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Review

Anodic Stripping Voltammetry for Simultaneous Determination of Lead and Cadmium using Bismuth-based Electrodes

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Abstract- Heavy metals are materials with many advantages. However, it is also harmful to the environment and human health. Lead and cadmium can cause many health problems, such as cancer, liver dysfunction, nervous system disorders, cardiovascular problems, and many more. Lead and cadmium can also accumulate in water, soil, and plants. Based on the problem, the development of lead and cadmium analytical methods was necessary to monitor its concentration level in the environment. One of heavy metal analysis's widest voltammetry methods is anodic stripping voltammetry (ASV). ASV involves the accumulation and stripping step to improve the analysis sensitivity toward heavy metals ions. ASV applied a three-electrode system and the working electrode played an essential role in obtaining an excellent analysis performance. Recently, bismuth-material was widely used for a working electrode in voltammetry methods, especially heavy metals analysis. Bismuth can form alloys with lead and cadmium ions during the deposition step in ASV and improve sensitivity. Bismuth also has low toxicity than mercury. Therefore, this review described the recent development of bismuth-based electrodes and their modification with other materials. We also briefly explained the ASV principle and its important parameter that needs optimization. In several previous studies, the modification of bismuth-based electrodes with various materials, such as carbon nanomaterials, conductive polymers, and metal nanoparticles, can give a synergic effect and enhancement the performance of lead and cadmium analysis.

Keywords- Heavy metals; Anodic stripping voltammetry; Bismuth; Lead; Cadmium

1. INTRODUCTION

Heavy metals are valuable elements with many advantages but can damage human health in a particular concentration. Lead and cadmium are the most poisonous heavy metals affecting human health. Lead and cadmium exposure can cause many health problems such as cancer, liver dysfunction, nervous system disorders, cardiovascular problem, and others [1-3]. Lead and cadmium are released into the environment via electroplating, metallurgical step, and paper industries [4]. These elements can contaminate crops through accumulation in water and soil. Cadmium and lead ions can be dissolved in the water and absorbed to plant tissue. Cadmium has been found in wheat and rice, while lead also is found in cabbage and spinach [5]. WHO determined the limit of lead and cadmium in drinking water are 3 μg L^{-1} and 10 μg L^{-1}, respectively [6]. Accordingly, the analytical method is required for analyzing and monitoring lead and cadmium contaminants in the environment.

The determination for monitoring heavy metals have been developed with several analytical methods, including electrothermal atomic absorption spectrometry (ET-AAS), flame atomic absorption spectrometry (FAAS), inductively coupled plasma mass spectrometry (ICP-MS), and inductively coupled plasma optical emission spectrometry (ICP-OES) [7]. These analytical methods have well precision, but they require high-maintenance instrumentation, time-consuming, well-trained operator, and lengthy procedures for sample preparation [8,9]. Recently, electrochemical methods became an alternative for determining heavy metal ions. The electrochemical analysis provides a portable analysis device, simple operation, rapid response of analysis, and only needs a small number of samples compared with other methods [10]. One of the most popular and sensitive techniques for determining heavy metals is anodic stripping voltammetry (ASV). The sensitivity of the ASV technique was due to the effective pre-concentration step followed by the electrochemical analysis stripping step of accumulation analytes. The metal ions were reduced and deposited in the surface of the working electrode in the pre-concentration step. Then, the metal was rapidly oxidized back so that oxidation peak was measured proportionally with the metal ions concentration [11-14].

ASV measurement used a three-electrodes system, i.e., reference electrode (RE), counter electrode (CE), and the working electrode (WE). WE material selection and modification are very important in the voltammetry technique to develop highly sensitive methods. The appropriate electrode material could increase measurement performance, including selectivity, sensitivity, reproducibility, and stability [4,15–17]. In the recent decade, a modified electrode with bismuth-based materials was developed successfully to replace the mercury electrode due to low toxicity compared with mercury, has a wide potential window, and the ability to form a fused alloy with various heavy metals. The ability of bismuth form fused alloy with heavy metal promote the nucleation process during the accumulation step and increases the sensitivity of heavy metal determination. Accordingly, bismuth material was developed for the voltammetric determination of Pb^{2+} and Cd^{2+} [15,17–19].

The modified bismuth-based electrode could combine with other materials that give a synergic effect for electrode. In recent years, bismuth was combined with various materials such as carbon nanomaterials, conductive polymer, and metal nanoparticles. This review reviewed several recent developments of anodic stripping voltammetry technique with bismuth-based modified electrode for determination Pb^{2+} and Cd^{2+}. In the next section, we briefly describe the principle and parameters of ASV. We also mentioned several bismuth-based modified electrodes and compared several modified electrode's performance for simultaneous determination of Pb^{2+} and Cd^{2+}.

2. ANODIC STRIPPING VOLTAMMETRY FOR Pb^{2+} AND Cd^{2+} DETERMINATION

One of the most powerful and sensitive electroanalytical techniques for metal analysis is anodic stripping voltammetry (ASV). This technique can analyze in various environmental matrices. ASV consists of a pre-concentration and stripping step that can improve analysis sensitivity [11,14]. The common technique for analyses Pb^{2+} and Cd^{2+} are square wave anodic stripping voltammetry (SWASV) and differential pulse anodic stripping voltammetry (DPASV). The principle of square wave stripping voltammetry is to apply square wave and staircase potential simultaneously. The first step is to deposit the heavy metal ions on the surface of the working electrode by applying the cathodic potential so that heavy metal ions are reduced. Furthermore, square wave stripping voltammetry was applied to measure heavy metals by electron involved in the electrochemical reaction [20]. The potential waveform in this technique can be thought of as a superposition of a regular square wave onto an underlying staircase. The key parameter of the potential waveform are pulse height, step, and frequency [21]. Therefore, the differential pulse voltammetry measured the differential current. The current is measured twice at the end of the forward pulse and the end of the reverse pulse. Due to this measurement, the capacitive current is possibly minimized. There are two current waveforms, the forward and reverse current waveforms that are similar to the current in cyclic voltammetry. Because the differential current peak is proportional to the analyte concentration, the technique can be used for quantitative analytical purposes, especially heavy metal ions in environmental media [21,22].

The previous studies also developed the double stripping voltammetry. The methods involve twice in each step, pre-concentration and stripping step, to improve the sensitivity of the Pb^{2+} and Cd^{2+} [23,24]. Zhao et al used SWASV with double deposition and stripping steps with different modified electrodes in each step. The technique operated with three system electrodes (Figure 1). Pb^{2+} and Cd^{2+} were deposited in the working electrode’s surface that was used, in-situ plated bismuth-film graphite carbon paste electrode (Bi/GCPE). Due to the large specific surface area and excellent ability to adsorb heavy metal ions of GCPE, it is applied in the first deposition step for concentrate ions [25,26]. After the first deposition, Bi/GCPE is quickly moved to another micro electrolytic cell that is filled with buffer solution for the first stripping step. Furthermore, the second deposition step is performed with another working electrode, in-situ plated bismuth-film multiwalled carbon nanotube–Nafion composite modified glassy carbon electrode (Bi/MWCNT–NA/GCE).

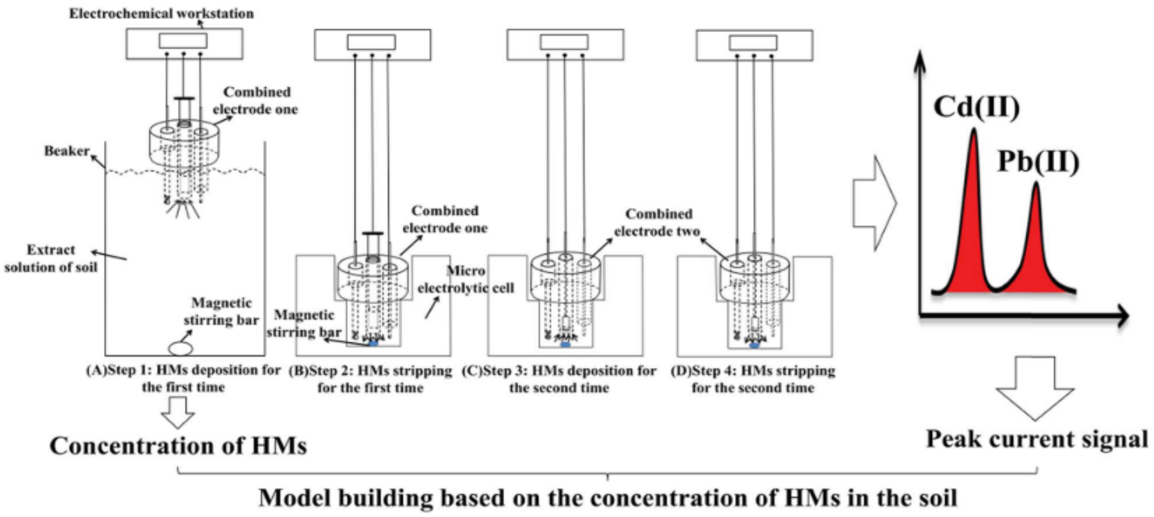

Figure 1. Schematic illustration of double stripping SWASV in determination of Pb^{2+} and Cd^{2+}; Reprinted with the permission from [23]

The previous ion from the stripping step was deposited again on the surface of the second working electrode following the stripping step for measuring the current signal from ions oxidation. Zhao et al also compared the results with standard stripping voltammetry. The results indicated that double stripping voltammetry provided the higher sensitivity until 7 times and has a lower detection limit than standard stripping voltammetry. That results probably due to the small volume of the buffer solution in the micro-electrolytic cell in the second deposition and stripping step. The concentration of analyte becomes higher than in bulk solution. That caused the low detection limit in the double stripping voltammetry technique. The limit detection was estimated at 0.03 $\mu g\ L^{-1}$ for Pb^{2+} and 0.02 $\mu g\ L^{-1}$ for Cd^{2+} [23]. Compared with other methods, this method has the lowest limit detection for Pb^{2+} and Cd^{2+}. That result indicated that the double stripping SWASV technique could increase the sensitivity of the determination method.

In the other work, Zhang et al also applied DPASV with a double stripping technique to determine Pb^{2+} and Cd^{2+}. The measurement used ionic liquid-graphite-based paste working electrode (ILGPE) as a working electrode with the presence of Bi^{3+} in the solution. ILGPE was carried out in the first deposition and stripping step. Pb^{2+} and Cd^{2+} were deposited again in the surface of GCE and analyzed in the second stripping step onto buffer solution with the DPASV technique. Zhang et al measured the concentration of Pb^{2+} and Cd^{2+} in the first pre-concentration step to evaluate its efficiency. The obtained concentration indicated that the surface of ILGPE effectively deposited ~15% Pb^{2+} and Cd^{2+} in the bulk solution [24]. However, this method does not have a wide concentration linear range than others provided in Table 1. The limit detection was also not significantly different from the common ASV (single stripping technique).

The performance of ASV is greatly influenced by several important parameters, including deposition potential, deposition time, and pH [10,27,28]. In the determination of Pb^{2+} and Cd^{2+}, The optimum deposition potential was obtained in the range of -1.1 V to -1.4 V from most previous work. The optimum deposition potential was determined to produce the maximum stripping current peak. Al-Hossainy et al measured Pb^{2+} and Cd^{2+} with gold nanoparticle-graphene-selenocysteine modified bismuth film glassy carbon electrode (Au-GNSeCys/GCE). They applied the deposition potential in the range of -0.09 V to -1.20 V. The results showed that the peak current increased by the negative shift of potential in -0.90 to -1.0 V and decreased in potential above it. The potential of -1.0 V was selected for the optimum deposition potential for measurement [29]. A similar result was also obtained by Kilic et al that used graphene/bismuth nanocomposite film modified pencil graphite electrode (Gr/Bi PGE). Kilic et al also obtained the optimum deposition potential in -1.0 V [6].

The most work obtained -1.2 V for optimum deposition potential. Hwang et al. was observed a stripping current peak in the range -1.4 to -0.6 with nanoporous bismuth electrode (modified-NPBiE) as a working electrode. The results show that the stripping current peak increased along with potential enhancement negatively and reached the maximum peak in -1.2 V. In the more negative potential, the stripping current peak was decreased. It probably happened because the hydrogen gas evolution was started [10]. The competing and decreasing of active sites on the electrode surface due to hydrogen could happen and affect the measurement of the heavy metal ions and possibly harm bismuth film and the metal alloys deposition on the surface of the electrode [10,30–32]. The same results were also obtained with a nanocomposite functionalized multiwalled carbon nanotubes with polypyrrole film (PPy) and bismuth particles carbon paste electrode (Bi/PPy/MWCNT/CPE) [9], polymer/bismuth film modified glass carbon electrode (GCE) [33], GCPE combined with MWCNT–Nafion/GCE [34], Bi/Nafion/RGO-GNPs/GCE [35], and gold nanoparticle-graphene-cysteine composite (Au-GN-Cys) modified bismuth film GCE [36]. The optimum deposition potential was also determined due to the good repeatability and sensitivity of the analysis [33].

In deposition potential more than -1.3 V, the electrode could not reduce enough metal ion, while hydrogen evolution was started in the potential less than -1.3 V [37]. Due to behavior, Zhang et al selected -1.3 V for optimum deposition potential and because of the highest stripping peak current with bismuth oxycarbide (BOC)/Nafion modified GCE [38]. However, Other studies were obtained -1.4 V and -1.5 V for optimum deposition potential [24,39–41]. In the study of Albalawi et al, Pb^{2+} and Cd^{2+} current peak was not detected in the potential under the potential of -1.4 V and selected optimum deposition potential at -1.5 V because the maximum current peak was obtained [41]. The results indicated that hydrogen evolution might not interfere with the deposition and stripping process of Pb^{2+} and Cd^{2+} on the electrode surface.

Deposition time is also the key parameter in ASV. It can be enormously involved in the sensitivity and the detection limit of the electrode of the method [9,10]. Oularbi et al studied the influence of deposition time in the determination of Pb^{2+} and Cd^{2+} with Bi/PPy/MWCNT/CPE. The deposition time was varied from 60 to 400 s in deposition potential of -1.2 V/SCE and showed the linear enhancement of stripping current peak with the longer deposition time. However, after 240 s, the current peak gradually decreased due to saturation of the electrode surface. Based on the results, the deposition time of 240 s was selected as optimum deposition time [9]. Moreover, the longer deposition time can be applied in the low concentration sample to improve the sensitivity of the analysis and linearity range. In the study of Rojas-Romo et al, deposition time of 60 s was chosen for the optimum deposition time because the peak increased linearly until deposition time of 60. The longer deposition time was evaluated between 60 s and 180 s. The results indicated that the deposition time of 180 s has a wide range of linear concentration than the deposition time of 60 s. especially in the analysis of the real samples. Rojas-Romo et al used 120 s as deposition time for the analysis of the real samples [40].

Another important parameter that affected the ASV performance was pH. The pH greatly affects the deposition and stripping steps in Pb^{2+} and Cd^{2+} analysis [27]. In several previous studies, the pH influence was evaluated. The results indicated that optimum pH was obtained from pH 3 until pH 5.5 [17,29,33,35,39,41,42,43]. Liu et al used carbon paste electrode with BiOCl (bulk modifier) to determine Pb^{2+} and Cd^{2+} in NaCl solution. The maximum current peak was obtained at pH 3 [43]. On the other study from Bahinting et al, Pb^{2+} and Cd^{2+} determination were conducted with bismuth film-coated gold ultramicroelectrode array (BF-UMEA) in acetate buffer solution. The optimum pH was obtained in pH 4 that showed the maximum stripping current peak [42]. Furthermore, Zhao et al was obtained optimum pH at 5.5 using multi-walled carbon nanotube (MWCNT)-emeraldine base polyaniline (EBP)-Nafion (NA) composite modified glassy carbon electrode (MWCNT-EBP-NA/GCE) in acetate buffer solution [17]. In the determination of Pb^{2+} and Cd^{2+}, the interference of H^+ can occur and cause competition with metal ions on the electrode surface in the lower pH. However, in the higher pH, the stripping current peak also decreased due to hydrolysis of Pb^{2+} and Cd^{2+} [29,44]. Consequently, evaluating the parameter of ASV, including deposition potential, deposition time, and pH, is important to obtain the optimum condition for effective deposition and stripping process on the modified electrode surface. The optimum condition parameter can lead to the excellent performance of the methods, such as sensitivity, linearity, limit detection, and reproducibility of the electrode.

3. BISMUTH-BASED ELECTRODES FOR ELECTROCHEMICAL ANALYSIS OF LEAD AND CADMIUM IONS

Recently, bismuth-based electrodes have become an excellent alternative to mercury electrodes due to their low toxicity, environmentally friendly, and has similar behavior to mercury. Bismuth-electrode has several advantages, including excellent sensitivity, simple modified process, insensitivity to dissolved oxygen, great peak resolution, low background and redox potential of hydrogen, and a wide electrochemical window [15,17,44–46]. Bismuth also can form fused alloys with heavy metals that generate the nucleation process during the deposition step and improve the sensitivity of heavy metal determination [18]. Compared with the bare electrode, bismuth-electrode showed a higher stripping current peak for Pb^{2+} and Cd^{2+} signals. The results indicated that the presence of bismuth could generate the reduction of Pb^{2+} and Cd^{2+} due to the ability of bismuth to form alloys with the heavy metals ion [23]. Accordingly, bismuth was much developed and has an important role in voltammetry analysis for Pb^{2+} and Cd^{2+}, especially in anodic stripping voltammetry technique [10,18,47].

To form film in the electrode surface, Bi^{3+}, Pb^{2+}, and Cd^{2+} were simultaneously reduced and formed alloys based on the reaction:

$Bi^{3+} + 3e^- \rightarrow Bi$
$Pb^{2+} + 2e^- + Bi \rightarrow Pb(Bi)$
$Cd^{2+} + 2e^- + Bi \rightarrow Cd(Bi)$

where Pb(Bi) and Cd(Bi) are metal-bismuth alloys [48]. The nucleic generation was occurred and formed a thin bismuth film and condensation centers on the active site of the electrode surface. Then, Pb^{2+} and Cd^{2+} are deposited together with bismuth [49]. Furthermore, different pulse or square wave was applied at a certain potential that could be oxidized again Pb^{2+} and Cd^{2+} and produced the stripping current peaks at different potentials [48]:

$Cd(Bi) \rightarrow Cd^{2+} + 2e^-$
$Pb(Bi) \rightarrow Pb^{2+} + 2e^-$
$Bi \rightarrow Bi^{3+} + 3e^-$

The popular approach for preparing bismuth-electrode was in-situ plating and ex-situ plating methods. The in-situ plating method was carried out by electrodeposited simultaneously bismuth and metal ions that dissolved in the electrolyte solution [50]. Bismuth deposited on the electrode surface with metal ions. Therefore, the electrodeposition of bismuth in the ex-situ plating method was conducted on the electrode surface before immersed the electrode into the electrolyte solution that contains the metal ions [51]. Due to good repeatability and sensitivity, the in-situ method was much developed to prepare bismuth-based electrodes [52]. The previous study by Zhang et al compared the bismuth-based electrode with in-situ and ex-situ methods. The results showed that the peak current of Pb^{2+} and Cd^{2+} produced by the in-situ method was 2.2-fold higher than the ex-situ method. The work also confirmed the study by Quintana and co-workers' finding that also has excellent sensitivity [53]. Compared with in-situ methods, the repeatability of ex-situ methods is not good enough because of the loss of deposited Bi from the electrode surface during the cleaning and stripping step. To prevent the loss of bismuth, the electrode surface could be modified directly with the bismuth material to form a bismuth-film electrode [54].

4. THE MODIFIED BISMUTH-BASED ELECTRODES FOR ELECTROCHEMICAL ANALYSIS OF LEAD AND CADMIUM IONS

Recently, a modification of bismuth electrode was developed by combining bismuth material with other materials such as carbon nanomaterials, polymer, and metal nanoparticles, to improve the electrode performances (Table 1). Zhao and Liu combined $(BiO)_2CO_3$ on the single-walled carbon nanotube (SWCNT) nanocomposite and Nafion as a dispersant for modifying the glassy carbon electrode (GCE) for determination of Pb^{2+} and Cd^{2+} based on SWASV. SWCNT has good properties for electrochemical analysis, such as high electrical conductivity, large active surface area, and has catalytic capacity toward certain analytes. SWCNT was functionalized with carboxyl groups to increase the bound site with bismuth. SEM image showed that $(BiO)_2CO_3$ nanoparticles were extensively distributed and formed large surfaces of bismuth film on the three-dimensional interconnected SWCNT network. The composite of $(BiO)_2CO_3$ nanoparticles@SWCNT-Nafion on GCE caused a synergic effect that improve the electrode sensitivity due to increased electron transfer rate and degree of delocalization in the electrode surface because of the presence of SWCNT. Therefore, the modified electrode surface also has a high specific surface area for forming Bi-Pb^{2+} and Bi-Cd^{2+} alloys on the electrode surface. The interference study of $(BiO)_2CO_3$ nanoparticles@SWCNT-Nafion/GCE indicated that current response was not influenced with common metal ions in the real sample until a concentration ratio of 1:100. However, Cu^{2+} has affected the measurement significantly with the decrease of current signal 20.54% and 19.38% for Cd^{2+} and Pb^{2+}, respectively. Cu^{2+} could compete with analytes for the active site on the electrode surface. Therefore, this method has low limit detection of Pb^{2+} and Cd^{2+} at 0.05 µg L^{-1} and 0.03 µg L^{-1} [52].

In several works, bismuth was combined with multi-walled carbon nanotube (MWCNT) [9,17,23,39,55]. Zhao et al [17] was conducted an electrochemical analysis of Pb^{2+} and Cd^{2+} with a multi-walled carbon nanotube (MWCNT)-emeraldine base polyaniline (EBP)-Nafion (NA) composite modified glassy carbon electrode (MWCNT-EBP-NA/GCE) with in-situ bismuth modified based on SWASV. The nanocomposite provided excellent properties and synergic effects including large active surface area, high electrical conductivity, excellent mechanical stability, good ion exchange, and anti-interference abilities. Anti-interference ability of the electrode was caused by the MWCNT-EBP-NA nanocomposite that has a fibrous hairs-like structure. The hairs like structure can prevent the adsorption of macromolecules and other interferences on the electrode surface [17]. The nanocomposites also improved surface active area for bismuth and heavy metal form alloys and degree of electron delocalization in the MWCNT-EBP composite film due to strong interaction between MWCNT and the conjugated structure of polyaniline via p-stacking. The detection limit was estimated at 0.04 µg L^{-1} for Cd^{2+} and 0.06 µg L^{-1} for Pb^{2+} [56].

MWCNT is also combined with in-situ bismuth film for a working electrode in double stripping technique based SWASV. Zhao et al [23] prepared in situ plated bismuth-film multiwalled carbon nanotube–Nafion composite modified glassy carbon electrode (Bi/MWCNT–NA/GCE) as the working electrode in the second deposition and stripping step after used in situ plated bismuth-film GCPE (Bi/GCPE) for the first working electrode. The Bi/MWCNT–NA/GCE plays an important role to increase the sensitivity due to the high electrical conductivity, large specific surface area, and excellent Pb^{2+} and Cd^{2+} preconcentration and stripping abilities [23]. Oularbi et al [9] synthesized a nanocomposite consisting of functionalized multi-walled carbon nanotubes, polypyrrole film (PPy), and bismuth particles modified carbon paste electrode(CPE) (Bi/PPy/MWCNT/CPE). Functionalized MWCNT was deposited on the electrode surface followed by electropolymerization of Ppy. Bismuth modification was conducted with the in-situ plating method [9].

In the other studies, MWCNT was combined with bismuth oxide nanoparticles (Bi_2O_3 nanoparticles) developed by Cui and Li [39]. MWCNT and Bi_2O_3 nanoparticles were coated on the surface of the screen-printed electrode (SPE) (BONP-MSPE). Then, Bi_2O_3 nanoparticles were reduced to bismuth nanoparticles with immersed the BONP MSPE into 0.1 M KOH solution and applied potential 0f -1.4 V [39]. Moreover, Cerovac et al [55] compared two multi-walled carbon nanotubes composites combined with bismuth (Bi/MWCNT) and bismuth-oxychloride particles (BiOCl/MWCNT) to modify GCE for Pb^{2+} and Cd^{2+} electrochemical determination. Both modified electrodes were prepared by ex-situ modification methods. The results showed that BiOCl/MWCNT produced the stripping current peak three times higher than the Bi/MWCNT modifier in acetate buffer solution [55].

One of the widely interesting carbon nanomaterials was graphene due to its excellent properties, such as large surface areas, remarkable electrical and thermal conductivities properties, excellent mechanical strength, and simple modification [57]. Based on that properties, Lin et al [58] developed an electrochemical method for Pb^{2+} and Cd^{2+} analysis based on the synthesis of graphene-based carbon nanomaterials by one-step laser etching of polyimide (PI) sheets (LEGCNs). A suspension containing LEGCNs, Nafion, and ethanol was dropped on the GCE surface following the in-situ modification of bismuth film. The synthesized LEGCNs has a nanosheet structure with many edge plane sites that provide a large electrochemical active surface area. It can improve the effectiveness of heavy metal ions deposition on the electrode surface. It was indicated by the increases of electrochemical activity surface area of LEGCN-GCE was twice larger than bare-GCE. LEGCNs also has excellent electrical conductivity and electron transfer abilities that could improve the electrochemical analysis performance [58]. Kilic et al [6] also developed simple and low-cost graphene and bismuth nanocomposite film modified pencil graphite electrode (G/Bi/PGE) for determination of Pb^{2+} and Cd^{2+}. Graphene was prepared from oxidized graphite to graphene oxide followed by reducing it. The results indicated that graphene-modified PGE has a larger electroactive surface area than bare-PGE. Graphene increased the surface area and the sensitivity of the PGE [6].

A nanocomposite combining gold nanoparticles (AuNPs), graphene (GN), cysteine was developed by Zhu et al [36] based on bismuth film electrode for Pb^{2+} and Cd^{2+} detection. The results showed that the bismuth film-modified Au-GN-Cys/GCE improved the sensitivity of the analysis at 236% and 65.1% peak current signal enhancement for Cd^{2+} and Pb^{2+}, respectively compared to bismuth film-modified GCE. The peak potential also shifted negatively for Cd^{2+} and Pb^{2+} with the bismuth film-modified Au-GN-Cys/GCE. The results were obtained due to the properties of the graphene that large surface area and high electric conductivity that generated the electron transfer of the metal ions. Moreover, citrate with a negative charge around AuNPs could improve the accumulation ability of the electrode surface because of their good affinity for metal ions [36].

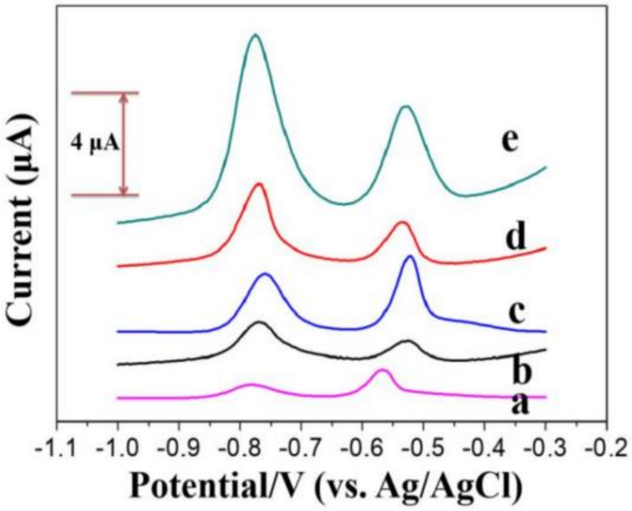

Figure 2. SWASV curve of Pb^{2+} and Cd^{2+} determination with (a) bare-GCE, (b) rGO/GCE, (c) NA/GCE, (d) $(BiO)_2CO_3$/rGO/GCE, and (e) $(BiO)_2CO_3$/rGO/NA/GCE; Reprinted with permission from [54]

The bismuth film is also combined with reduced graphene oxide (rGO) to improve the conductivity and specific surface area of the electrode surface which conducted by Zhao et al and Zhao et al [35,54]. Zhao et al fabricated a nanocomposite film containing AuNPs, rGO, and Nafion modified bismuth film electrode based on SWASV. The nanocomposite modified bismuth film electrode significantly increased the stripping current peak of Pb^{2+} and Cd^{2+}. The results could be due to the strong adsorptive ability of the electrode surface with the presence of large specific surface area rGO [35]. Similarly, Zhao et al developed a nanocomposite containing bismuth subcarbonate ($(BiO)_2CO_3$), rGO, and Nafion for GCE modification ($(BiO)_2CO_3$/rGO/NA/GCE). $(BiO)_2CO_3$/rGO/NA/GCE has the highest stripping current peak response of Pb^{2+} and Cd^{2+} compared with bare-GCE, rGO/GCE, NA/GCE, and $(BiO)_2CO_3$/rGO/GCE (Figure 2). Those results indicated that each component contributed to providing a synergic effect for the improvement of the GCE performance [54].

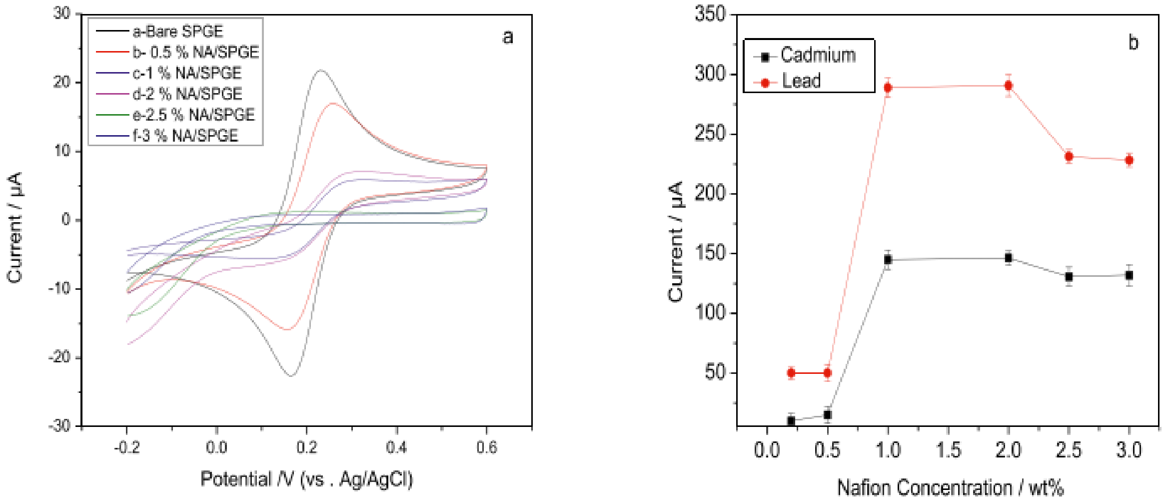

Figure 3. (a) Cyclic voltammograms of bare SPGE and NA/SPGE/ (0.5–3 wt%) in 1.0 mM $K_3Fe(CN)_6$ (1.0 M KCl) (b) Nafion concentration effect on the stripping signals of 300 μg/L Pb^{2+} and Cd^{2+} using NA/SPGE; Reprinted with permission from [41]

The other material that is commonly used to modify the electrode surface is polymers. The modification with polymers can improve the sensitivity, stability, and reproducibility of the electrode [59]. Nafion is one of the most frequently used to modify the bismuth-based electrode. Nafion polymer has been widely used for modification electrode surface due to biocompatibility properties, resistance to chemical attack, good mechanical stability, and conductive [41,60]. Nafion contained a negative charge of the sulfonate group that can act as a cation-exchanger and improve the ability of the metal ions adsorption [35,54]. Nafion was also applied to modify bismuth-based electrode for Pb^{2+} and Cd^{2+} determination. Due to the mechanical stability of Nafion, Albalawi et al coated it and combined it with in-situ bismuth nanoparticles modification on the screen-printed gold electrode surface. The study evaluated the performance of the modified electrodes at 0.2 – 3% Nafion concentration. The current peak was increased with increased of Nafion concentration until concentration of 1% and 2% (Figure

3). Moreover, the thinner Nafion films provided more good reproducibility. Accordingly, a Nafion solution of 1% concentration was chosen for the optimum measurement condition [41]. Nafion was also used by Zhao et al to synthesize the composite of MWCNT-EBP-NA that was previously described. The hydrophobic MWCNT site is wrapped by Nafion caused the separation of hydrophobic and hydrophilic regions. Nafion also influenced the formation of the EBP fibers structure and helped the electrodeposition of in-situ bismuth modification. The composite provided a synergic effect that improve the electrochemical performance of Pb^{2+} and Cd^{2+} determination [17].

Frutos-Puerto et al used Nafion for polymeric protection on commercial sputtered-bismuth screen-printed electrodes (BiSPSPEs). Polymeric cover of Nafion could keep the original 3D superficial structure of the electrode. Frutos-Puerto evaluated the effect of Nafion thickness on the electrode surface. The results showed that Nafion concentration higher than 2% increased the current signal but also increased the conditioning time of measurement. Based on the result, 2% of Nafion concentration is used for the electrode surface modification. Compared with bare- BiSPSPEs, Nafion protected-electrode showed 2.4 times and 1.6 times higher in the peak signal of Pb^{2+} and Cd^{2+}, respectively. BiSPSPEs, Nafion protected-electrode has a concentration linear range at 30 – 90 µg L^{-1}. Moreover, the detection limit was estimated at 3.83 and 3.62 for Pb^{2+} and Cd^{2+}, respectively. That result was not low enough compared with other methods. Furthermore, RSD values also are relatively high for repeatable measurement and with the different electrodes. That result suggested for calibration of each electrode before being applied in the measurement of real samples [60]. Based on the report, the electrode is required further improvement for better analysis performance.

Besides Nafion, other polymers were also developed for the modified bismuth-based electrode. Yifru et al fabricated polymer/bismuth film modified electrode for Pb^{2+} and Cd^{2+} determination. Different polymers such as 5-aminonaphthalene-1-sulphonic acid (5AN1SA), 2aminonaphthalene-1-sulphonic acid (2AN1SA), 8-aminonaphthalene-2-sulphonic acid (8AN2SA), and 4-amino3-hydroxynaphthalene-1-sulphonic acid (4A3HN1SA) which aminonaphetalenesulphonic acid derivates was developed for low-cost modifier and sensitive electrode that could replace Nafion. Each polymer was polymerized on the GCE surface followed by in-situ bismuth electrodeposition. All polymers modified electrode was evaluated and the results showed that poly (8-AN2SA) modified bismuth electrode has the highest stripping current peak signal compared with bare-GCE and other polymers modified GCE that indicated good electrochemical behavior of poly (8-AN2SA) [33]. The conductivity and other properties including electrocatalytic and sensing improved on electrodeposition of metal ions in conducting polymers layers [61].

In another work, Ourlarbi et al conducted nanocomposite bismuth particles, polypyrrole, and combined with MWCNT modified CPE for Pb^{2+} and Cd^{2+} analysis. MWCNT was deposited following with electropolymerization of polypyrrole film on the CPE surface. In the next step, bismuth particles are also deposited with metal ions by in-situ methods on the prepared modified CPE. The presence of polypyrrole and MWCNT could grow uniform and homogeneous bismuth particles on the electrode surface. The structure can provide a larger active surface area that is effective for the reduction of Pb^{2+} and Cd^{2+}. The combined MWCNT and polypyrrole gave a synergic effect that showed by enhancement of the current peak response of Pb^{2+} and Cd^{2+} compared with only polypyrrole-modified CPE. Those results indicated that MWCNT plays a role to generate more easy electron transfer ability of the polypyrrole due to the larger surface area of the modified CPE and improved conductivity.

Table 1. Several modified bismuth-based electrodes for determination of lead and cadmium ions

Electrode	**Technique**	**Linear range (μg L^{-1})**		**LOD (μg L^{-1})**		**Sample**	**Ref.**
		Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}		
Bi/GCPE Bi/MWCNT–NA/GCE	Double SWASV	1 – 45	1 – 45	0.03	0.02	Soil	[34]
Bi/ILGPE	Double DPASV	2.0 – 36	2.0 – 36	0.4	0.3	Seawater	[24]
$(BiO)_2CO_3$@SWCNT/NA/GCE	SWASV	1 – 50	1 – 50	0.05	0.03	Soil	[52]
Bi/ MWCNT-EBP-NA/GCE	SWASV	1 – 50	1 – 50	0.06	0.04	Soil	[17]
Bi-PPy/ MWCNT/CPE	SWASV	0.11 – 150	0.16 – 150	0.099	0.157	Water	[9]
Bi_2O_3NPs/MSPE	SWASV	0.5 – 40	0.5 – 40	0.05	0.22	Paint	[39]
BiOCl/MWCNT/GCE	SWASV	5 – 50	5 – 50	0.57	1.2	Water	[55]
Bi/LEGCN/GCE	SWASV	5 – 120	7 – 120	0.41	0.47	Water	[58]
Gr/Bi/PGE	SWASV	5 – 100	5 – 100	0.29	0.12	Water	[6]
Bi/Au-Gr-Cys/GCE	SWASV	0.5 – 40	0.5 – 40	0.05	0.10	Water	[36]
Bi/NA/rGO-AuNPs/GCE	SWASV	1 – 90	1 – 90	0.12	0.08	Soil	[35]
$(BiO)_2CO_3$/rGO/NA/GCE	SWASV	1 – 60	1 – 60	0.24	0.16	Water	[54]
Bi/NA/SPGE	SWASV	20 – 300	20 – 300	3	4	Water	[41]
Bi_{SP}SPEs	SWASV	30 – 90	30 – 90	3.83	3.62	Water	[60]
Bi/poly(8AN2SA)/ GCE	SWASV	1 – 40	1 – 40	0.38	0.08	Water	[33]
Bi_2O_3/CS/GCE	DPASV	108 – 758	89.93 – 629.5	31.05	5.62	Water	[39]

The larger surface area can improve the amount of the reduction of metal ions during the deposition step. Furthermore, in-situ bismuth deposition also increased the stripping current peak twice due to the ability of bismuth to form alloy with metal ions. The modified electrode also provided a wide linear concentration range for Pb2+ and Cd2+ in the range of 0.11 – 150 µg L^{-1} and 0.16 – 150 µg L^{-1} [9].

Hao et al prepared a composite electrode with chitosan and bismuth oxide nanoparticles (Bi_2O_3) (BiF-CS-GCE) for Pb^{2+} and Cd^{2+} detection. The modification was conducted by dropping the emulsion of Bi_2O_3 and chitosan in a certain mass ratio on the GCE surface. The presence of chitosan provided a good film form of bismuth on the electrode surface. BiF-CS-GCE showed excellent electrochemical properties than bare-GCE. The stripping current peak of Pb^{2+} and Cd^{2+} was approximately nine times higher with modified GCE. That result due to not only caused by the ability of bismuth to form alloy with metal ions but also increased absorption capacity toward metals ions by chitosan on GCE surface [16]. However, the electrode has a high detection limit for the analysis of trace metal ions.

5. CONCLUSION

Contamination of heavy metals, including lead and cadmium, is still a recent crucial problem in the environment. Therefore, it is necessary to develop analytical methods to monitor the presence of heavy metals in the environment. The development of anodic stripping voltammetry technique based on bismuth electrode is a potential method for lead and cadmium ions analysis. Bismuth-based modification is a potential material used for working electrode because of its excellent properties and is environmentally friendly compared to mercury. In anodic stripping voltammetry, optimizing parameters, including deposition potential, deposition time, and pH, is very important to obtain good analysis results. In addition, the modification of bismuth electrodes with other materials also plays an important role in increasing the sensitivity, reproducibility, and accuracy of lead and cadmium ions measurements. Using materials with remarkable properties, such as large active site surface area, excellent conductivity, good stability, and mechanical strength for electrode modification, can increase the deposition metal ions on the electrode surface and increase the sensitivity of the analysis. The use of polymers other than Nafion can also be further developed to support the improvement of electrode performance. It is based on a specific functional group's presence on the polymer, which can increase the interaction with metal ions to produce electrodes with good analysis performance.

REFERENCES

[1] R. T. Daher, Anal. Chem. 67 (1995) 405.
[2] S. J. S. Flora and S. Agrawal, Reproductive and Developmental Toxicology, Academic Press (2017).

[3] M. Valko, H. Morris, and M. T. D. Cronin, Curr. Med. Chem. 12 (2005) 1161.

[4] A. A. Saeed, B. Singh, M. Nooredeen Abbas, and E. Dempsey, Electroanalysis 28 (2016) 2205.

[5] K. Tyszczuk-Rotko, and K. Domańska, J. Electrochem. Soc. 164, H537–H544 (2017).

[6] H. D. Kiliç, and H. Kizil, Anal. Bioanal. Chem. 411 (2019) 8113.

[7] L. Zhao, S. Zhong, K. Fang, Z. Qian, and J. Chen, J. Hazard. Mater. 239–240 (2012) 206.

[8] L. S. Guenang, P. Gupta, V. C. Basseto, and M. S. Jovic, Am. J. Anal. Chem. 11 (2020) 1.

[9] L. Oularbi, M. Turmine, and M. El Rhazi, Synth. Met. 253 (2019) 1.

[10] J. H. Hwang, X. Wang, D. Zhao, M. M. Rex, H. J. Cho, and W. H. Lee, Electrochim. Acta 298 (2019) 440.

[11] J. Wang, Analytical Electrochemistry 3rd edition, Wiley, Hoboken, New Jersey (2006).

[12] D. Abd El-Hady, and A. K. Youssef, Anal. Chim. Acta. 772 (2013) 68.

[13] J. Ping, Y. Wang, J. Wu, and Y. Ying, Food Chem. 151 (2014) 65.

[14] V. Jovanovski, and N. I. Hrastnik, Microchem. J. 146 (2019) 895.

[15] I. Švancara, C. Prior, S. B. Hočevar, and J. Wang, Electroanalysis 22 (2010) 1405.

[16] C. Hao, Y. Shen, J. Shen, K. Xu, X. Wang, Y. Zhao, and C. Ge, Microchim. Acta 183 (2016) 1823.

[17] G. Zhao, Y. Yin, H. Wang, G. Liu, and Z. Wang, Electrochim. Acta. 220 (2016) 267.

[18] X. Xuan, and J. Y. Park, Sens. Actuators B 255 (2018) 1220.

[19] G. Kefala, A. Economou, and A. Voulgaropoulos, Analyst 129 (2004) 1082.

[20] D. Demetriades, A. Economou, and A. Voulgaropoulos, Anal. Chim. Acta 519 (2004) 167.

[21] A. Scandurra, and S. Mirabella, IEEE Sens. J. 21 (2021) 1.

[22] Z. Zeng, S. Fang, D. Tang, R. Xiao, L. Tang, B. Peng, J. Gong, B. Long, X. Ouyang, G. Zeng, Microporous Mesoporous Mater. 284 (2019) 177.

[23] G. Zhao, H. Wang, and G. Liu, RSC Adv. 8 (2018) 5079.

[24] X. Zhang, Y. Zhang, D. Ding, J. Zhao, J. Liu, J. Y. Wenrong, and K. Qu, Microchem. J. 126 (2016) 280.

[25] X. Zhang, M. Li, Y. Cui, J. Zhu, J. Zhao, B. Chen, and K. Qu, Int. J. Electrochem. Sci. 8 (2013) 4839.

[26] G. Zhao, H. Wang, G. Liu, and Z. Wang, Electroanalysis 29 (2017) 497.

[27] D. Li, J. Jia, and J. Wang, Microchim. Acta. 169 (2010) 221.

[28] G. Kefala and A. Economou, Anal. Chim. Acta. 576 (2006) 283.

[29] A. F. Al-Hossainy, A. A. I. Abd-Elmageed, and A. T. A. Ibrahim, Arab. J. Chem. 12 (2019) 2853.

[30] J. Yukird, P. Kongsittikul, J. Qin, O. Chailapakul, and N. Rodthongkum, Synth. Met. 245 (2018) 251.

[31] A. Afkhami, H. Ghaedi, T. Madrakian, and M. Rezaeivala, Electrochim. Acta 89 (2013) 377.
[32] F. Dong, Q. Li, Y. Sun, and W. K. Ho, ACS Catal. 4 (2014) 4341.
[33] A. Yifru, G. Dare, T. B. Demissie, S. Mehretie, and S. Admassie, Heliyon 7 (2021) 1.
[34] G. Zhao, H. Wang, and G. Liu, RSC Adv. 8 (2018) 5079.
[35] G. Zhao, H. Wang, G. Liu, Z. Wang, and J. Cheng, Ionics 23 (2017) 767.
[36] L. Zhu, L. Xu, B. Huang, N. Jia, L. Tan, and S. Yao, Electrochim. Acta 115 (2014) 471.
[37] Z. Guo, D. Li, X. Luo, Y. Li, q. Zhao, M. Li, Y. Zhao, T. Sun, and C. Ma, J. Colloid Interface Sci. 490 (2017) 11.
[38] Y. Zhang, C. Li, Y. Su, W. Mu, and X. Han, Inorg. Chem. Commun. 111 (2020) 1.
[39] H. Cui, and Q. Li, Int. J. Electrochem. Sci. 14 (2019) 6154.
[40] C. Rojas-Romo, M. E. Aliaga, V. Arancibia, and M. Gomez, Microchem. J. 159 (2020) 1.
[41] I. Albalawi, A. Hogan, H. Alatawi, and E. Moore, Sens. Bio-Sensing Res. 34 (2021) 1.
[42] S. E. D. Bahinting, A. P. Rollon, S. Garcia-Segura, V. C. C. Garcia, B. M. B. Ensano, R. R. M. Abarca, J. Yee, and M. D. G. de Luna, Sensors 21 (2021) 1.
[43] L. Liu, C. Yu, X. Zhang, H. Ma, C. Ma, Y. Fu, and X. Dong, Int. J. Electrochem. Sci. 14 (2019) 4469.
[44] L. Chen, Z. Li, Y. Meng, P. Zhang, and S. Yao, Sens. Actuators B 191 (2014) 94.
[45] S. Palisoc, A. J. Gonzales, A. Pardilla, L. Racines, and M. Natividad, Sens. Bio-Sensing Res. 23 (2019) 100268.
[46] K. C. Bedin, E. Y. Mitsuyasu, A. Ronix, A. L. Cazetta, O. Pezoti, and V. C. Almeida, Int. J. Anal. Chem. (2018) 1.
[47] J. Wang, J. Lu, S. B. Hocevar, P. A. M. Farias, and B. Ogorevc, Anal. Chem. 72 (2000) 3218.
[48] D. Soulis, M. Trachioti, C. Kokkinos, A. Economou, and M. Prodromidis, Sensors 21 (2021) 1.
[49] N. Papageorgiou, and M. Skyllas-Kazacos, Electrochim. Acta 37 (1992) 269.
[50] B. Petovar, K. Xhanari, and M. Finšgar, Anal. Chim. Acta 1004 (2018) 10.
[51] A. Scandurra, F. Ruffino, M. Urso, M. G. Grimaldi, and S. Mirabella, Nanomaterials 10 (2020) 1.
[52] G. Zhao, and G. Liu, Sens. Actuators B 288 (2019) 71.
[53] J. C. Quintana, F. Arduini, A. Amine, F. Punzo, G. L. Destri, C. Bianchini, D. Zane, A. Curulli, G. Palleschi, and D. Moscone, Anal. Chim. Acta 707 (2011) 171.
[54] G. Zhao, M. Sedki, S. Ma, C. Villarreal, A. Mulchandani, and D. Jassby, Sensors 20 (2020) 1.
[55] S. Cerovac, V. Guzsvány, Z. Kónya, A. M. Ashrafi, I. Švancara, S. Rončević, A. Kukovecz, B. Dalmacija, and K. Vytřas Talanta. 134 (2015) 640.
[56] J. E. Huang, X. H. Li, J. C. Xu, and H. L. Li, Carbon N. Y. 41 (2003) 2731.

[57] Y. Xin, J. G. Liu, Y. Zhou, W. Liu, J. Gao, Y. Xie, Y. Yin, and Z. Zou, J. Power Sources 196 (2011) 1012.

[58] X. Lin, Z. Lu, Y. Zhang, B. Liu, G. Mo, and J. Li, Microchim. Acta 185 (2018) 438.

[59] M. Pawlak, and E. Bakker, Electroanalysis 26 (2014) 1121.

[60] S. Frutos-Puerto, C. Miró, and E. Pinilla-Gil, Sensors (Switzerland). 19 (2019) 1.

[61] S. Ivanov, and V. Tsakova, Electrochim. Acta. 49 (2004) 913.