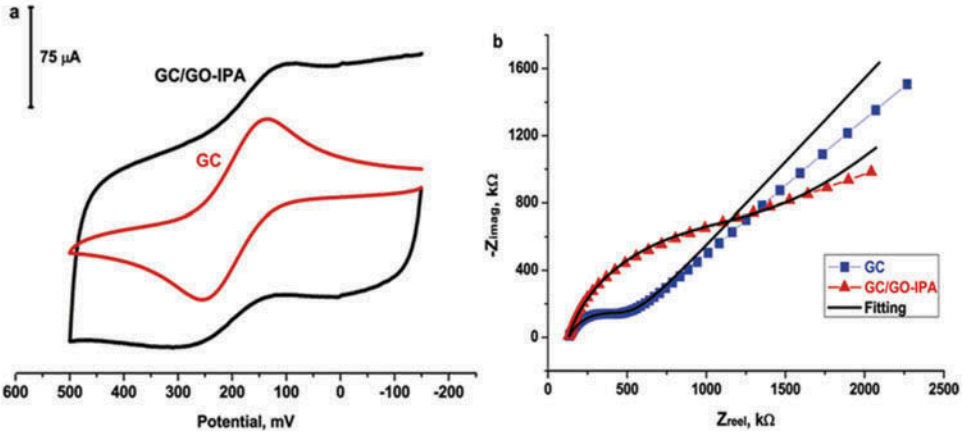


Figure 3. A: Cyclic voltammograms and B: Nyquist plots of 2 mM $Fe(CN)_6^{3-/4-}$ on the bare GC electrode and GC/GO-IPA.

and GC/GO-IPA surfaces are shown. The acquired data were fitted to a constant phase element (CPE; Y_o and α values) circuit with diffusion (i.e., Randles equivalent circuit with a Warburg impedance element, Z_w). The impedimetric values are shown in Table 1. The supported electrolyte included solution resistance (R_s) was determined between 129–134 Ω. The charge transfer resistances (R_{ct}) of the redox couple at the GC and GC/GO-IPA were 368.9 ± 11.40 and 1.331 ± 0.06 kΩ, respectively, calculated from fitting the curves to the equivalent circuit. The R_{ct} of redox couple probes for GC/GO-IPA was fitted to a higher valued curve than the bare GC. Fitting of the Nyquist datas of the redox couple gave strong evidence that GC/GO-IPA surface was formed on the GC surfaces, which increase the charge transfer resistant of the redox couple.

Table 1. Fitting values of EIS data for 2 mM $Fe(CN)_6^{3-/4-}$ redox probe couple on bare GC and GC/GO-IPA in 100 mM KCl supported electrolyte.

Samples	R_s (Ω)	Y_o for CPE ($S.s^{1/2}$)	α for CPE	Z_w (Ω)	R_{ct} (Ω)
GC	133.6 ± 1.5	(7.81 ± 0.10) × 10^{-6}	0.734 ± 0.016	(3.83 ± 0.005) × 10^{-4}	368.9 ± 11.4
GC/GO-IPA	129.8 ± 1.3	(4.489 ± 0.004) × 10^{-6}	0.803 ± 0.010	(1.27 ± 0.006) × 10^{-4}	(1.331 ± 0.061) × 10^3

Effect of pH, deposition time, and suspension solution volume

The effect of pH, deposition time and suspension solution volume on the analysis systems was investigated for the range from 3.50 to 5.50, 10–50 s, 5–20 µL, respectively. The results are illustrated in Fig. 4. The maximum signals were observed at pH 4.5 for Cd(II) and Bi(III) analyst (Fig. 4a). Optimum deposition time for this method was obtained to be 30 s, and then observed signal was constant by 50 s for all analytes (Fig. 4b). Also suspension volumes were performed range of 5–20 and 10 µL suspension volume qualified for maximum signal of Cd (II) and Bi (III) ions (Fig. 4c). The optimum parameters were used to remainder experiments.

Influence of different concentrations on the SWASV of Cd (II) and Bi (III)

Figure 5 presents SWASV responses of concentrations of Cd^{2+} and Bi^{3+} on the GC/GO-IPA surface. The determination limits of Cd (II) and Bi (III) have been supported by SWASV experiments at the on the GC/GO-IPA in 0.1 M acetate buffer (pH 4.5) range of 1×10^{-8} M – 1×10^{-12} M Cd^{2+} and Bi^{3+}, as shown in Fig. 5. The heights of the stripping peaks of Bi^{3+} were more intensively than that of Cd^{2+}. Hence, the GC/GO-IPA surface exhibited the highest sensitivity and the best stability for assay of Bi^{3+} and Cd^{2+}. The acetate groups of IPA can electrostatically attract Bi^{3+} and Cd^{2+} cations. The oxygen atom can be binding with Bi^{3+} and Cd^{2+} ions, and both of two factors affect the GC/GO-IPA-enhanced sensitivity.[56] The authors have not considered which factor predominates the enhanced sensitivity in this study.

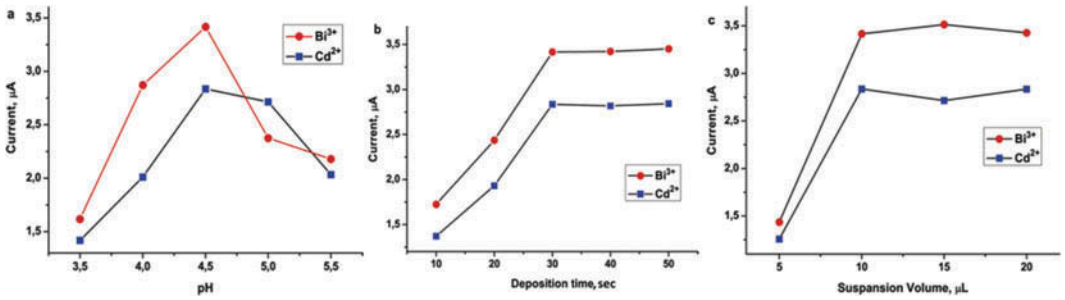


Figure 4. The effect of A: pH, B: deposition time, and C: suspension solution volume.

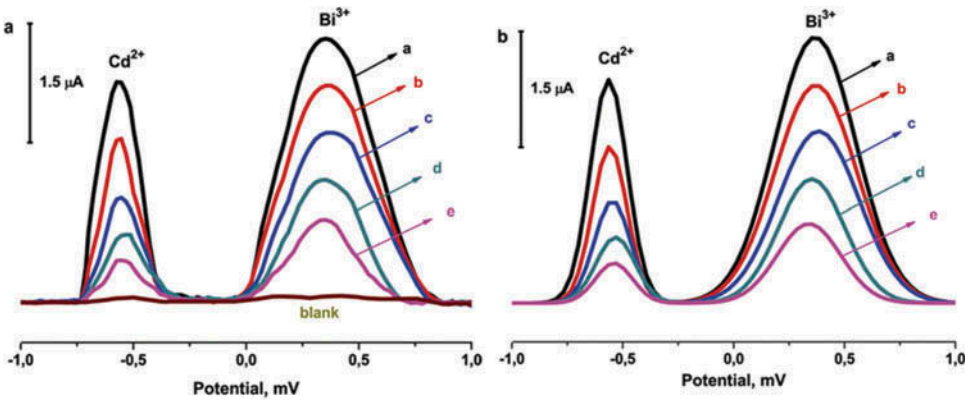


Figure 5. SWASV responses of A: 1×10^{-8} M, B: 1×10^{-9} M, C: 1×10^{-10} M, D: 1×10^{-11} M, and E: 1×10^{-12} M Cd^{2+} and Bi^{3+} on the GC/GO-IPA surface (pulse size: 25 mV, Frequency: 25 Hz.).

Figure 6 shows calibration curves of different concentrations of Cd^{2+} and Bi^{3+} on the GC/GO-IPA. The analysis of Cd^{2+} and Bi^{3+} under the optimum conditions was performed by changing the concentration of both of two species. As shown in Fig. 6, the peak current of Cd^{2+} and Bi^{3+} are linear with its concentration from 1×10^{-8} M to 1×10^{-12} M at a sensitivity (slope) of 0.5–3.5 μA, respectively. The linear curves of Bi^{3+} and Cd^{2+} are $y = -0.604x + 8.2416$ ($R^2 = 0.9996$) and $y = -0.578x + 7.2724$ ($R^2 = 0.9653$), respectively. The responses of species are practically unaltered with the increase of another species concentration. The detection limits of Cd^{2+} and Bi^{3+} were 8.1×10^{-13} M and 1.06×10^{-13} M, respectively. Especially, the Bi^{3+} calibration curve slope is more vertical than that of Cd^{2+}. This is clearly showing that this method is more selectivity for Bi^{3+} than Cd^{2+}. Some researchers calculated detection limit of Cd^{2+} species by voltammetry method were 2.1 pM and 1.5 nM,[13,14] respectively. And also someone found detection limit of Bi^{3+} was 110 ppb.[17] However, this method results are under these limits. These optimum parameters were more advantage according to some literatures as pH, deposition time, and suspension solution volume.[12–14,17,19] The researchers will continue to develop new methods for the growing world.

Analysis of the tap water and milk samples

To determine the effectiveness of our method, recoveries of Bi (III) and Cd (II) experiments were carried out. Therefore, the recoveries of Bi (III) and Cd (II) can be shown that fraction of the Bi (III) and Cd (II) determined after addition of a known amount of the Bi (III) and Cd (II) to a sample.[57] The method was evaluated by the application in the simultaneous determination of Bi^{3+} and Cd^{2+} in two tap water samples using standard addition method. The recoveries of Bi^{3+} and Cd^{2+} in tap water and milk samples ($n = 5$) are shown in Table 2. GC/GO-IPA electrode was also applied successfully for the simultaneous determination of Bi^{3+} and Cd^{2+} in tap water and milk samples. The recoveries of the Bi^{3+} and Cd^{2+} were up to 95%, so analytical recovery was obtained for all species and in the real sample. Also, these values were very good as comparison with the literature.[58,59]

The selectivity of the method for the determination of various metal ions was evaluated for various ions including Bi^{3+} and Cd^{2+} solutions. In this study, interferences of equimolar concentrations of Hg^{2+}, Fe^{2+}, Cu^{2+}, and Zn^{2+} were studied at different pHs. The peak current of Bi^{3+} and Cd^{2+} did not affect for equimolar range. The peak current responses of the ions were reduced by about 2% by the presence of 100-fold excess of other heavy metal ions.

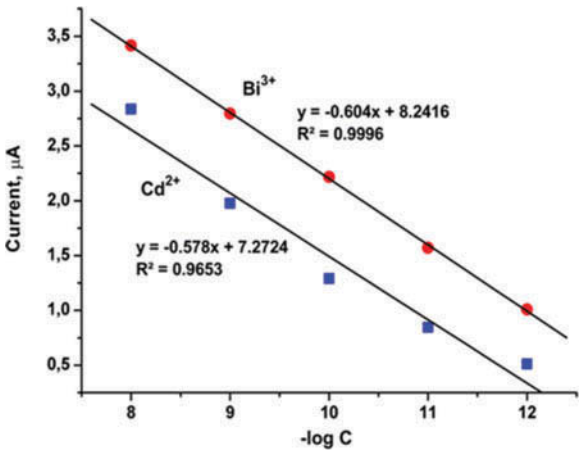


Figure 6. Calibration curves of A: 1×10^{-8} M, B: 1×10^{-9} M, C: 1×10^{-10} M, D: 1×10^{-11} M, and E: 1×10^{-12} M Cd^{2+} and Bi^{3+} on the GC/GO-IPA.

Table 2. The recoveries of Bi^{3+} and Cd^{2+} in tap water and milk samples (n = 5).

	Added*, nM		Determined, nM		ICP-OES, nM		Recovery, %	
Samples	Bi^{3+}	Cd^{2+}	Bi3+	Cd2+	Bi3+	Cd2+	Bi3+	Cd2+
Tap water-1	–	–	1.23 ± 0.06	1.48 ± 0.07	1.27 ± 0.06	1.45 ± 0.08	–	–
	1.0	1.0	2.27 ± 0.05	2.53 ± 0.07	2.31 ± 0.06	2.13 ± 0.11	98.2	98.0
	2.0	2.0	3.18 ± 0.07	3.52 ± 0.08	3.23 ± 0.07	3.48 ± 0.09	98.5	98.9
	4.0	4.0	5.31 ± 0.08	5.40 ± 0.11	5.43 ± 0.06	5.47 ± 0.08	98.5	98.5
Tap water-2	–	–	2.77 ± 0.07	1.03 ± 0.05	2.69 ± 0.07	1.17 ± 0.08	–	–
	1.0	1.0	3.69 ± 0.09	2.10 ± 0.08	3.72 ± 0.07	2.23 ± 0.08	97.9	96.6
	2.0	2.0	4.83 ± 0.08	2.98 ± 0.07	4.91 ± 0.08	3.05 ± 0.09	98.7	98.3
	4.0	4.0	6.70 ± 0.07	5.07 ± 0.09	6.59 ± 0.07	5.21 ± 0.08	99.0	99.2
Milk-1*	–	–	5.65 ± 0.07	1.17 ± 0.06	5.77 ± 0.07	1.26 ± 0.09	–	–
	1.0	1.0	6.73 ± 0.09	2.21 ± 0.07	6.80 ± 0.04	2.27 ± 0.07	98.8	98.2
	2.0	2.0	7.59 ± 0.07	3.13 ± 0.09	7.65 ± 0.06	3.08 ± 0.08	99.2	98.7
	4.0	4.0	9.73 ± 0.09	5.23 ± 0.07	9.68 ± 0.07	5.31 ± 0.07	99.2	98.8
Milk-2*	–	–	3.73 ± 0.06	0.98 ± 0.07	3.84 ± 0.08	1.11 ± 0.07	–	–
	1.0	1.0	4.84 ± 0.07	2.03 ± 0.05	4.78 ± 0.11	2.01 ± 0.06	97.7	97.5
	2.0	2.0	5.77 ± 0.06	2.95 ± 0.08	5.82 ± 0.07	2.88 ± 0.07	99.3	99.0
	4.0	4.0	7.89 ± 0.07	5.01 ± 0.06	7.93 ± 0.09	4.97 ± 0.08	97.9	99.4

*Twice diluted sample.

Conclusions

The GO was synthesized via electrochemical exfoliation method. It was characterized by using Tem and XRD. IPA attached GO was modified on GC electrode surface under the IR lamp. The modified electrode was electrochemically characterized with CV and EIS techniques assisted with a $Fe(CN)_6^{3-/4-}$ redox probe couple. An XPS spectrum measurement of the modified surface was shown that it was included presence of the amide's N_{1s} and functionalized various C_{1s}. The proposed this method, which is using GC/GO-IPA surface, is proven to be an efficient, simple and rapid separation method that can be used for Cd (II) and Bi (III) and tap water and milk samples. Effects of this procedure were investigated for analytical parameters such as pH, deposition time, and suspension solution volume. The detection limits of the method are comparable with the literature.[12–14,17,19,56] Simultaneous Cd (II) and Bi (III) ions by SWASV is one of the most important advantages of the proposed method, which has been applied on tap water and milk samples. And also the recoveries of Bi^{3+} and Cd^{2+} were higher than the literature.[60,61] This mean is that GC/GO-IPA electrode show more sensitive for Bi^{3+} and Cd^{2+} ions according to literature.[62,63]

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