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Abstract

In this project, a new voltammetric method for the lead (Pb) heavy metal in the washing water obtained from the sugar beet washing step that is one of the stages of the process using in sugar plants have been developed. The working electrode was produced by coating a commercial glassy carbon electrode with bismuth. A new analytical method has been enhanced for quantitative analysis of lead in 0.1 M KNO_3 in acetate buffer by using square wave anodic stripping voltammetry (SWASV). It was found that the new bizmuth electrode could work with 0.01 µM as the limit of quantitation and in 0.1 µM – 1 µM concentration range as linear working range.

Keywords: Lead, Square Wave Voltammetry, Heavy Metal, Bismuth Electrode.

INTRODUCTION

Voltammetry, one of the electroanalytical techniques, is a potential-controlled technique where the net current is different from zero. In the mid-1960s, several advantages were sought when selecting voltammetric methods for determinations. With its low cost, high sensitivity, and ease of application, interest in these methods has increased for the determination of many species, particularly in pharmaceutical, environmental, and biological contexts (Yavaş, 2014).

The validation of bismuth film electrodes for the determination of cobalt and cadmium in soil samples has been studied. Bismuth film electrodes were used either by in-situ coating or by being pre-prepared. The deposition potential was set at -1.0 V and the deposition time at 120 s with 0.1 M acetate buffer. While determining cobalt, the bismuth film electrode was prepared in a separate solution. A glassy carbon electrode was immersed in a solution containing 0.1 M acetate buffer and 100 mg/L Bi(III) and stirred for 5 minutes at -1.0 V (Hutton, 2004).

Economou (2005) has compiled a review on the recent developments of bismuth film electrodes. He noted that the conditions for bismuth film coating could vary, suggesting an acidic medium since bismuth may hydrolyze at high pH. He mentioned that coating could be performed by stirring a solution containing 5-200 mg/L Bi(III) at -0.5 to -1.2 V for 1-8 minutes. For instant coating, he emphasized that Bi(III) ions in the range of 400-1000 mg/L could be directly added to the sample. Another method is the bulk modification of the electrode with Bi_2O_3 at -1.0 V. Bi_2O_3 is reduced to metallic bismuth and can accumulate on the electrode surface (Economou, 2005).

Gentamicin selective electrode, poly β-cyclodextrin-p-toluene sulfonic acid/glassy carbon electrode was prepared by electropolymerization technique. Characterization of the prepared poly p-cyclodextrin-p-toluene sulfonic acid/glassy carbon electrode was carried out using cyclic voltammetry and electrochemical impedance spectroscopy. Then, the effects of various parameters were investigated using square wave anodic stripping voltammetry in citrate buffer containing 4.0 mmolL^{-1} gentamicin. From the calibration chart, the correlation coefficient and detection limit were obtained as 0.9999 and 3.7 µmolL^{-1}, respectively (Burç, 2024).

A novel Pb^{2+} selective sensor based on ionic imprinted polymer has been investigated using differential pulse voltammetry (DPV) for the determination of trace lead levels in natural water and fruit juice. The new polymer was used to modify a GCE to create a new electrochemical sensor. Highly suitable voltammetric performance was achieved for the electrochemical detection of lead with a low detection limit (0.05 ngmL^{-1}) over a wide linear concentration range (0.1–80 ngmL^{-1}) (Dahaghin, 2020).

In another study, where bismuth electrodes were prepared by the direct addition of 400 ppb (µg/L) bismuth (III) to the sample, bismuth and the target metal were deposited on glassy carbon or carbon fiber material. Using stripping voltammetry, Cd, Pb, and Zn were determined at microgram per liter levels (Wang, 2000).

The bismuth electrode was investigated as an alternative electrode for the analysis of Pb, Cd, and Zn in anodic stripping voltammetry. In this study, the electrode was prepared by coating it with bismuth, yielding results with similar sensitivity to those obtained with bismuth-based electrodes. Metal accumulation was conducted using a square wave voltammetric stripping technique from -1.4 V to 0.35 V for 180 seconds. Detection limits of 93, 54, and 396 ng/L were obtained for Pb(II), Cd(II), and Zn(II), respectively, within a calibration range of 10-100 µg/L. The optimized method successfully determined heavy metals in river water using bismuth as an alternative electrode (Kristie, 2010).

Lead is the first metal to cause significant damage to the ecological system through human activities. It is a soft metal with a bluish or silver-gray color. Lead is the most important heavy metal causing environmental pollution, as it is released into the atmosphere in the form of metal or compounds, both of which exhibit toxic properties. According to the World Health Organization (WHO), the permissible limit in the workplace is 0.1 mg/m^3 (Özkan, 2009).

According to Özbolat (2016), lead is a heavy metal and neurotoxin that does not participate in biochemical reactions and has been known and used by humans for thousands of years. It is one of the most significant heavy metals threatening human health. Inorganic lead is found in the atmosphere as particles, whereas organic lead is volatile and often contaminates food and drinking water. Therefore, organic lead affects living organisms more than inorganic lead. The widespread industrial use and prevalence in environmental elements make lead a significant exposure factor both environmentally and occupationally (Gülçin, 2002).

Lead exposure occurs through environmental and industrial pathways (Özbolat and Tuli, 2016). A significant portion of environmental lead pollution originates from tetraethyl lead, which is released from the combustion of gasoline used in motor vehicles. Lead contamination in marine life is observed as a result of industrial waste being transported by water. For lead to have a toxic effect in the body, it must accumulate to a certain level in the blood or soft tissues. The impact varies depending on several factors, such as age, nutrition, and physiological conditions. For children, toxic symptoms can be observed at 40-80 µg Pb/100 mL, and lead poisoning occurs at 80 µg Pb/100 mL.

The concentration of lead detected in waters close to metal industries is higher compared to other waters. The chemical form of lead plays a significant role in its biological effects. For example, lead tetraethyl can easily diffuse through the skin and mucous membranes into the body. Only 5-10% of lead entering the digestive system enters the bloodstream. About 30-40% of lead taken in through the respiratory tract enters the bloodstream. Once in the bloodstream, some lead accumulates in bones, while the rest is excreted in urine. This mechanism prevents lead accumulation in soft tissues. Lead inhibits the synthesis of hemoglobin, a crucial component of red blood cells, leading to anemia. Reduced red blood cell synthesis results in anemia in poisoned individuals. Studies on adults generally show low levels of lead in the blood (Gündüz, 1998).

In humans, acute lead poisoning can lead to brain damage and death, while chronic poisoning, to which infants and children are particularly sensitive, can result in intellectual impairment, learning disabilities, hyperactivity, hypertension, chronic anemia, and peripheral nerve damage from early exposure to lead (Çağlarırmak and Hepçimen, 2010). These heavy metals also enter the bodies of all living organisms through the food chain and can cause serious damage to organs when consumed in excessive amounts. Therefore, in today's industrial production, the importance of treating industrial wastewater in compliance with standards has become even more crucial (Dinç and Yılmaz, 2013).

This study aims to develop a practical, cost-effective, and rapid analysis method for determining the amount of lead in untreated sugar beet washing water entering a wastewater treatment plant. For this purpose, voltammetric stripping technique, known for its cost advantages in terms of equipment and consumables, as well as its repeatability, will be employed. There are numerous studies in the literature on the voltammetric determination of heavy metals in various samples. However, mercury electrodes have been predominantly used in existing studies. Mercury electrodes are considered the most successful electrodes due to their large surface area, high sensitivity, good repeatability, and renewability. However, awareness of environmental protection has led to a reduction in mercury electrode applications. Due to the toxic effects of mercury, recent studies have focused on alternative electrode materials. Particularly, bismuth-based electrodes are suggested for use in the voltammetric stripping technique for the determination of heavy metals.

Bismuth film electrodes have become attractive to electroanalytical researchers in the past decade. These electrodes are important for maintaining the negligible toxicity of bismuth and its salts, while preserving all the advantages of mercury film electrodes (Huang, 2012). In the proposed study, experiments were conducted to produce a new bismuth electrode based on literature findings. The usability of the obtained electrode for heavy metal determination was investigated. By employing new methods during the metal accumulation and stripping stages, the aim was to develop a new method with lower detection limits and a wider working range compared to previous studies.

Since lead is a heavy metal that is harmful to human health, waste should be controlled and the amount of lead released into the environment should be monitored. By preventing contamination of soil and water resources, toxic substances can be prevented from entering the food chain in agricultural activities.

Because environmental protection laws and regulations require industrial wastes to be managed in accordance with certain standards, lead determination is necessary to comply with these regulations.

Lead from sources such as industrial waste and vehicle exhaust can migrate into the soil and disrupt the ecosystem. In addition, it may leak into water sources, threatening drinking water quality and causing dangerous consequences for human health. Lead exposure, especially in children, can negatively affect brain development, leading to learning disabilities, attention deficits, and behavioral problems. In adults, lead may increase the risk of high blood pressure and other cardiovascular diseases. Long-term lead exposure can cause deterioration in kidney function. Lead can inhibit the production of blood cells, leading to anemia.

MATERIAL AND METHODS

Reagents

All chemicals used in the experimental stage [$Pb(NO_3)_2$, $BiCl_3$, CH_3COOH, KNO_3, NaOH, ferrosen, dopamine, KCl, ACN, NaCl, H_2SO_4] were procured from Sigma-Aldrich. 0.05 M $BiCl_3$ (Reidel de Haen) solution and 0.2 M acetate buffer (pH 3.50 - 8.00) were used as supporting electrolytes. Buffers and supporting electrolytes were prepared using CH_3COOH (100%), H_3PO_4 (Carlo Erba, 35%), and NaOH. Acetonitrile was used as the solvent for both pure water and organic environments. Potassium nitrate (KNO_3) and sodium chloride (NaCl) were used as supporting electrolytes in aqueous environment studies, while tetrabutylammonium tetrafluoroborate (TBATFB) salts were used in organic environment studies. Electrodes were polished using P2400 grit sandpaper followed by polishing with suspensions prepared using pure water and alumina powders of particle sizes 1 micron, 0.3 micron, and 0.05 micron. High purity nitrogen gas was used in the study.

Apparatus and instrumentation

The CHI660C model electrochemical analysis system was used for voltammetric studies. Experiment solutions were analyzed using the Entek C-4 solid electrode working cell integrated into this system. A three-electrode design was employed in the experiments. Initially, a bare glassy carbon electrode was used as the working electrode, followed by a bismuth electrode obtained by coating this electrode with bismuth(III). An Ag/AgCl (saturated with KCl) electrode was used as the reference electrode, and a platinum wire served as the counter electrode. pH measurements were conducted using a PL-700PV pH meter. Deionized water used in preparing the solutions was obtained using a TKA Smart 2 Pure ultra-pure water system (conductivity of 0.055 µS/cm).

Procedure for preparing bismuth chloride solution

A 0.1 M stock solution of $Pb(NO_3)_2$ was prepared from a 0.1 M KNO_3 solution, and different concentrations of standard solutions were freshly prepared before each study. A coating solution of 100 ppm $BiCl_3$ was prepared. KNO_3 was used as the supporting electrolyte. The coating solution was prepared in an acetic acid/sodium acetate buffer environment.

A dopamine solution was prepared in 0.1 M H_2SO_4 with the presence of 10^{-3} M NaCl as the supporting electrolyte, while a ferrocene solution was prepared in acetonitrile with the presence of 0.1 M TBATFB as the supporting electrolyte.

Method

Alternating current voltammetry (CV), bulk electrolysis (BE), and SWASV techniques were employed in electrochemical studies. A glassy carbon electrode was coated with a bismuth film using amperometry technique at an appropriate potential. To characterize the developed bismuth electrode, the behaviors of the bare glassy carbon electrode and the modified electrode in the mediator medium were compared using cyclic voltammetry. Once it was determined that the electrode was modified, the behavior of lead on this surface was studied and compared with that on the bare glassy carbon electrode. Based on the high oxidation peak current and its dependence on concentration, anodic stripping voltammetry was employed for the determination process.

RESULTS AND DISCUSSION

Modifying the glassy carbon electrode

The behaviors of three different bare glassy carbon electrodes to be coated were examined in 10^{-3} M dopamine and 10^{-3} M ferrocene solutions. Differences in the peak changes in cyclic voltammetry were investigated. The accuracy of the working electrode to be modified was determined. The bare glassy carbon electrode was cleaned with sandpaper and polished with alumina powders of different sizes before each use. The glassy carbon electrode was coated with Bi(III) using the amperometry technique at a constant potential (-1 V) and used as the working electrode. A coating solution of 100 ppm $BiCl_3$ was prepared. The coating durations were tested at 300 s and 600 s.

As a result of the comparisons, it was observed that the reduction and oxidation peaks of the GC electrode coated for 300 seconds were not very regular. It was decided to continue the studies with 600 s coating.

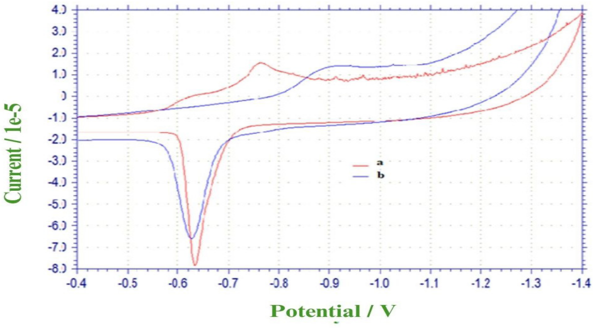

Figure 1. Comparison of cyclic voltammograms of GC electrodes coated with Bi(III) for (b) 300 s and (a) 600 s in 10^{-4} M Pb(II) solution

Electrochemical characterization of the bismuth-coated glassy carbon electrode in a 10^{-3} M dopamine solution

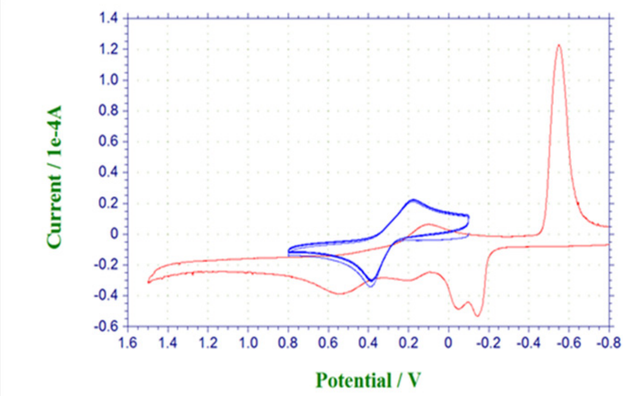

Figure 2. Simultaneous display of cyclic voltammograms obtained for a) Bi(III)-coated GC and b) bare GC immersed in 10^{-3} M dopamine solution (prepared in 0.1 M H_2SO_4 with 10^{-3} M NaCl supporting electrolyte), *v*= 100 mV/s (vs. Ag/AgCl).

When comparing the dopamine voltammograms obtained with the bare glassy carbon electrode and the bismuth-coated glassy carbon electrode, it is observed that the electrode has been successfully coated.

Electrochemical characterization of the bismuth-coated glassy carbon electrode in a 10^{-3} M ferrocene solution

When examining the behavior of ferrocene on bismuth-coated and bare glassy carbon electrodes, a shift in cathodic and anodic peak potentials was observed. Ferrocene is a mediator that undergoes rapid electron transfer. The change in peak separation on the two different surfaces indicates the presence of the coating.

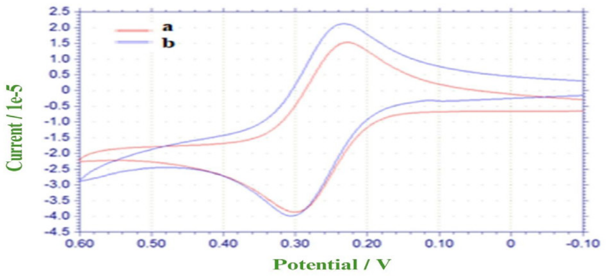

Figure 3. The combined appearance of cyclic voltammograms for (a) bare and (b) bismuth-coated GC immersed in a 10^{-3} M ferrocene solution (prepared in acetonitrile with 0.1 M TBATFB as the supporting electrolyte), v = 100 mV/s (vs. Ag/AgCl)

According to the obtained results, it has been understood that the peaks unrelated to dopamine arise from the oxidation of bismuth. The anodic peak at -0.2 V is attributed to the oxidation of bismuth.

With these results, when attempting to display the dopamine peak together with other peaks on the bare glassy carbon electrode, the situation depicted in Figure 4 below has emerged.

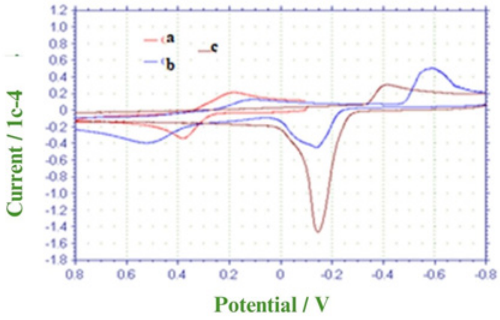

Figure 4. (a) Cyclic voltammograms obtained with a bare glassy carbon electrode and a bismuth-coated glassy carbon electrode in the presence of supporting electrolyte, (b) in environments with dopamine, (c) in environments without dopamine, *v* = 100 mV/s (vs. Ag/AgCl)

Based on the obtained results, it is understood that the anodic peaks are attributed to dopamine, while the other peaks not associated with dopamine are due to the oxidation and reduction of bismuth.

In these comparative experiments, the electrode was subjected to coating for 600 seconds. The same control was performed for bismuth behavior in an environment with and without ferrocene. In Figure 5, it is observed that the reduction and oxidation currents of ferrocene are larger on the bismuth-coated electrode. Additionally, no current was observed with the bismuth electrode in the presence of only the supporting electrolyte.

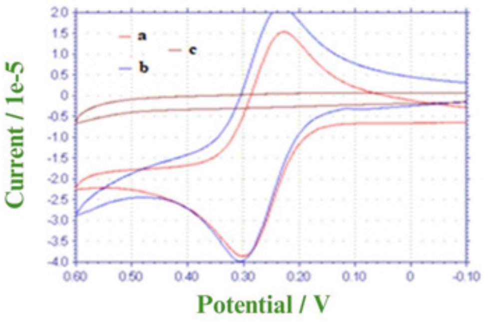

Figure 5. (a) Cyclic voltammograms obtained with the bare glassy carbon electrode and the bismuth-coated glassy carbon electrode in the presence of the supporting electrolyte, (b) in environments with ferrocene, and (c) in environments without ferrocene, v = 100 mV/s (vs. Ag/AgCl)

According to the obtained results, when comparing the bare glassy carbon electrode and the bismuth-modified electrode immersed in the ferrocene solution, it is observed that the anodic peaks belong to ferrocene, while the cathodic peaks at -0.2 V and -0.4 V correspond to the oxidation-reduction peaks of bismuth.

As seen in the figure, the peak separation in the cyclic voltammogram of ferrocene, which is a reversible system, has increased. This result indicates that the surface has been coated with bismuth. Moreover, the conductivity of the surface has not been significantly affected by this coating process.

The glassy carbon electrode was coated with Bi(III) using the Constant Potential Amperometry (*i*-t) technique. The surface was characterized using the Cyclic Voltammetry (CV) technique, confirming that the electrode was successfully coated. To explain the reduction and oxidation of lead ions on this electrode surface, as well as to perform deposition and stripping on the electrode surface, CV and SWASV electroanalytical techniques were used. The reduction and oxidation of Pb(II) ions on the prepared modified electrode surface were examined using the cyclic voltammetry technique. For the analytical determination of lead, deposition and stripping processes were applied using Square Wave Voltammetry with the optimization of necessary parameters.

Examination of lead (II) in bare GC electrode

Before coating, the reduction of lead on the bare glassy carbon electrode surface was examined in an aqueous medium. Nitrogen gas was passed through a 10^{-4} M $Pb(NO_3)_2$ solution for five minutes, and the cyclic voltammetry response was obtained. One reduction peak and one oxidation peak were observed. The observed peaks were identified as corresponding to lead (II) based on the cyclic voltammetry results obtained at different concentrations.

A $1x10^{-4}$ M $Pb(NO_3)_2$ solution was prepared from a 0.1 M stock solution in a 0.1 M KNO_3 supporting electrolyte medium. Initially, a CV experiment was conducted for the $1x10^{-4}$ M $Pb(NO_3)_2$ solution, and then 0.05 mL increments of the stock $Pb(NO_3)_2$ solution were added to this analysis sample. The changes in voltammetric measurement results were monitored.

Investigation of Lead on the Bismuth-Coated Electrode

In this section of the experimental studies, following the bismuth coating procedure, the electrochemical behavior of lead on this surface was investigated. The same CV experiments conducted for Lead (II) on the bare GC electrode were repeated on the modified bismuth electrode surface. The experimental results obtained are presented in graph form in Figure 6.

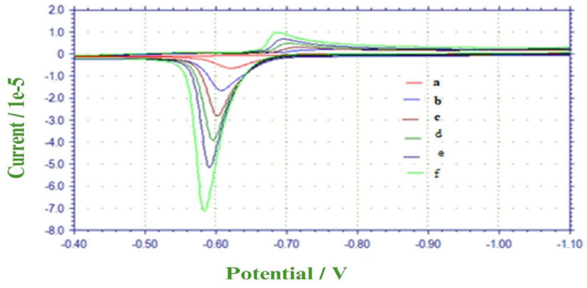

Figure 6. In the presence of a supporting electrolyte and 10^{-4} M Pb(II), cyclic voltammograms were obtained with (a) the bismuth-coated GC electrode in the same experimental cell, with additions of stock $Pb(NO_3)_2$ solution of (b) 0.05 mL, (c) 0.10 mL, (d) 0.15 mL, (e) 0.20 mL, and (f) 0.30 mL, *v*= 100 mV/s (vs. Ag/AgCl)

Analyses of the reduction of Pb(II) ions on the surface of the modified bismuth-coated electrode were conducted in the range of 0.1 µM to 1 µM. When the obtained reduction peaks were superimposed, it was confirmed that this signal belonged to Pb(II).

As observed in the study, on the surface of the modified GC electrode, a cathodic peak around -0.750 V and both cathodic and anodic peaks around -0.600 V were detected. Accordingly, the difference between the cathodic and anodic peak potentials is approximately 50 mV, which is consistent with Nernstian behavior.

SWASV Optimization on Bi(III)-Coated Electrode

The coating durations necessary for preparing the bismuth electrode were tested for 300 s and 600 s. Based on this comparison, the 600 s coating duration was preferred due to the smaller difference between the cathodic and anodic peak potentials and the higher peak intensities.

Comparisons revealed that the reduction and oxidation peaks of the GC electrode coated for 300 seconds were not very regular. Therefore, it was decided to continue the experiments with a 600-second coating.

Square Wave Anodic Stripping Voltammetry (SWASV) Results

Upon examining the lead peaks recorded by cyclic voltammetry, it was observed that the oxidation peaks were sharper and there were more significant increases in the anodic current with increasing concentration. Therefore, a method development involving accumulation and stripping using SWASV technique was decided. Experimental parameters for SWASV were investigated. The effects of Pb(II) accumulation time (t_{acc}), accumulation potential (E_{acc}), and accumulation frequency (f_{acc}) on peak height were studied and optimized in the modified electrode. These parameters' impact on peak height in SWASV studies was examined. After determining the experimental parameters, the effect of increasing Pb(II) concentration on peak height was investigated.

Optimization of Accumulation Time

In the study, using a modified electrode with a 600-second coating time in 10^{-5} M $Pb(NO_3)_2$ solution, cyclic voltammograms were taken to optimize the accumulation time, which was explored at intervals of 30, 60, 90, 120, 150, 210, 240, and 270 seconds. Considering the need for increased peak height without compromising peak symmetry, an accumulation time of 210 s was determined.

Table 1. Current values at different accumulation times obtained from 10^{-5} M Pb(II) in SWSV (currents are the average of three measurements)

Current (ip) x 10^{-4}	Accululation Time (s)
0.437	30
1.252	60
1.532	90
1.711	120
1.883	150
2.059	210
2.183	240
2.346	270

Optimization of accumulation frequency (f)

To optimize the frequency, one of the parameters of square wave voltammetry, square wave voltammograms were compared at 14 different frequencies starting from 15 Hz and increasing by 15 Hz increments, using a 210 s accumulation time with a 10^{-5} M $Pb(NO_3)_2$ solution. It was determined that the optimal frequency where the peak shape remained undistorted was 15 Hz. At other frequencies, although peak currents increased, peak shapes became distorted and broadened. These characteristics rendered the peaks unsuitable for quantitative purposes, thus they were not preferred.

Optimization of Accumulation Potential

With an accumulation time of 210 s and a frequency of 15 Hz, the optimization of accumulation potential was conducted at -0.7, -0.8, -0.9, and -1.0 V. Upon comparing these four different potentials, it was determined that the optimal accumulation potential is -0.8 V.

Table 2. SWASV results of current values at different accumulation potentials obtained from 10^{-5} M Pb(II) (currents are averages of two measurements)

Current (ip) x 10^{-4}	Accumulation Potential (V)
0.032	-0,7
2.059	-0,8
1.090	-0,9
1.047	-1

Determining the Analytical Working Range

After optimizing the necessary parameters, the concentration-current relationship for lead was investigated under these conditions. According to the optimization studies, the accumulation potential was set at -0.8 V, accumulation time at 210 s, and frequency at 15 Hz. Current values were plotted in the range of 0.1-1 µM concentration.

Table 3. Under optimum conditions, current values obtained at different concentrations (standard deviations calculated from three measurements)

Concentration, µM	Current, 10^{-5} A
1	1.372±0.02
0.8	1.142±0.05
0.6	0.794±0.03
0.4	0.392±0.04
0.2	0.109±0.02
0.1	0.03±0.01

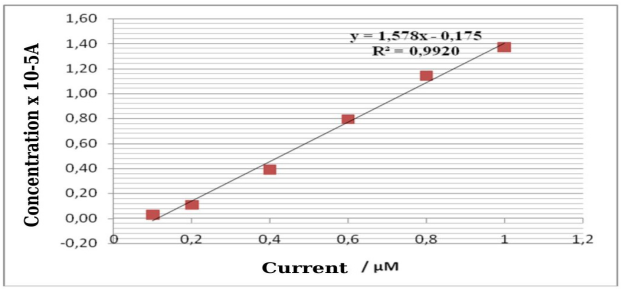

Figure 7. Calibration curve obtained at different concentrations for Pb(II) ion using bismuth-coated GC electrode under optimum conditions. Standard $Pb(NO_3)_2$ concentrations: 0.1 µM, 0.2 µM, 0.4 µM, 0.6 µM, 0.8 µM, and 1 µM.

Table 4. Analytical determination parameters according to the working graph obtained in the range of 0.1-1 µM (pH = 4.50) in 0.2 M acetate buffer

Parameters	Results
Concentration Range (µM)	0.1 – 1
Slope 10^{-5}A μM^{-1}	1.578
Standard Deviation of Slope (S_m)	0.099
Correlation Coefficient, r	0.996
Regression Standard Deviation, s_r	0.057
Number of Measurements, n	3
Detection Limit, LOD(M)	3.3 x 10^{-9}
Lower Detection Limit, LOQ(M)	1.1 x 10^{-8}

Upon examination of Figure 7 and Table 4, the optimal linear range was determined to be 0.1 µM-1 µM.

Calculation of LOD (limit of detection) and LOQ (limit of quantification)

By measuring at the lowest detectable concentration of $1x10^{-8}$ M, the average and standard deviation were calculated. The LOD value was determined as 3xS/m and the LOQ value as 10xS/m using the formula specified in Table 4 (Skoog, 2004).

Voltametric determination and recovery of lead(II) in sugar beet wash water using a bismuth-modified electrode

A mixture was prepared by taking 50 mL of sugar beet wash water as the sample and 50 mL of 0.2 M KNO_3 solution as the supporting electrolyte. Separate cells were used for each set of three measurements taken. The measured current values were substituted into the calibration graph equation obtained as y=1.78×-0.175 to calculate the amount of lead(II).

For recovery, a concentration of 2×10^{-6} M of 10^{-4} M $Pb(NO_3)_2$ solution was added to wastewater sample containing 1.6×10^{-7} M Pb(II). Three separate cells were prepared, and three measurements were taken in each cell. The amount of lead(II) corresponding to the added Pb(II) substance was calculated in milligrams based on the obtained current value. The recovery of the wastewater sample was calculated as 97.5% by comparing the added lead(II) amount with the found lead(II) amount.

Table 5. Measurement of lead(II) amount in wastewater sample and recovery of lead

Parameters	Results
Relative standard deviation (%R.S.D)	2.344
Added	4.144×10^{-3} mg
Found	8.84×10^{-3} mg
Recovery (%)	97.5

Table 6. Comparison of analytical performance measurements of bismuth coated GC with different modified electrodes in the literature for the determination of heavy metal ions.

Electrode	Technique	LOD	Ref.
N^1-hydroxy-N^1,N^2-diphenylbenzamidine-Carbon paste electrode(CPE)	ASWSV	0.0094 nM (Pb)	(29)
(Ag)/ (Au)-(NP)glassy carbon electrode(GCE)	DPASV	0.03×10^{-2} µg /L (Pb)	(30)
Bi oxycarbide /GCE	DPASV	3.97 µg /L (Pb)	(31)
Bi/carboxyphenyl-modified GCE	ASWSV	10 µg /L (Pb)	(32)
Graphene quantum dots and Nafion modified GCE	ASWSV	8.49 µg /L (Pb)	(33)
BE-MCPE	DPASV	4.89×10^{-8} M	(34)
Bismuth coated GC	ASWSV	3.3×10^{-9} M	This work

It is shown in Table 6 that the Bismuth coated GC exhibits good sensitivity and selectivity for the detection of Pb(II). It can be said that it is an electrode that can be used for trace amounts of lead analysis. Table 6 also compares the analytical performance measurements of the Bismuth coated GC with other modified electrodes reported in the literature. When compared with the literature, it is seen that a very suitable LOD value for Pb^{+2} detection of bismuth-coated GC is achieved. In addition, this electrode can be prepared quickly and is cost-effective.

CONCLUSION

In this study, a method was first developed for the electrochemical determination of Pb(II) ions using SWASV on a bismuth-coated glassy carbon electrode. The developed method was then applied to a sugar beet washing water sample. The current value obtained for the sample was substituted into the calibration equation to determine the amount of Pb(II).

The working concentration range of the developed method was determined to be 0.1 µM – 1 µM. Since no current reading can be obtained for control solutions without any electroactive species in electrochemical determination methods, the lower detection limit was determined as 0.01 µM, which is the lower limit of the working range and the smallest concentration at which a current reading can be made.

In the analytical application of this method, the amount of Pb(II) in the sugar beet washing water sample taken from Çorum Sugar Factory was found to be (0.16±0.09) µM. Measurements were taken for three different samples, and the standard deviation value was calculated using these three measurements. The amount of Pb in the washing water sample corresponds to 0.03 ppm. This value is below the highest level of 0.14 ppm that can be found in industrial waters or nearby areas (Gündüz, 1998).
As seen in Table 5, the recovery rate was found to be 97.5%, leading to the conclusion that the presence of Pb(II) does not interfere with our method.

According to the simultaneous results obtained from an external laboratory for the sugar beet washing water sample taken from Çorum Sugar Factory, the amount of Pb(II) was determined to be '< 0.04 µM'.

Voltammetric stripping techniques are used for the determination of trace amounts of substances in aqueous and non-aqueous environments. Along with atomic absorption, neutron activation, fluorometric, and chromatographic methods, voltammetric stripping methods are considered among the five important methods used in trace analysis. Among these methods, the two most widely used in inorganic analysis are atomic absorption and stripping methods. While atomic absorption is only used for inorganic determinations, stripping techniques can be used for both inorganic and organic determinations. Additionally, atomic absorption is a destructive method, whereas stripping methods are non-destructive. The equipment used in stripping techniques is simpler and cheaper. The same sample can be analyzed multiple times using stripping techniques.

In conclusion, an effective method has been developed for the rapid, easy application, low cost, and low detection limit determination of lead ions, one of the heavy metals found in the wash waters resulting as waste in the production process of sugar factories.

Sugar beet processing water is the waste of water used in the process of obtaining sugar from beet along with dissolved organic and inorganic substances. This wastewater contains a variety of components and can have environmental impacts.
Process water contains various substances such as sugar, acids, organic substances, nitrogen and phosphorus components. With appropriate treatment processes, process water can be reused in various fields, such as irrigation in agriculture or energy production. It is important to manage and treat wastewater in accordance with environmental protection laws. As a result, it can be said that sugar beet processing water wastes may cause environmental problems if not managed correctly. Therefore, studies should be carried out to develop treatment methods and keep waste under control**.**

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